Université de Montréal

Étude de la complexation simultanée d'un groupe carbonyle par deux sites acides de Lewis

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SOMMAIRE

En synthèse organique, la fonction carbonyle est d'une utilité capitale. Sa réactivité fait qu'elle soit transformable en une multitude de fonctions chimiques. La complexation d'un groupe carbonyle par un acide de Lewis monodentate exalte sa réactivité. Cette augmentation de la réactivité est en fait la conséquence de la coordination de l'un des deux doublets libres de l'oxygène par l'acide de Lewis. Dans cette thèse, nous nous proposons d'exploiter la présence du deuxième doublet libre de l'oxygène pour complexer doublement l'oxygène de la fonction carbonyle par deux sites acides de Lewis. En principe, un tel complexe est réalisable par le biais des acides de Lewis bidentates et sera encore plus activé que dans le cas d'une complexation monodentate. Les acides de Lewis bidentates et chiraux offriront au chimiste un outil fort appréciable permettant également une induction asymétrique plus efficace, résultat d'une complexation bidentate de structure plus rigide.

Nous sommes parvenus à démontrer avec succès qu'une cétone simple est intrinsèquement assez basique pour accepter conjointement deux ponts hydrogène et nous avons essayé d'étendre ce résultat aux acides de Lewis métalliques en empruntant deux voix distinctes. Dans la première, nous avons construit une variété de molécules, possédant deux sites basiques disposés symétriquement par rapport à une fonction cétone centrale. Notre objectif était d'utiliser la chélation pour fixer deux métaux dans une orientation favorisant une double complexation de la cétone par la présence unique de liens de coordination. Malheureusement, nos études cristallographiques et nos études par la résonance magnétique nucléaire à température variable n'ont pas montré que le groupe cétone dans ces molécules est doublement complexé.

Dans un effort parallèle visant la double complexation des composés carbonylés, nous avons synthétisé des acides de Lewis bidentates dérivant de l'addition de deux équivalents de AlR_3 ou de $TiCl_4$ sur une diversité structurale de diphénols. Les bis(dialkylphénoxydes) d'aluminium et les bis(trichlorophénoxydes) de titane ainsi élaborés ont une structure rigide et incorporent une disposition potentiellement convergente des sites acides de Lewis. Ces réactifs ont été conçus pour interagir doublement avec un composé carbonylé et le maintenir fixe dans l'espace.

Nous avons été en mesure de caractériser deux complexes dérivés des acides de Lewis bidentates générés par cette stratégie. Un cas, un butadiynediylbis(trichlorophénoxyde) de titane complexe deux équivalents d'acétate d'éthyle et dans l'autre, un trichlorophénoxyde de titane dérivé d'un fluorènediol, complexe deux équivalents de diméthylbenzophénone. Dans les deux cas, nos études cristallographiques ont montré que chaque atome de titane est pentacoordoné et interagit avec un seul motif carbonylé.

Nos essais avec les bis(dialkylphénoxydes) d'aluminium n'étaient pas fructueux vu que ceux-ci réduisent les dérivés carbonylés plutôt que de les complexer. Nous avons alors opté pour d'autres candidats basiques et avons réussi à isoler le complexe d'un bis(diisobutylphénoxyde) d'aluminium contenant un équivalent de diméthoxy-1,2 éthane. Une étude cristallographique a montré que le complexe est un oligomère alors que les études en solution par la résonance magnétique nucléaire à température variable ont avéré que le complexe est plutôt monomérique.

Nos travaux ont montré l'efficacité de la stratégie empruntée pour la construction des acides de Lewis bidentates forts et de propriétés différentes à partir d'un même diol approprié. Les distances séparant les deux oxygènes hydroxyles dans les différentes structures des diols utilisés sont inconvenables pour générer des acides de Lewis bidentates forts et capables de participer dans une double complexation d'un groupe carbonyle. Nos études synthétiques, structurales et thermodynamiques contribueront grandement dans l'élaboration future des acides de Lewis bidentates forts et plus efficaces.

TABLE DES MATIÈRES

Page

DESCRIPTION DE LA THÈSE

Nos travaux sont présentés sous forme de thèse par articles. Au corps de la thèse ont été ajoutés les manuscrits de cinq articles qui ont été publiés ou accéptés pour publication. Les manuscrits ajoutés au corps de la thèse ont été reproduits dans leurs versions intégrales en anglais. La numérotation des composés, des figures, des schémas, des tables et des références adoptée lors de la soumission des manuscrits a été conservée. Ainsi, une liste de références apparaît à la fin de chaque article. La numérotation des composés, des figures, des schémas et des références du corps de la thèse en français est indépendante de celle des sections par articles en anglais. Les références du corps de la thèse en français sont regroupées à la page **160** et leur numérotation est consécutive tout au long de la thèse. Le matériel supplémentaire déposé avec les articles est reproduit en annexes à la fin de ce document.

LISTES DES COMPOSÉS

LISTES DES FIGURES

Article 1

Article 2

Article 3

Article 4

Article 5

LISTES DES SCHÉMAS

LISTES DES TABLES

Article 3

Article 4

Article 5

LISTE DES ABRÉVIATIONS

Ac	: Acétyle
ACS	: Société chimique américaine
Å	: Angstrœm
Anal. Calcd	: Analyse élémentaire
AL ou LA	: Acide de Lewis
BL ou LB	: Base de Lewis
BuLi	: Butyllithium
i-Bu	: Isobutyle
t-Bu	: Tertiobutyle
° ou deg	: Degré
°C	: Degré Celsius
δ	: Déplacement chimique
$\Delta\delta$	: Différence de déplacement chimique
ΔH	: Différence d'enthalpie
DME	: Diméthoxy-1,2 éthane
DMF	: N,N-diméthylformamide
DMSO	: Diméthylsulfoxyde
ΔS	: Différence d'entropie
EI	: Impact électronique
eq	: Équation
Et	: Éthyle
FAB	: Bombardement rapide d'atomes
$\Delta G^{\ddagger}$	: Différence d'énergie libre d'activation
g	: Gramme
h	: Heure
HRMS	: Spectre de masse haute résolution
Hz	: Hertz
IR	: Infrarouge
J	: Constante de couplage
Kcal	: Kilocalorie

M	: Molaire
Me	: Méthyle
m/e	: Thomson
mg	: Milligramme
MHz	: Mégahertz
min	: Minute
mL	: Millilitre
mm	: Millimètre
mmol	: Millimole
mol	: Mole
mp	: Point de fusion
N	: Normale
NuH	: Nucléophile
p	: Para
Ph	: Phényle
py	: Pyridine
RMN ou NMR	: Résonance magnétique nucléaire
T	: Température
Tc	: Température de coalescence
THF	: Tétrahydrofuranne
Tf	: Trifluorométhanesulfonyle
TMEDA	: N,N,N',N'-tétraméthyl-1,2-diaminoéthane

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À la mémoire de Ommi Zbeida

CHAPITRE 1

INTRODUCTION

1.1 INTRODUCTION

La fonction carbonyle est très utile en synthèse organique pour sa commodité d'être transformée en d'autres fonctions chimiques[1]. Elle est réactive, susceptible à des attaques nucléophiles et suffisamment polarisée pour subir l'addition des meilleurs nucléophiles[2]. Cependant, pour des nucléophiles moins réactifs, il devient impératif d'augmenter la polarisation de la fonction carbonyle afin qu'elle puisse réagir. Une telle polarisation est causée par la complexation de la fonction carbonyle par les acides de Lewis. Cette complexation a des conséquences éminentes et pratiques qui ont été utilisées pour promouvoir une vaste gamme de réactions fondamentales telles que la réaction de Friedel-Crafts[3], la condensation aldolique[4], la réaction ène[5], la réaction de Diels-Alder[6] et tant d'autres[7]. La complexation affecte considérablement le substrat carbonylé et le rend chimiquement plus activé pour supporter aisément des additions nucléophiles. Dans ce chapitre, nous présentons les facteurs responsables de cette modification chimique de la fonction carbonyle suite à sa complexation par un acide de Lewis.

1.2 DÉFINITIONS

1.2.1 ACIDE DE LEWIS

Un acide de Lewis est toute espèce chimique, atome ou molécule, qui possède une ou plusieurs orbitales vacantes capable d'accepter une ou plusieurs paires d'électrons. Plusieurs acides de Lewis incorporent des métaux de transition vu qu'ils possèdent des orbitales d vacantes. D'autres acides de Lewis contiennent des éléments du groupe principal ayant des orbitales p vacantes tels que le bore et l'aluminium.

1.2.2 BASE DE LEWIS

Une base de Lewis est toute espèce chimique, atome ou molécule, capable de céder une paire d'électrons à une orbitale vide d'un acide de Lewis. Cette paire d'électrons peut être soit d'une orbitale non liante tel qu'un doublet d'une fonction éther ou amine, ou bien d'une orbitale faiblement liante telle qu'une liaison π d'un alcène.

1.2.3 NOTION DE COMPLEXE

Le partage de la paire d'électrons d'une base de Lewis à un acide de Lewis forme un complexe dans lequel les deux unités sont liées par un lien de coordination (Schéma 1). La formation du lien de coordination crée une charge positive partielle sur la base de Lewis et contribue à modifier sa réactivité chimique.

Schéma 1

$$A + :B \longrightarrow \overset{\delta-}{A} \leftarrow \overset{\delta+}{:B}$$

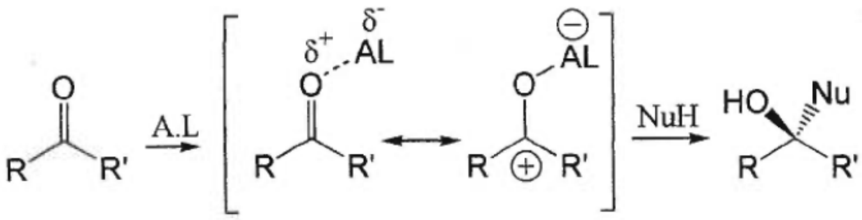
A = Acide de Lewis **Complexe**

:B= Base de Lewis

1.3 CONSÉQUENCES DE LA COMPLEXATION D'UN COMPOSÉ CARBONYLÉ PAR UN ACIDE DE LEWIS

La coordination de la fonction carbonyle à un acide de Lewis (AL) amplifie la charge positive sur le carbone du lien carbonyle et le rend plus susceptible à des additions nucléophiles (Schéma 2).

Schéma 2



Plusieurs études visant à éclaircir les détails de cette coordination ont été publiées. Par exemple, Reetz et collaborateurs ont estimé par des calculs MNDO que la charge sur le carbone du groupe carbonyle de l'acétaldehyde est de + 0.242 alors que celle de la forme complexée par le BF_3 est de + 0.363[8]. Ils ont constaté également une diminution importante de l'énergie de l'orbitale π^*_{CO} et ont noté que cette nouvelle énergie est plus similaire à celle de l'orbitale non liante d'un nucléophile.

Kojima et son équipe ont étudié la réaction de cycloaddition entre l'acrylate de méthyle et le butadiène et ont démontré que la réaction catalysée par le $AlCl_3$ est de 10^5 fois plus rapide que celle non catalysée[9]. Ils ont démontré aussi que l'énergie d'activation de la réaction catalysée est nettement inférieure à celle de la non catalysée. L'origine de cette accéleration peut être rationnalisée par la diminution de l'énergie de la LUMO du diénophile en la rapprochant d'avantage de l'énergie de la HOMO du diène. La diminution de l'écart énergétique entre les deux orbitales est responsable d'une plus forte interaction entre celles-ci et réduit ainsi l'énergie d'activation[10].

1.4 MODE DE COORDINATION D'UN COMPOSÉ CARBONYLÉ À UN ACIDE DE LEWIS

La coordination de la fonction carbonyle par un acide de Lewis peut-se faire de deux manières distinctes[11]. Dans la première, l'acide de Lewis interagit avec l'un des deux doublets libres de l'oxygène du groupe carbonyle en formant un lien σ. Dans ce cas, l'acide de Lewis se trouve à proximité du plan du groupe carbonyle. La deuxième possibilité est la formation d'un complexe π qui peut se faire soit par l'interaction d'une orbitale vide de l'acide de Lewis avec l'orbitale π de la fonction carbonyle ou encore par l'interaction d'une orbitale occupée de l'acide de Lewis avec l'orbitale π^* de la fonction carbonyle. Dans cette alternative, l'acide de Lewis se trouve hors du plan du carbonyle (Figure 1).

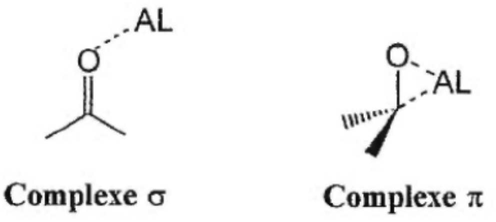
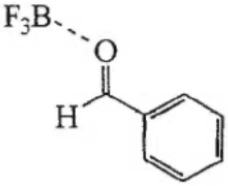


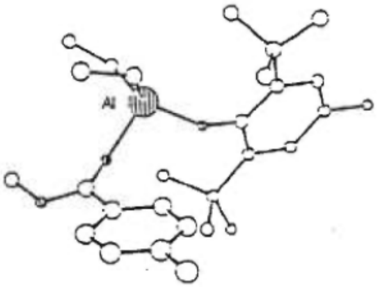
Figure 1: Deux modes de coordination d'un composé carbonylé à un acide de Lewis

D'après la littérature[12], les complexes isolés et caractérisés sont surtout du type σ. Dépendamment du métal et des ligands autour de lui, la complexation peut être du type π. Reetz et collaborateurs ont isolé le complexe **1** où le benzaldéhyde est coordiné au trifluorure de bore[8]. Une étude cristallographique par la diffraction des rayons-X a montré que le BF_3 se trouve dans le plan du groupe carbonyle, disposé *anti* au groupe phényle, et forme un complexe σ avec l'aldéhyde.



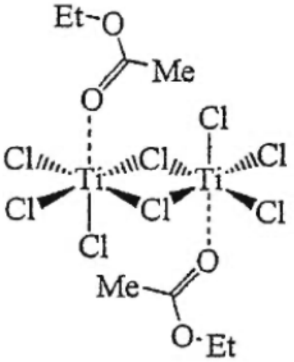
1

La complexation d'un groupe carbonyle par un acide de Lewis est sensible à l'encombrement stérique. Ainsi, la structure du complexe cristallin **2** formé par un phénoxyde d'aluminium encombré et le *p*-toluate de méthyle suggère que l'aluminium est forcé de s'éloigner du plan du carbonyle par l'effet stérique du ligand 2,6-di-tert-butyl-4-méthylphénoxyde[13].



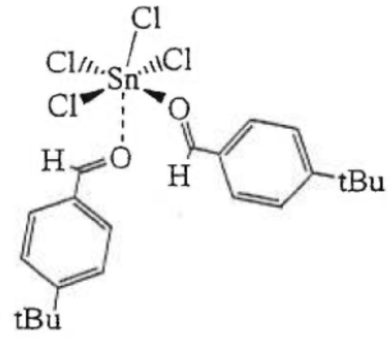
2

L'adduit cristallin 1:1 de $TiCl_4$ et d'acétate d'éthyle est une structure dimérique **3** contenant deux unités de titane octaédrique liées par des ponts chlore[14]. Les atomes de titane du $TiCl_4$ sont pratiquement coplanaires aux deux groupes carbonyles. Une structure cristalline analogue a été obtenue avec l'anisate d'éthyle et le $TiCl_4$ mais cette fois-ci, les atomes de titane du $TiCl_4$ sont hors du plan des deux groupes carbonyles montrant à quel point l'effet stérique peut affecter le mode de la coordination[15].



3

Le $SnCl_4$ forme avec le 4-tert-butylbenzaldéhyde le complexe 1:2 **4** où l'atome d'étain du $SnCl_4$ est coplanaire aux deux groupes carbonyles. La géométrie autour de l'étain est octaédrique et les deux aldéhydes sont dans une disposition *cis*[16].



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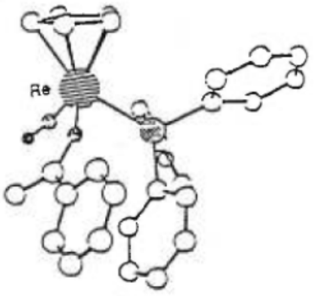
La formation des complexes π est observée chez les métaux riches en électrons avec les composés carbonylés pauvres en électrons tels que les aldéhydes. De cette façon, il peut y avoir rétrodonation des électrons du métal à l'orbitale π* du groupe carbonyle. Par exemple, Gladysz et colaborateurs ont étudié deux complexes formés par le même cation $[(Cp)(PPh_3)(NO)Re]^+$ avec l'acétophénone et le phénylacétaldéhyde. Avec la cétone, le cation forme le complexe σ 5 alors qu'avec l'aldéhyde, c'est le complexe π **6** qui se forme[17].



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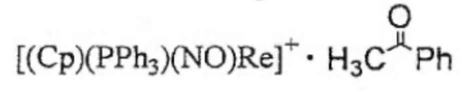
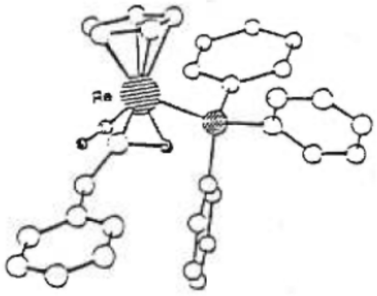

$[(Cp)(PPh_3)(NO)Re]^+ \cdot H_3C\text{–}C(=O)\text{–}Ph$



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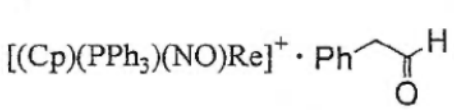

$[(Cp)(PPh_3)(NO)Re]^+ \cdot Ph\text{–}CH_2\text{–}C(=O)H$

1.5 COMPLEXATION BIDENTATE D'UN COMPOSÉ CARBONYLÉ

1.5.1 INTRODUCTION

Les composés carbonylés forment des adduits cristallins avec les acides de Lewis et le mode de coordination le plus fréquent est celui qui met l'acide de Lewis à proximité du plan du carbonyle selon la direction du doublet libre de l'oxygène en formant un complexe σ. En principe, ce mode de coordination laisse sur l'oxygène un deuxième doublet libre qui est disponible pour se lier à un second équivalent d'acide de Lewis pour former un complexe trimoléculaire du type **8** (Figure 2). En principe, la coordination simultanée de l'oxygène du groupe carbonyle par deux acides de Lewis rendrait la fonction carbonyle plus déficiente en électrons et par conséquent, plus réactive.

7 **8**

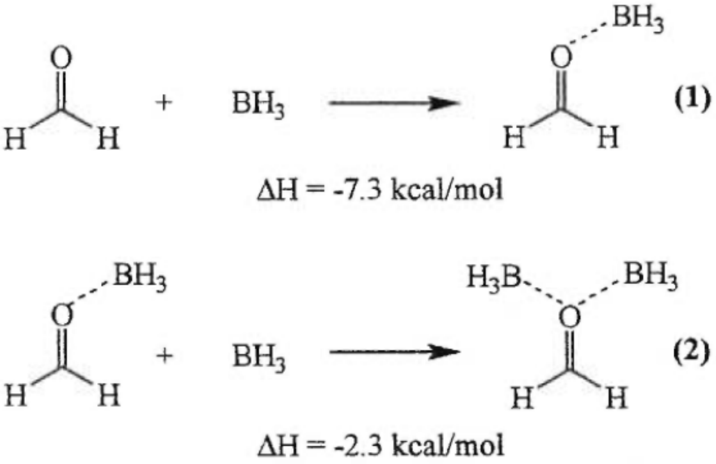
Figure 2 : Complexation monodentate et complexation bidentate

Les complexes bidentates dans lesquels l'oxygène est simultanément lié par deux acides de Lewis indépendants en formant un complexe trimoléculaire du type **8** posent un problème entropique relié à la difficulté d'assembler deux acides de Lewis séparés et un composé carbonylé. D'autre part, il peut se créer de la répulsion stérique entre les acides de Lewis liés à l'oxygène et également de la répulsion électrostatique entre ceux-ci causées par la création des charges partielles négatives.

Néanmoins, en 1963, les travaux de Palm et collaborateurs ont confirmé la possibilité de juxtaposer deux métaux sur l'oxygène d'un composé carbonylé[18]. Leur étude cristallographique a montré que dans le complexe $(NH_2)_2CO{\cdot}NaCl{\cdot}H_2O$, l'oxygène de l'urée intéragit simultanément avec deux cations Na^+. Une structure semblable a été obtenue avec le DMF.

Par ailleurs, des calculs *ab initio* ont montré que la coordination d'une molécule de BH_3 sur l'oxygène du formaldéhyde est exothermique (-7.3 kcal/mol) et forme un complexe σ (eq. 1) (Schéma 3). L'addition d'un second équivalent de BH_3 au formaldéhyde déjà complexé est modestement exothermique (-2.3 kcal/mol) et les deux acides de Lewis se coordonnent σ aux deux doublets de l'oxygène du formaldéhyde[19] (eq. 2) (Schéma 3).

Schéma 3

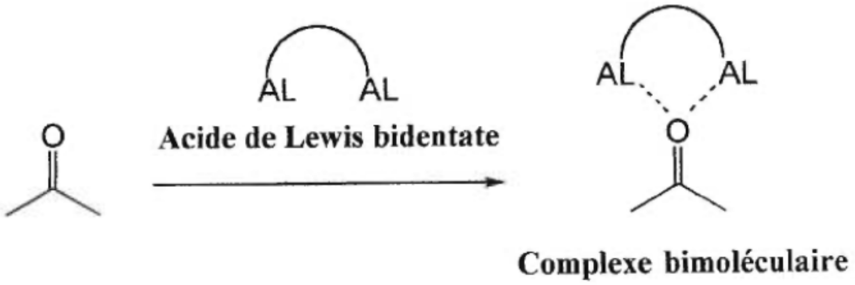


Ces résultats théoriques suggèrent que le doublet de l'oxygène demeure basique après sa coordination à un équivalent de BH_3 et confirment la faisabilité de la coordination conjointe des deux doublets de l'oxygène d'un carbonyle par deux acides de Lewis.

1.5.2 BUT DU PROJET

Dans le but de rendre la double complexation des composés carbonylés par les acides de Lewis chimiquement accessible, nous pensions qu'il serait plus logique que les deux sites acides de Lewis soient reliés par un squelette organique rigide formant ainsi un acide de Lewis bidentate. De cette facon, il est possible de surmonter les problèmes d'entropie et de répulsion électrostatique afin de complexer conjointement l'oxygène de la fonction carbonyle en formant un complexe bimoléculaire (Schéma 4).

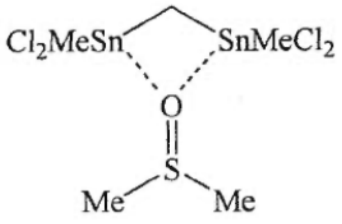
Schéma 4



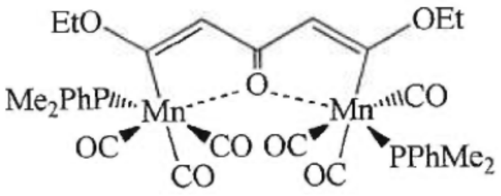
Dans une complexation monodentate entre un composé carbonylé et un acide de Lewis, il peut y avoir une multitude de conformères possibles à cause de la rotation facile du substrat autour du lien de coordination[19]. L'utilisation d'un acide de Lewis bidentate chiral pourrait solutionner ce problème en maintenant le composé carbonylé dans une conformation rigide et favorable à des transformations hautement stéréosélectives.

1.5.2.1 COMPLEXATIONS BIDENTATES EFFECTIVES

Kuivila et collaborateurs ont montré que l'oxygène du DMSO peut se coordiner simultanément à deux atomes d'étain d'un acide de Lewis bidentate pour former le complexe **9**[20]. En 1991, Adams et collaborateurs ont publié une structure incorporant, dans la même molécule **10**, deux atomes de manganèse interagissant simultanément avec l'oxygène d'une cétone[21]. Les deux métaux sont dans le même plan de la fonction carbonyle .

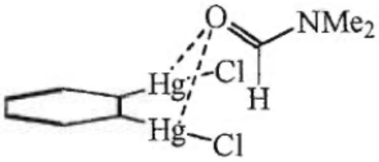


9



10

Wuest, Beauchamp et collaborateurs ont publié la structure du complexe **11** où l'oxygène du diméthylformamide interagit simultanément avec les deux atomes de mercure d'un acide de Lewis bidentate[22]. C'est le premier exemple où le design d'un système bidentate a été fructueux dans la reconaissance et la double complexation d'un composé carbonylé. Le plan défini par l'oxygène et les deux sites acides de Lewis est approximativement perpendiculaire à celui de la fonction carbonyle, donc le mode de complexation est un hybride σ−π de type trois centres-deux électrons.



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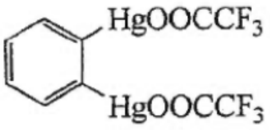
Wuest et Zacharie ont montré que le composé **12** forme des complexes bidentates avec des thiocétones et que cette complexation permet une désulfuration réductive en diarylméthanes[23]. L'utilisation des acides de Lewis monodentates ayant une structure similaire ne produit qu'un faible pourcentage de diarylméthanes. C'est le premier exemple rapporté dans la littérature concernant l'effet sur la réactivité que procure la double coordination d'un composé carbonylé par un acide de Lewis bidentate.



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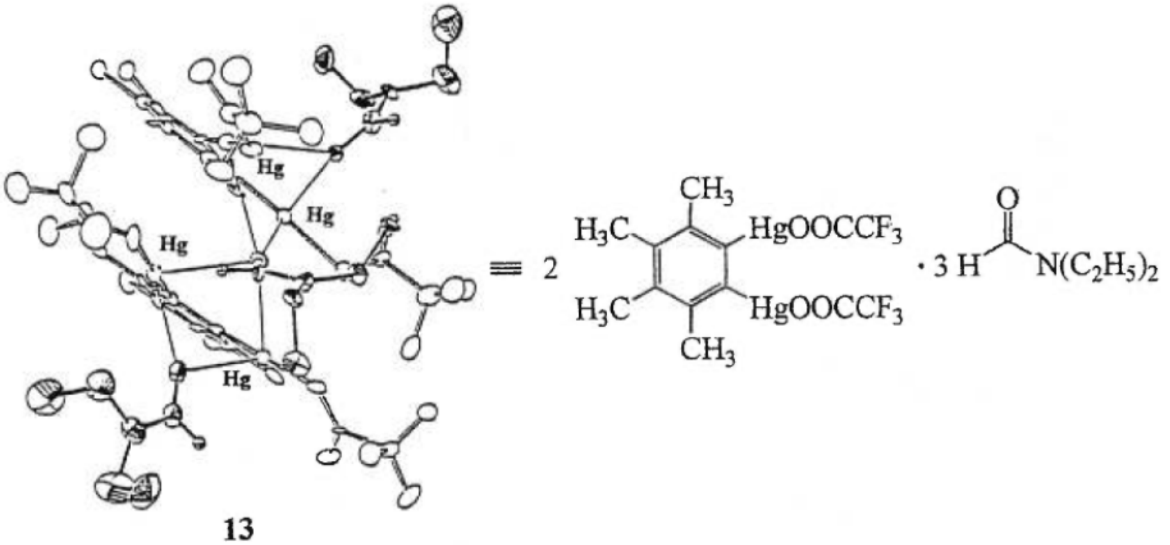
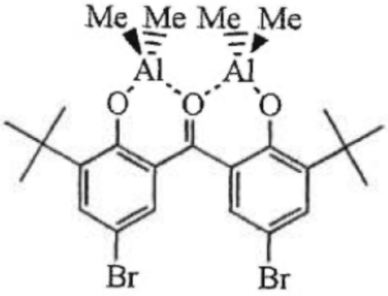
Wuest et Vaugeois ont trouvé que le tétraméthyl-3,4,5,6 bis(trifluoroacétate) phénylènedimercure-1,2 forme avec le diéthylformamide le complexe 2 :3 **13** dans lequel deux amides sont doublement coordonnés et le troisième oxygène amide est tétracoordonné[24]. Dans ce complexe, chaque unité phénylènedimercure forme deux liens Hg-O avec les amides liés dont l'un est plus court que l'autre. Les liens les plus courts se situent à proximité du plan du carbonyle alors que les plus longs sont dans un plan approximativement perpendiculaire au plan du carbonyle. Ceci suggère que les fortes intéractions se trouvent près du plan du carbonyle alors que les plus faibles sont hors de ce plan. Ces résultats sont théoriquement très importants car ils établissent qu'à l'état solide, l'oxygène de la fonction carbonyle peut être coordiné à plusieurs sites acides de Lewis. Cependant, les acides de Lewis bidentates de mercure sont tellement faibles et mous qu'ils ne peuvent être facilement utilisés dans la complexation des composés carbonylés et des bases organiques plus dures.



13

Wuest et Sharma ont réussi à isoler et caractériser le complexe **14** dans lequel les deux sites acides de Lewis –AlMe$_2$ greffés d'une manière covalente sur deux oxygènes phénoxy d'une benzophénone coordonnent simultanément l'oxygène de la fonction cétone centrale[25]. C'est le premier exemple de complexation bidentate d'une fonction carbonyle par deux acides de Lewis du groupe principal rapporté dans la litérature. La préférence conformationelle caractéristique des benzophénones met les deux atomes d'aluminium hors du plan du carbonyle.



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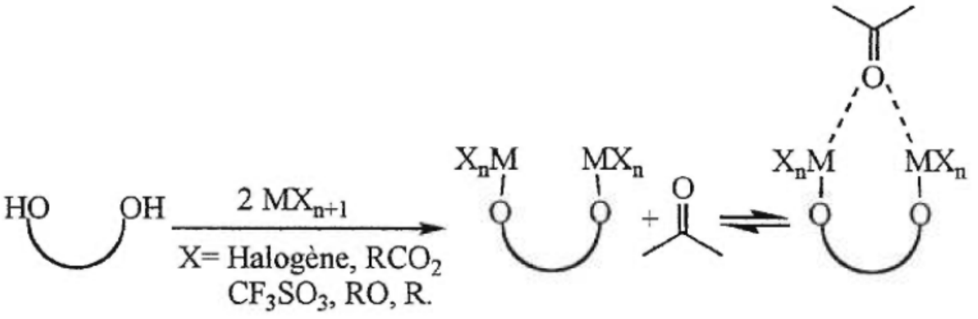
1.5.2.2 STRATÉGIE DE SYNTHÈSE DES ACIDES DE LEWIS BIDENTATES

Les relevés bibliographiques énoncés ci-haut prouvent que la complexation bidentate d'un composé carbonylé est une idée concrètement réalisable et nous incitent à aller de l'avant afin de déterminer le squelette et le métal idéaux qui constitueront l'acide de Lewis bidentate approprié pour une coordination simultanée d'un substrat carbonylé.

Les étapes décisives dans l'élaboration d'un acide de Lewis bidentate capable de reconnaître, fixer et activer vigoureusement un composé carbonylé sont les choix du squelette organique et du métal greffé sur le squelette. Les synthèses des premiers acides de Lewis bidentates rapportées dans la littérature ont utilisé pour la plupart des liaisons carbone-métal pour lier les métaux au squelette organique[22,26]. Cependant, les liens carbone-métal diminuent souvent l'acidité du métal, ce qui rend moins probable la formation des complexes doublement liés. En plus, il peut y avoir un problème de réactivité de la liaison carbone-métal vis-à-vis de la fonction carbonyle. Par exemple, les organozinciques[27], les organomagnésiens[28] et les alkyles de titane[29] réagissent avec des cétones et des aldéhydes pour former les alcools correspondants.

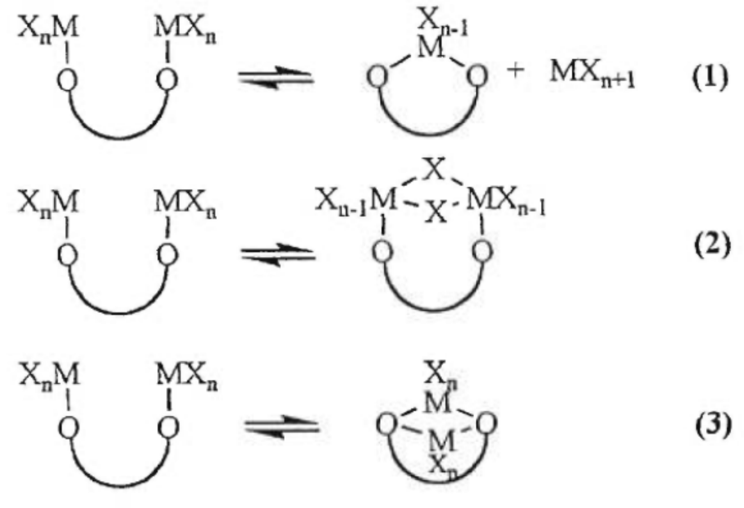
Pour contourner tous ces problèmes, il est préférable de remplacer le lien carbone-métal par le lien oxygène-métal dans la construction des acides de Lewis bidentates. D'une part, l'oxygène est plus électronégatif que le carbone, ce qui rendra le métal plus acide de Lewis que dans le cas du lien carbone-métal. D'une autre part, il suffira de choisir un diol et de le traiter avec un sel de métal pour générer un acide de Lewis bidentate. Un choix intelligent du sel du métal et du squelette hydroxylé est primordial dans la formation d'un acide de Lewis bidentate dont les sites métalliques sont à une distance idéale pour intéragir simultanément avec un substrat carbonylé (Schéma 5).

Schéma 5

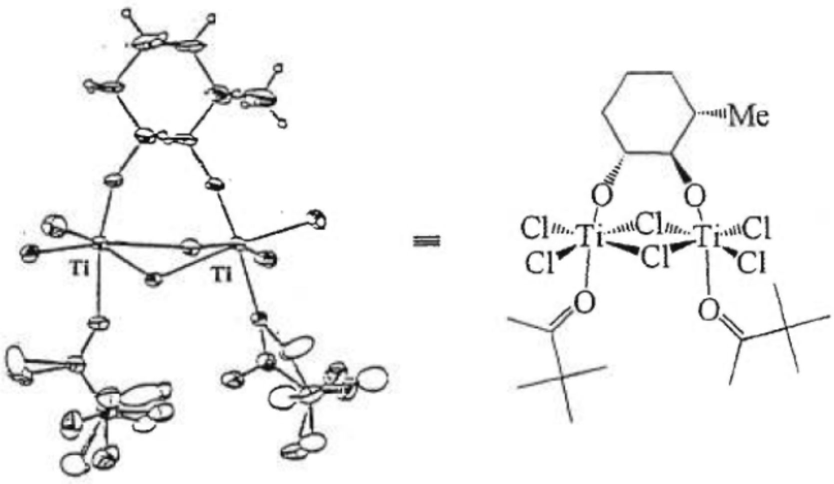


La distance séparant les deux métaux doit être bien ajustée pour une complexation simultanée de l'oxygène d'un groupe carbonyle et défavorable à toute autre alternative de redistribution des ligands autour du métal. Par exemple, si la distance est assez courte, il peut se former un dialkoxyde cyclique aux dépens du motif bidentate[30] (eq. 1) (Schéma 6). L'éloignement entre les sites métalliques doit désavantager également la formation des structures pontées (eq. 2 et 3)[31,32] (Schéma 6).

Schéma 6



Les travaux de Wuest et Bachand témoignent de la formation des structures pontées (eq. 2) (Schéma 6)[31]. Ils ont caractérisé le complexe 1 :2 **15** où l'acide de Lewis bidentate dérivé du trans-cyclohexanediol-1,2 présente des ponts chlore entre les atomes de titane et chaque métal complexe une pinacolone. Une structure analogue a été obtenue avec l'iode à la place du chlore.



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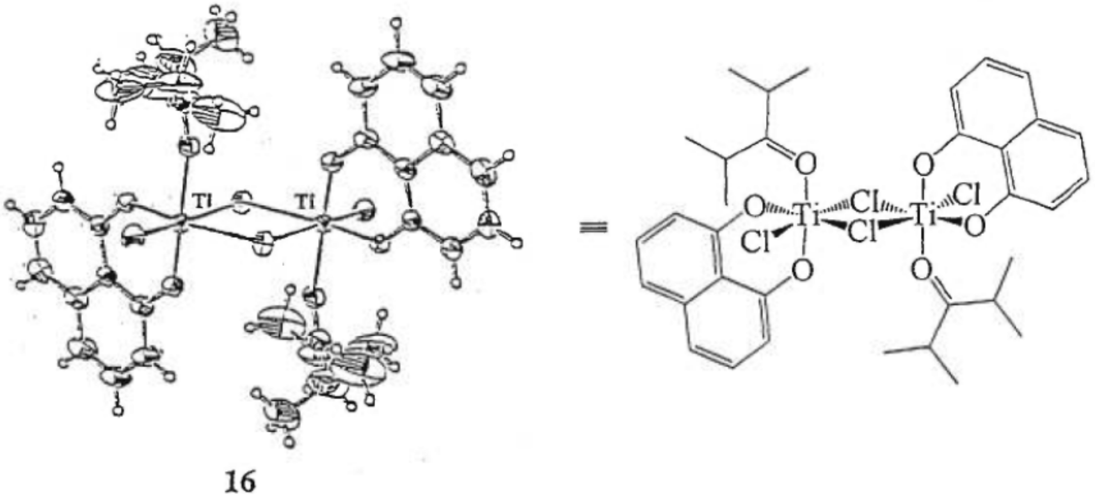
Wuest et Poirier ont également obtenu le complexe dimérique **16** dont la structure manifeste la formation des dialkoxydes cycliques (eq. 1) (Schéma 6)[30]. Les oxygènes du naphtalènediol sont liés au même atome de titane constituant en fait un acide de Lewis monodentate. Les atomes de titane sont liés par des ponts chlore et chaque titane complexe une cétone.



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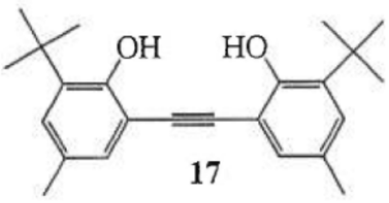
Cela étant, il est nécessaire que la distance séparant les deux sites acides de Lewis soit raisonnable pour une complexation conjointe d'un substrat carbonylé. Nous avons choisi les diols **17-19** parce qu'ils ont des stuctures rigides sur lesquelles nous pouvons greffer un sel de métal de façon à obtenir un acide de Lewis bidentate.



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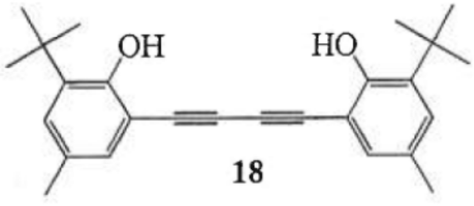

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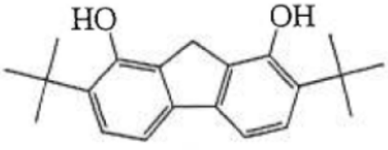

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En ce qui concerne le choix du métal pour étudier la complexation de la fonction carbonyle, il est conseillé d'utiliser des acides de Lewis qui ne réagissent pas avec le lien carbonyle. Par exemple, le Ti(III) réagit avec des aldéhydes et des cétones pour former les alcools correspondants[33]. Il est donc nécessaire que le métal doit avoir un potentiel d'oxydation élevé pour éviter la réduction de la fonction carbonyle par transfert d'électrons et pour simplifier sa manipulation. Il est également requis que le métal choisi ne soit pas paramagnétique et qu'il s'adapte bien à la technique de la RMN, outil essentiel pour étudier la complexation de la fonction carbonyle. Enfin, il est également utile que la chimie des alkoxydes du métal convenu soit bien connue dans la littérature[34,35] vu que nous utiliserons des diols pour construire les acides de Lewis bidentates. Pour ces raisons, nous avons choisi le tétrachlorure de titane et les composés trialkylaluminium parce qu'ils sont des acides de Lewis durs[36] et remplissent toutes les conditions spécifiées pour la bonne marche de l'étude envisagée.

CHAPITRE 2

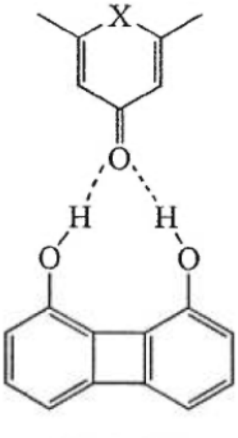
COMPLEXE DANS LEQUEL L'ATOME D'OXYGÈNE D'UNE CÉTONE SIMPLE ACCEPTE DEUX PONTS HYDROGÈNE INTERMOLÉCULAIRES

2.1 PRÉAMBULE

Certaines fonctions carbonylées plus basiques qu'une cétone[37] peuvent intéragir *intermoléculairement* avec deux sites acides de Brønsted ou de Lewis voisins[22,24,38,39]. Les structures dans lesquelles l'oxygène d'une cétone simple accepte *intramoléculairement* deux sites acides de Brønsted ou de Lewis voisins sont également bien connues[25,40]. Par contre, les complexes dans lesquels une cétone simple intéragit *intermoléculairement* avec deux sites acides de Brønsted sont extrêmement rares[41,42] et ceux avec deux sites acides de Lewis sont inexistants.

2.2 COMPOSÉS CARBONYLÉS CONJOINTEMENT LIÉS À DEUX SITES ACIDES DE BRØNSTED

Les travaux de Hine et collaborateurs ont révélé que le 1,8-biphénylènediol et ses dérivés sont des excellents acides de Brønsted bidentates capables de céder leurs deux hydrogènes hydroxyles aux atomes d'oxygène carbonyles pour former les complexes **20** et **21**[39b]. Cette double complexation se manifeste aussi bien à l'état solide qu'en solution.



20: X = NMe

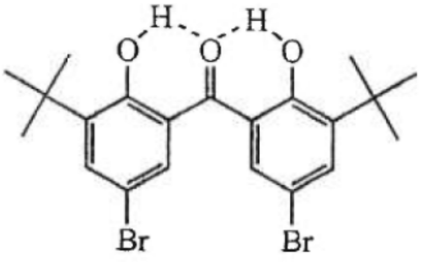
21: X = O

Kelly et collaborateurs ont étudié une réaction de Diels-Alder catalysée par un dérivé du 4,5-dinitrobiphénylènediol où les diènophiles sont des aldéhydes et des cétones α,β-insaturées[43]. Leurs résultats indiquent que les rendements des réactions catalysées par le diol sont jusqu'à six fois supérieurs à ceux obtenus en utilisant un acide de Brønsted monodentate dont le pKa est similaire.

Ces résultats suggèrent que la double activation intermoléculaire d'un groupe carbonyle est réalisable par le biais de diols appropriés et nous ont stimulés à confirmer qu'une cétone simple est intrinsèquement assez basique pour interagir conjointement et intermoléculairement avec deux sites acides de Brønsted ou de Lewis.

2.3 STRUCTURES DE COMPOSÉS CÉTONIQUES SIMULTANÉMENT LIÉS À DEUX SITES ACIDES DE BRØNSTED OU DE LEWIS

Wuest et collaborateurs ont montré que les atomes d'oxygène cétoniques de la 2,2'-dihydroxybenzophénone **22** et de la 1,8-dihydroxyfluorènone **23** acceptent intramoléculairement deux ponts hydrogène approximativement symétriques[40]. Ces résultats sont très importants vu qu'ils illustrent l'habilité de la fonction cétone à interagir simultanément avec deux sites acides de Brønsted.



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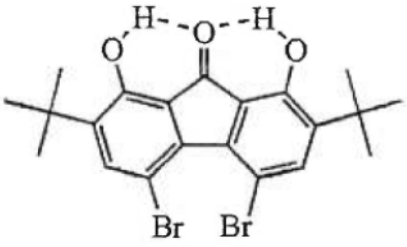
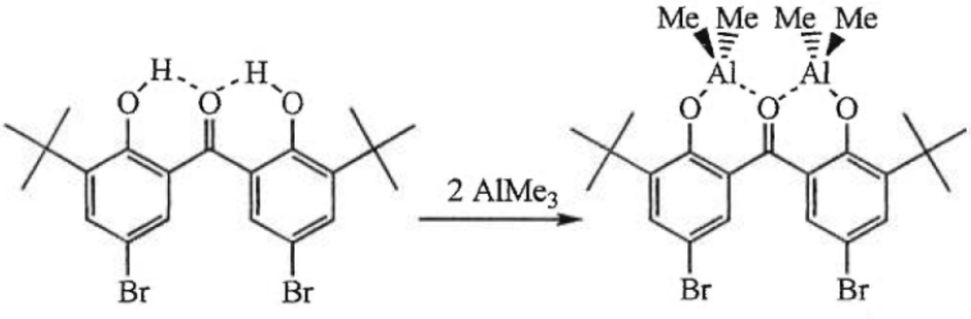


23

Par ailleurs, Wuest et Sharma ont réussi à convertir la 2,2'-dihydroxybenzophénone **22** en phénoxyde d'aluminium (Schéma 7) en le traitant avec deux équivalents de $AlMe_3$[25]. L'orientation des deux sites acides de Lewis greffés sur les oxygènes phénoxy de la benzophénone a permis leur interaction simultanée avec la cétone centrale. C'est le premier exemple publié de la double complexation d'une fonction cétone par deux acides de Lewis du groupe principal.

Schéma 7



22 **14**

Ces observations nous ont démontrés que la double coordination *intramoléculaire* de la fonction cétone par deux sites acides de Brønsted ou de Lewis est faisable et nous ont incités à tester la faisabilité de la double coordination *intermoléculaire* d'une cétone simple par deux liaisons hydrogène afin d'extrapoler ultérieurement aux acides de Lewis.

Nous avons synthétisé l'éthynediylbisphénol **17**[32] qui incorpore deux groupes hydroxyles dans une orientation possiblement convergente[44] et bien organisée pour la double coordination d'un composé carbonyle. Nous avons co-cristallisé le composé **17** avec des cétones simples et d'autres composés carbonylés plus basiques et nous rapportons nos observations dans l'article suivant.

2.4 ARTICLE 1 : *J. Org. Chem.* Accepté le **28/01/98**

Complexes in Which the Carbonyl Oxygen Atom of Simple Ketones Accepts Two Intermolecular Hydrogen Bonds

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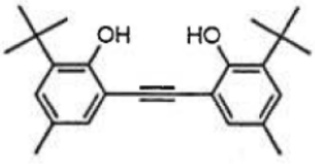
Abstract: Co-crystallization of equimolar amounts of 3,3,5,5-tetramethylcyclohexanone and 2,2´-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (1), which holds two OH groups in a potentially convergent orientation, produces an unusual 1:1 adduct 3 in which the carbonyl oxygen atom of the bound ketone accepts two intermolecular hydrogen bonds. Both lie close to the carbonyl plane along the directions defined by the formal sp^2 lone pairs on oxygen, and they appear to be moderately strong, although somewhat weaker than those found in related adducts in which the carbonyl oxygen atom accepts only one hydrogen bond. These observations confirm that simple ketones are basic enough to accept multiple intermolecular hydrogen bonds, at least in the solid state.

Carbonyl oxygen atoms have two formal lone pairs of electrons in sp^2 orbitals.[2] In principle, both pairs are available for interaction with Brønsted or Lewis acids. Simultaneous binding of two or more Brønsted or Lewis acids by simple ketones is therefore plausible, even though ketones are among the least basic carbonyl compounds.[3] Such multiple coordination can be expected to have a variety of interesting consequences.[4-10] Of particular importance is the possibility that ketones interacting with multiple Brønsted or Lewis acids may experience an unusually high degree of electrophilic activation.[5-9] Structures in which the carbonyl oxygen atom of relatively simple ketones interacts *intra*molecularly with two nearby sites of Brønsted acidity are well-known,[4] and analogues involving two intramolecular sites of Lewis acidity have also been characterized.[5] In both cases, the multiple interactions have marked effects on the geometry, spectroscopic properties, and reactivity of the bound carbonyl group. Carbonyl compounds that are more basic than simple ketones can interact *inter*molecularly with multiple sites of Brønsted or Lewis acidity.[6,7,10] In contrast, complexes in which simple ketones interact *inter*molecularly with multiple Brønsted acids are extremely uncommon,[11,12] and analogues involving multiple Lewis acids are unknown. In this note, we establish that doubly hydrogen-bonded complexes of simple ketones can be formed with 2,2´-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (1),[13] which is particularly well designed to serve as a convergent donor of two hydrogen bonds.[14]



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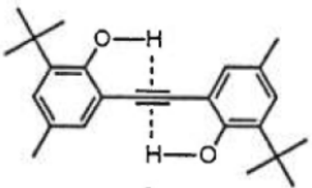
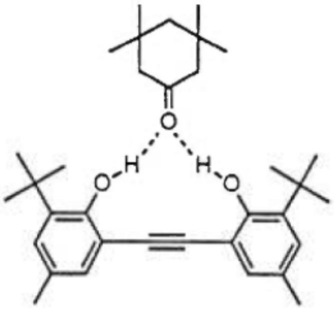


2

Evaporation of solvent from an equimolar mixture of diphenol **1** and 3,3,5,5-tetramethylcyclohexanone in pentane produced colorless crystals of a 1:1 adduct in 98% yield. Its IR spectrum (Nujol) revealed a sharp band at 1670 cm^{-1} and a broader band at 3329 cm^{-1}. In contrast, the carbonyl stretching band of the free ketone appears at 1717 cm^{-1} under similar conditions, and the OH stretching region of the IR spectrum of diphenol **1** contains a sharp peak at 3502 cm^{-1}, which indicates that both hydroxyl groups are equivalent and doubly π-bonded to the central triple bond in the approximately symmetric manner suggested by structure **2**.[13] Together, these data suggest that the 1:1 adduct has the novel structure **3**, in which the two OH groups of diphenol **1** are oriented convergently and act as donors of two hydrogen bonds to the oxygen atom of the ketone. This mode of binding has a notable effect on the position of the carbonyl band, which shifts by 47 cm^{-1} to lower frequency in the adduct.



3

An X-ray crystallographic study confirmed that the doubly hydrogen-bonded structure **3** is adopted in the solid state. The results of this study, which are summarized in Figure 1, show that

— Figure 1 —

the hydrogen bonds are equivalent by symmetry and have several interesting features. In particular, the intermolecular O(1)•••O(11) distances are relatively short (2.780(2) Å), suggesting that both hydrogen bonds are moderately strong. However, the distances are somewhat longer than those normally seen in singly hydrogen-bonded adducts of simple ketones and phenols (2.73-2.78 Å),[15] and they are also longer than those observed in a related doubly hydrogen-bonded 1:2 adduct of acetone and 4-hydroxybiphenyl (2.745(2) Å).[12] The observed lengthening may indicate that the average strength of a hydrogen bond in a doubly bonded adduct is slightly lower than that in a singly bonded analogue, or it may simply reflect constraints imposed by the rigid geometry of diphenol **1**. Indeed, the O(1)•••H—O(11) angles (150.4(1)°) show that the hydrogen bonds in adduct **3** deviate more substantially from linearity than those in unconstrained analogues.[11,12,15] Moreover, the C(11)—C(17)—C(17a) angle (171.85(12)°) reveals that the triple bond is slightly deformed, possibly in order to make the hydrogen bonds more nearly linear. The angle C(1)—O(1)•••O(11) (118.26(5)°) and the dihedral angle C(2)—C(1)—O(1)•••O(11) (2.33(4)°) are both similar to those found in related structures, and they confirm that both hydrogen bonds lie close to the carbonyl plane along the directions defined by the formal sp^2 lone pairs on oxygen.[16]

We have observed that diphenol **1** also forms solid 1:1 adducts with other carbonyl compounds. Their structures are presumably analogous to that of adduct **3**, but we did not characterize them in detail. Although double hydrogen bonding is a salient feature of the interaction of diphenol **1** with simple ketones in the solid state, it is apparently too weak to be retained in solution. For example, the IR spectrum of a 0.2 M solution prepared by dissolving adduct **3** in CH_2Cl_2 showed only bands at 1707 cm^{-1} and 3506 cm^{-1}, which are characteristic of free 3,3,5,5-tetramethylcyclohexanone and diphenol **1** under the same conditions. It is possible that more stable adducts will be formed by related diphenols with convergent OH groups that cannot form weak intramolecular hydrogen bonds such as those present in structure **2**. Nevertheless, our spectroscopic and crystallographic studies confirm that simple ketones, despite their inherently weak basicity, can accept multiple intermolecular hydrogen bonds.

Experimental Section

1:1 Adduct of 2,2´-(1,2-Ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (1) and 3,3,5,5-Tetramethylcyclohexanone. A mixture of diphenol **1** (15.9 mg, 0.0448 mmol)[13] and 3,3,5,5-tetramethylcyclohexanone (6.9 mg, 0.045 mmol) in pentane (1 mL) was stirred at 25 °C for 10 min. Evaporation of solvent then left a crystalline colorless residue of the 1:1 adduct **3** (22.3 mg, 0.0442 mmol, 98%): mp 110 °C; IR (Nujol) 3329, 1670 cm^{-1}.

X-ray Crystallographic Study of the 1:1 Adduct 3 of 2,2´-(1,2-Ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (1) and 3,3,5,5-Tetramethylcyclohexanone.[17] Crystals of 1:1 adduct **3** belong to the orthorhombic space group Pnma with $a = 9.542(2)$ Å, $b = 26.567(6)$ Å, $c = 12.398(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 3142.9(10)$ Å^3, $D_{\text{calcd}} = 1.067$ g cm^{-3}, and $Z = 4$. Data were collected at 293 K, and the structure was refined to $R1 = 0.039$, $wR2 = 0.080$ for 3041 reflections with $I > 2.00\ \sigma(I)$.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada, the Ministère de l'Éducation du Québec, and Merck Frosst for financial support. In addition, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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15. Ibragimov, B. T.; Gdaniec, M.; Dadabaev, B. N. *J. Incl. Phenom.* **1990**, *8*, 333. Ouahab, L.; Mousser, A.; Boultif, A.; Grandjean, D.; Jolibois, H. *Acta Crystallogr.* **1989**, *C45*, 1397. Osborn, R. S.; Rogers, D. *Acta Crystallogr.* **1975**, *B31*, 359. These three examples provide suitable models because in all cases a simple aliphatic ketone (acetone or cyclohexanone) accepts a single intermolecular hydrogen bond from a phenolic OH group that does not participate in any other hydrogen bonds.

16. For a discussion of the geometry of hydrogen bonds in organic crystals, see: Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320.

17. The authors have deposited X-ray crystallographic data, a description of the structure

determination, and tables of atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and refined and calculated hydrogen atom coordinates with the Cambridge Crystallographic Data Centre. The data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

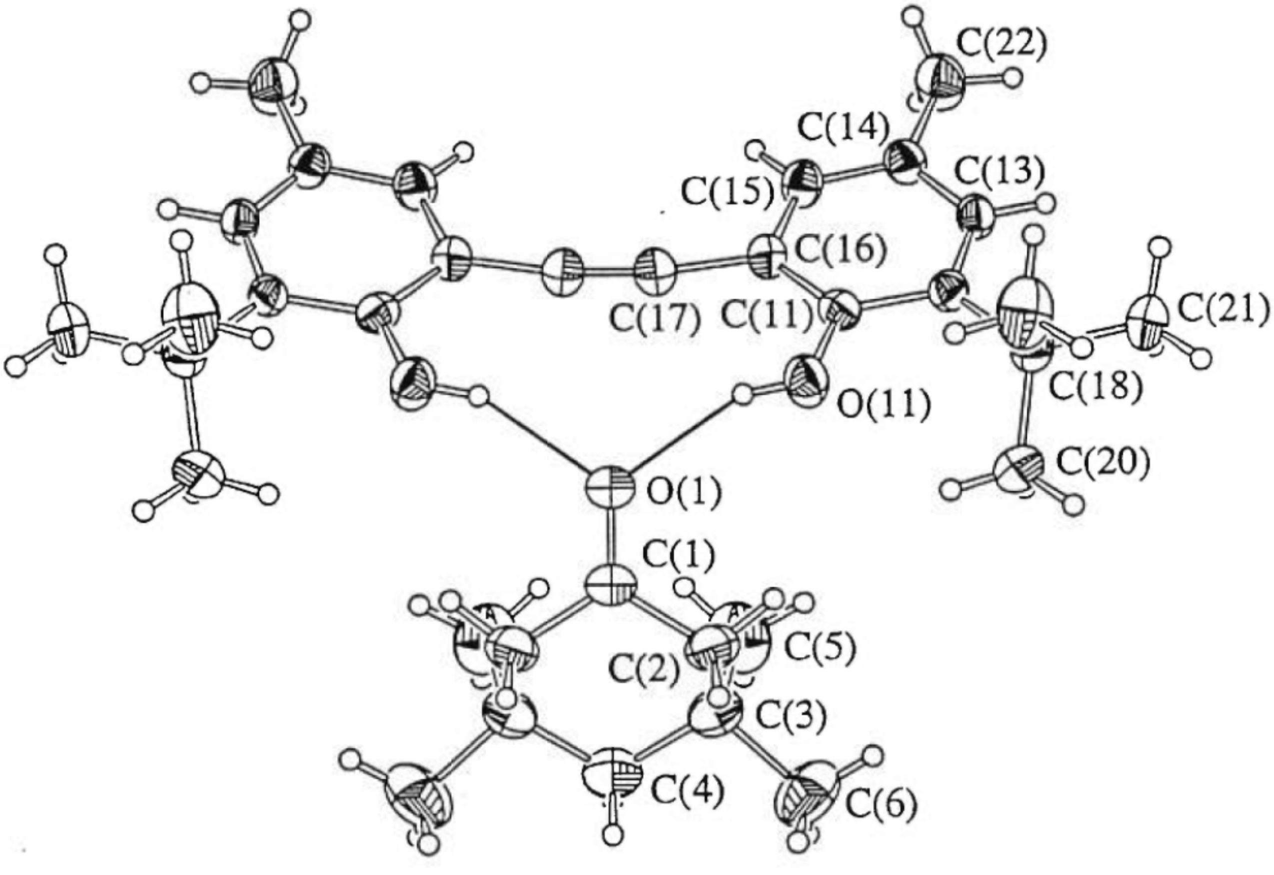


Figure 1. ORTEP view of the structure of the doubly hydrogen-bonded adduct **3** formed by the interaction of diphenol **1** and 3,3,5,5-tetramethylcyclohexanone. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, and hydrogen bonds are represented by narrow lines.

2.5 CONCLUSION

Nous avons été en mesure de confirmer qu'à l'état solide, une cétone simple est suffisamment basique pour être simultanément liée par deux ponts hydrogène. La double coordination de l'oxygène cétonique par deux sites acides de Brønsted s'est avéré trop faible pour être maintenue en solution. Cependant, l'étude IR d'un complexe obtenu par la co-cristallisation d'un mélange équimolaire du diol **17** et de la 2,6-diméthylpyrone a montré que la double coordination du groupe carbonyle pyronique est présente en solution. Ce résultat confirme les observations de Hine et collaborateurs[39b] et suggère que la coordinatioin simultanée d'un groupe carbonyle par deux sites acides de Brønsted en solution n'est faisable qu'avec des composés carbonylés plus basiques qu'une cétone simple[37].

En principe, la double coordination d'une cétone simple par deux sites acides de Lewis métalliques sera plus forte. Nous avons donc décidé de convertir le diol **17** en acide de Lewis bidentate qui serait capable d'interagir conjointement et fortement avec l'oxygène d'une cétone simple. Ces études sont résumées dans le chapitre 4.

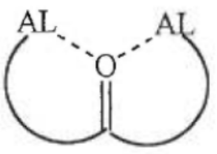
CHAPITRE 3

ESSAIS DE COORDINATION SIMULTANÉE D'UNE CÉTONE PAR DEUX SITES ACIDES DE LEWIS PAR CHÉLATION

3.1 INTRODUCTION

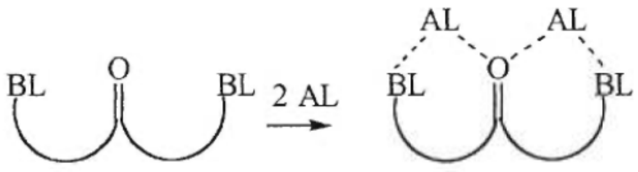
Dans le chapitre précédant, nous nous sommes inspirés des travaux de Wuest et collaborateurs[25,40] qui ont confirmé la faisabilité de la double coordination *intramoléculaire* de la fonction cétone par deux sites acides de Brønsted ou de Lewis. Dans ce chapitre, nous résumons nos tentatives d'exploiter davantage ces mêmes travaux d'une manière plus ambitieuse.

Dans les complexes **24** de Wuest et collaborateurs[25], les deux sites acides de Lewis sont liés au squelette organique d'une manière covalente de telle sorte qu'ils soient pour ainsi dire forcés d'interagir simultanément avec l'oxygène de la fonction cétone centrale. Nous avons décidé de développer l'impact de cette découverte en adoptant des bases de Lewis tridentates **25** possédant deux sites basiques disposés symétriquement par rapport à une fonction cétonique centrale. Ces structures serviront à fixer deux sites acides de Lewis dans une orientation favorisant une double complexation de la cétone par la présence unique de liens de coordination comme l'illustre la structure **26** (Schéma 8).



24 (AL = Acide de Lewis)

Schéma 8



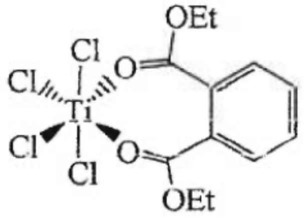
25 **26**

AL = Acide de Lewis, BL = Base de Lewis

Nous aurons la possibilité de choisir des structures qui sont symétriques afin de simplifier les études spectroscopiques et qui contiennent une fonction centrale cétonique simple et non conjuguée pour éviter tout phénomène de résonance[25]. De cette facon, nous serons en mesure d'affirmer si les deux doublets de l'oxygène d'une cétone simple sont intrinsèquement assez basiques pour être doublement coordonnés par deux sites acides de Lewis.

3.2 CHÉLATES FORMÉS PAR DES LIGANDS DICARBONYLÉS ET LE $TiCl_4$

Cette nouvelle stratégie utilisant la double chélation nous a semblé réalisable étant donné qu'il existe plusieurs études cristallographiques montrant que le $TiCl_4$ est capable de chélater deux groupes carbonyles d'un ligand bidentate[45]. Par exemple, le phtalate de diéthyle forme le chélate **27** possédant un cycle à sept chaînons où l'atome de titane du $TiCl_4$ est coplanaire aux deux groupes carbonyles[45d]. La 3,3-diméthyl-2,4-pentanedione produit également le chélate **28** en formant un cycle à six chainons où le titane est contenu dans le même plan que celui des deux carbonyles cétoniques[45e]. L'acénaphtènequinone produit également avec le $TiCl_4$ le chélate **29** à cinq chainons[45a].



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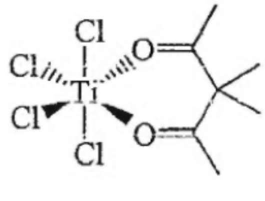

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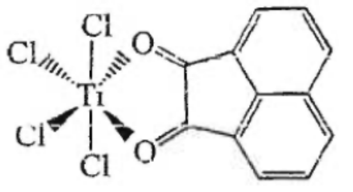

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Il est donc évident que le $TiCl_4$ forme des chélates cristallins et monomériques avec les composés dicarbonylés et qu'il serait possible de l'utiliser dans notre étude de la complexation bidentate d'une cétone simple par la double chélation.

Nous avons synthétisé des structures symétriques incorporant une fonction cétonique centrale simple et flanquée par deux sites bases de Lewis et nous avons étudié leurs comportements avec le $TiCl_4$ en solution par la technique de la RMN à basse température. De plus, nous avons réussi à isoler un chélate cristallin qui a été caractérisé par la cristallographie. Nos résultats sont résumés dans l'article suivant.

3.3 **ARTICLE 2 :** *Can. J. Chem.* Accepté le **05/03/98**

Complexes of Ketodiesters and Related Compounds with $TiCl_4$. Attempts to Use Chelation to Promote the Simultaneous Coordination of Ketones by Two Lewis Acids

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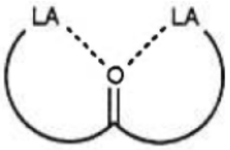
Abstract: Carbonyl oxygen atoms have two formal lone pairs of electrons. In principle, both can be used simultaneously to form complexes with two or more Lewis acids. This multiple coordination promises to have a variety of interesting consequences; unfortunately, however, complexes of carbonyl compounds with multiple Lewis acids are extremely rare. To promote multiple coordination, we have made a series of symmetric ketodiesters and related compounds in which the carbonyl group of a ketone is flanked by two additional sites of Lewis basicity. In such compounds, the flanking bases and both lone pairs of the central ketone are available for binding two equivalents of suitable Lewis acids, thereby producing symmetric double chelates in which the central ketone interacts with two Lewis acids at the same time. As expected, treatment of 3-oxoglutarates and 4-oxopimelates with $TiCl_4$ in a 1:1 ratio yielded unsymmetric single chelates in which the carbonyl groups of the ketone and one ester bind $TiCl_4$, while the other ester remains free. Unfortunately, treatment of the same ketodiesters with $TiCl_4$ in a 1:2 ratio did not produce the desired symmetric double chelates. Instead, 2:4 complexes were formed in which the free esters of the unsymmetric single chelates bind $TiCl_4$ in the normal way, without assistance from the keto group. We attribute this observation to the inherent reluctance of ketones to bind multiple Lewis acids, as well as to unfavorable Cl•••Cl interactions created in the hypothetical double chelates by the simultaneous attachment of two octahedrally coordinated atoms of titanium to a single carbonyl oxygen atom.

Introduction

Carbonyl oxygen atoms have two formal lone pairs of electrons in sp^2 orbitals,[2] and both are potentially available for interaction with Lewis acids. Simultaneous coordination of ketones by two or more Lewis acids is therefore plausible, although ketones are among the least basic carbonyl compounds.[3] Such multiple coordination can be expected to have a variety of interesting consequences.[4,5] Of particular importance to organic chemists is the possibility that ketones interacting with multiple Lewis acids may experience an unusually high degree of electrophilic activation.[4,5] Unfortunately, complexes of this type are extremely uncommon. No complexes in which simple ketones interact *inter*molecularly with multiple Lewis acids are known, although related structures involving carbonyl compounds more basic than ketones have been characterized.[4] In addition, we have established that the carbonyl oxygen atom of relatively simple ketones can form complexes **1** by interacting *intra*molecularly with two nearby sites of Lewis acidity when they are held by covalent bonds in a suitable orientation.[5] As expected, this double coordination has marked effects on the geometry, spectroscopic properties, and reactivity of the bound carbonyl group.[4-6] An even more ambitious objective is to construct related doubly coordinated complexes **2** in which the carbonyl group is flanked by two nearby sites of Lewis acidity that are held in place only by relatively weak dative bonds involving adjacent sites of Lewis basicity .[7] In such complexes, the carbonyl oxygen atom of the central ketone uses both of its lone



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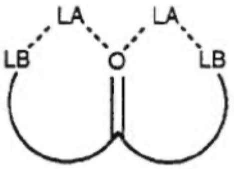


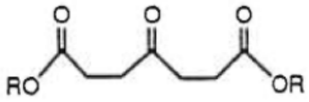
2

(LA = Lewis acid, LB = Lewis base)

pairs in order to participate in the simultaneous formation of two chelates. Chelation is thereby used to promote the simultaneous coordination of the ketone by two Lewis acids. In this paper, we describe our efforts to prepare novel complexes of this type by treating selected ketodiesters and related compounds with $TiCl_4$.

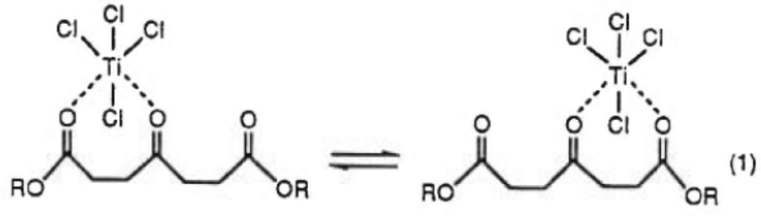
Results and Discussion

Transesterification of diethyl 4-ketopimelate provided the corresponding diphenethyl ester **3**, which forms complexes with $TiCl_4$ that proved to be soluble enough in CH_2Cl_2 to permit their



3 (R = CH_2CH_2Ph)

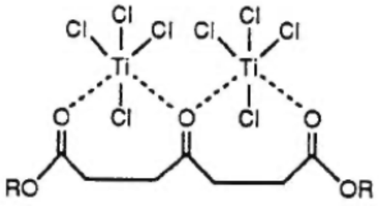
^1H and ^{13}C NMR spectra to be recorded at low temperatures. The carbonyl region of the ^{13}C NMR spectrum of ketodiester **3** ($CDCl_3$, 25 °C) showed two peaks at δ 172.4 and 206.7, which can be assigned to the carbonyl carbon atoms of the ester and the ketone, respectively. In the ^{13}C NMR spectrum of a solution prepared by mixing ketodiester **3** and $TiCl_4$ in a 1:1 ratio (0.50 M in CD_2Cl_2, 25 °C), the corresponding peaks appeared at δ 177.7 and 222.2. The pronounced downfield shifts indicate that complexation occurs, as expected, and that the ester and ketone groups must both participate. A similar spectrum recorded at -85 °C revealed a total of 19 peaks, including three in the carbonyl region at δ 171.6, 180.9, and 225.2. Together, these observations demonstrate that solutions prepared from equimolar amounts of ketodiester **3** and $TiCl_4$ must contain primarily a single 1:1 complex; moreover, the complex must be the unsymmetric chelate **4**,



4 (R = CH_2CH_2Ph)

in which the carbonyl groups of the ketone and one ester are bound to $TiCl_4$ and their carbonylcarbon atoms are shifted downfield, while the other ester remains free and essentially unshifted.[8] Symmetrization of the complex (eq. 1) is sufficiently rapid at 25 °C that the two esters can no longer be distinguished by ^{13}C NMR spectroscopy.

We hoped that the ^1H and ^{13}C NMR spectra of solutions prepared by mixing ketodiester **3** and $TiCl_4$ in a 1:2 ratio would provide evidence for the formation of the symmetric double chelate **5**. In fact, the carbonyl region of the ^{13}C NMR spectrum (0.33 M in CD_2Cl_2, 25 °C) showed two



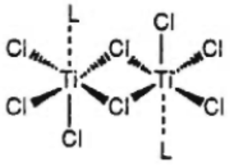
5 (R = CH_2CH_2Ph)

peaks at δ 180.4 and 223.2, which are both farther downfield than those observed in the spectrum of the 1:1 mixture under similar conditions (δ 177.7 and 222.2). The relatively large downfield shift of the upfield carbonyl carbon atom (Δδ 2.7) indicates that both ester groups must now be bound to $TiCl_4$; however, the downfield shift of the ketonic carbonyl carbon atom (Δδ 1.0) appears to be too small to be consistent with the formation of the desired symmetric double chelate

5. Furthermore, a similar spectrum recorded at -65 °C revealed three peaks in the carbonyl region at δ 181.5, 182.0, and 222.4 (Figure 1). This confirms that addition of an equimolar amount of

— Figure 1 —

$TiCl_4$ to the unsymmetric single chelate **4** under these conditions does not produce the symmetric double chelate **5**. Instead, we propose that the free ester group of unsymmetric chelate **4** behaves in the conventional way and binds $TiCl_4$ without assistance from the keto group, thereby forming a chloride-bridged complex **6a** of stoichiometry 2 **3** • 4 $TiCl_4$. This hypothesis is reasonable because a wide range of simple esters are known to form structurally analogous chloride-bridged 2:2 complexes with $TiCl_4$.[9]



6a (L = **4**, bound by free ester)
6b (L = **16**, bound by free ester)

Direct confirmation was provided by an X-ray crystallographic study of crystals of a CH_2Cl_2 solvate of complex **6a**, which were obtained by allowing pentane to diffuse into a solution prepared by mixing ketodiester **3** and $TiCl_4$ in CH_2Cl_2 in a 1:2 ratio. The results of this study are shown in Figure 2. Most of the observed bond lengths and angles are similar to those found in

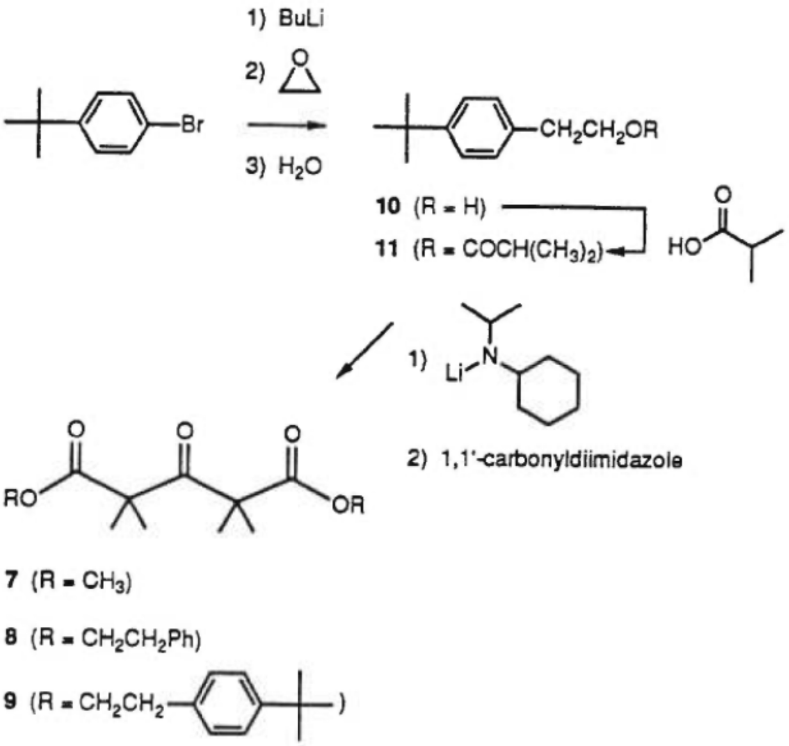
— Figure 2 —

related structures.[8,9] For example, normal values are observed for the average lengths of Ti(1)—Cl bonds trans to the chelating oxygen atoms (2.226(3) Å), Ti(1)—Cl bonds cis to the chelating oxygen atoms (2.287(3) Å), terminal Ti(2)—Cl bonds (2.208(3) Å), bridging Ti(2)—Cl bonds (2.450(3) Å), Ti(1)•••O bonds to the carbonyl groups of the chelating ester (2.076(6) Å) and ketone (2.141(6) Å), Ti(2)•••O bond to the carbonyl group of the non-chelating ester (2.050(7) Å), and C=O bonds of the chelating ester (1.206(11) Å), ketone (1.242(10) Å), and non-chelating ester (1.231(11) Å). Typically large values are observed for the carbonyl C=O•••Ti(1) angles involving the chelating ester (154.4(6)°) and the ketone (140.3(6)°), as well as for the carbonyl C=O•••Ti(2) angles involving the non-chelating ester (153.2(8)°). In addition, both atoms of titanium have approximate octahedral coordination. As expected, the dihedral angles Ti(1)•••O(4)—C(4)—C(3′) (2.0(2)°) and Ti(2)•••O(1)—C(1)—C(2) (-6.0(2)°) are small, indicating that normal $\eta^1(\sigma)$ complexation is favored by the ketone and the non-chelating ester, with Ti lying close to the carbonyl plane. However, an unusual value is observed for the dihedral angle Ti(1)•••O(1′)—C(1′)—C(2′) involving the chelating ester (23.0(2)°), which reveals that Ti(1) lies far from the carbonyl plane and that the interaction must therefore have important π character.[10]

In principle, the conversion of 2:4 complex **6a** into two equivalents of symmetric double chelate **5** is entropically favorable and should be favored by dilution. Even at the lowest concentrations that could be studied, however, low-temperature ^{13}C NMR spectra of solutions prepared by mixing ketodiester **3** and $TiCl_4$ in a 1:2 ratio provided no evidence for the formation of symmetric double chelate **5**.

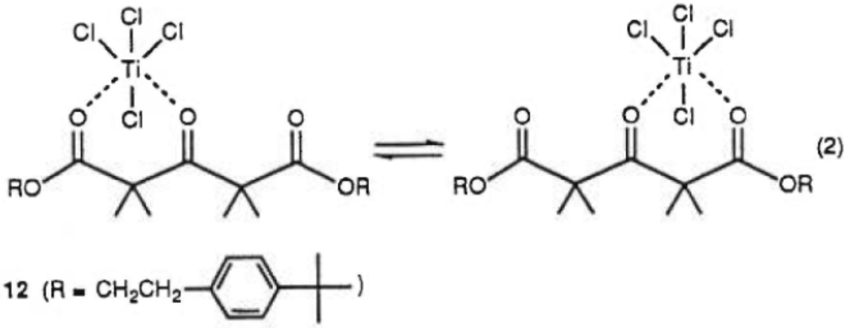
We reasoned that hypothetical structure **5** and other double chelates derived from 4-ketopimelates might be disfavored because they contain two seven-membered rings, so we also examined the interaction of representative 3-ketoglutarates with $TiCl_4$. Neither dimethyl 2,2,4,4-tetramethyl-3-oxopentanedioate (**7**)[11] nor the corresponding diphenethyl ester **8** formed complexes with $TiCl_4$ that were sufficiently soluble in CH_2Cl_2 at low temperatures, so we prepared derivative **9** by the route summarized in Scheme 1.[12] Lithiation of 1-bromo-4-(1,1-dimethylethyl)benzene,

Scheme 1



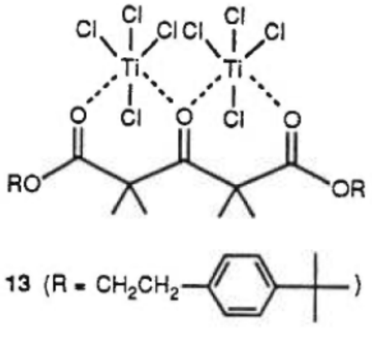
followed by the addition of excess ethylene oxide and then water, provided 4-(1,1-dimethylethyl)benzeneethanol (**10**) in 77% yield. Subsequent esterification then gave the corresponding 2-methylpropanoate **11** in 88% yield. Deprotonation of ester **11**, followed by treatment of the resulting enolate with 1,1′-carbonyldiimidazole, finally provided the required 3-ketoglutarate **9** in 43% yield.

The carbonyl region of the ^{13}C NMR spectrum of compound **9** (CD_2Cl_2, 25 °C) showed two peaks at δ 173.6 and 205.4, which correspond to the carbonyl carbon atoms of the ester and the ketone, respectively. As expected, the low-temperature ^{13}C NMR spectrum of a solution prepared by mixing ketodiester **9** and $TiCl_4$ in a 1:1 ratio (0.064 M in CD_2Cl_2, -85 °C) contained three peaks in the carbonyl region at δ 170.2, 179.1, and 218.6 (Figure 3). This provides strong evidence for the formation of the unsymmetric single chelate **12**. Low-temperature spectra of



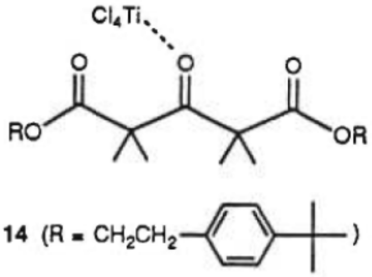
— Figure 3 —

solutions prepared by mixing ketodiester **9** and $TiCl_4$ in a 1:2 ratio were also recorded, but peaks in the carbonyl region remained too broad to permit detailed analysis; however, no conspicuous downfield shift of the carbonyl carbon atom of the ketone was observed, so we doubt that symmetric double chelate **13** is the principal product.



13

Although the two ester groups of unsymmetric single chelate **12** can be distinguished by ^{13}C NMR spectroscopy at -85 °C, symmetrization is nevertheless rapid (eq. 2). Variable-temperature ^{13}C NMR spectroscopy established that coalescence of the ester peaks occurred at T_c = -35 °C, enabling us to estimate that $\Delta G^{\dagger} = 10.2 \pm 0.2$ kcal mol^{-1} for the symmetrization of single chelate **12**.[13] In principle, this process can occur by three distinct mechanisms: 1) Intermolecular or intramolecular attack of the free ester on chelated $TiCl_4$, with displacement of the other ester; 2) complete dissociation of $TiCl_4$, followed by reassociation; or 3) partial dissociation to form the ketone complex **14**, followed by rapid syn-anti isomerization[14] and reassociation. Because



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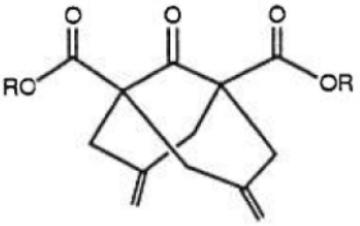
exchange in complexes of $TiCl_4$ normally occurs by dissociation,[14] mechanisms 2) and 3) are more probable. Furthermore, the observed $\Delta G^{\dagger}$ is closely similar to those measured for loss of a single ligand from 1:2 complexes of simple carbonyl compounds with $TiCl_4$.[14] We therefore propose that the symmetrizations of unsymmetric single chelates **4** and **12** both occur by dissociation of the bound ester and reassociation of the free ester.

The absence of the desired double chelates **5** and **13** is noteworthy, because previous experimental and theoretical studies have suggested that the simultaneous coordination of simple ketones by two Lewis acids is enthalpically feasible.[4,6,15] Two factors may account for our failure to observe double chelates derived from 4-ketopimelates and 3-ketoglutarates:

1) Simple ketones are inherently reluctant to form complexes with multiple Lewis acids, so the formation of double chelates by the addition of $TiCl_4$ to unsymmetric single chelates **4** and **12** may not be sufficiently exothermic to compete with the formation of 2:4 complexes such as structure **6a**, even at low concentrations; moreover, ΔS for the formation of double chelates **5** and **13** is made particularly unfavorable by the conformational mobility of ketodiesters **3** and **9**.
2) Careful examination of the octahedral coordination geometry of Ti in complex **6a** and other simple chelates of $TiCl_4$[8] reveals that hypothetical double chelates **5** and **13** are likely to be destabilized by non-bonded Cl•••Cl interactions created when a single carbonyl oxygen atom binds two molecules of $TiCl_4$ at the same time.

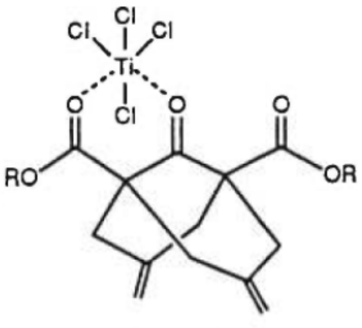
In order to evaluate the importance of conformational mobility, we decided to study the interaction of $TiCl_4$ with bicyclic 3-ketoglutarate **15**, which is a more rigid analogue of ketodiesters



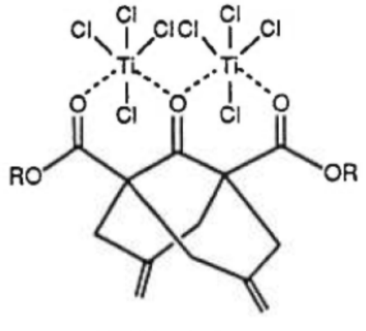
15 ($R = CH_2CH_3$)

7-9. Compound **15** could be made in a single step in 34% yield by treating diethyl 3-ketoglutarate with two equivalents of 3-chloro-2-(chloromethyl)-1-propene in refluxing toluene in the presence of K_2CO_3 and catalytic amounts of $(PPh_3)_2PdCl_2$.[16] The carbonyl region of the ^{13}C NMR spectrum of bicyclic ketodiester **15** (CD_2Cl_2, 25 °C) showed two peaks at δ 170.7 and 207.6, which correspond to the carbonyl carbon atoms of the ester and the ketone, respectively (Figure 4a). In the low-temperature ^{13}C NMR spectrum of a solution prepared by mixing bicyclic ketodiester **15** and $TiCl_4$ in a 1:1 ratio (0.050 M in CD_2Cl_2, -85 °C), a total of thirteen peaks appeared as anticipated, including three in the carbonyl region at δ 167.9, 176.6, and 221.2 (Figure 4b). This provides strong evidence for the formation of the expected unsymmetric single chelate **16**. A similar low-temperature spectrum of a solution prepared by mixing bicyclic

— Figure 4 —



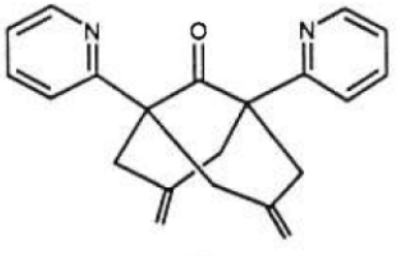
16 (R = CH_2CH_3)



17 (R = CH_2CH_3)

ketodiester **15** and $TiCl_4$ in a 1:2 ratio (0.050 M in CD_2Cl_2, -85 °C) also consisted of thirteen peaks, including three at δ 175.8, 175.9, and 219.3 (Figure 4c). We conclude that the behavior of bicyclic ketodiester **15** resembles that of its more flexible analogues **3** and **9**, and that detectible amounts of symmetric double chelate **17** are not formed when compound **15** and $TiCl_4$ are mixed in a 1:2 ratio, even at the lowest accessible concentrations. Instead, the principal product must again be a 2:4 complex, presumably structure **6b**.

In a final effort to exploit the double chelation of $TiCl_4$ to promote the simultaneous coordination of a ketone by two Lewis acids, we decided to replace ketodiesters by analogues in which the ketone is flanked by stronger Lewis bases.[3] In bicyclic ketone **18**, for example, the carbonyl group is flanked by two pyridines, and we hoped that strong binding of $TiCl_4$ by the pyridines would favor formation of the double chelate **19** by helping compensate for the weakly exothermic double coordination of the central carbonyl group. Compound **18** could be prepared conveniently in one step in 21% yield by treating 1,3-bis(2-pyridyl)-2-propanone[17] with 2-methylene-1,3-propanediol diacetate[18] in refluxing toluene in the presence of K_2CO_3 and catalytic amounts of $Pd(OOCCH_3)_2$ and PPh_3. The carbonyl region of the ^{13}C NMR spectrum of bicyclic dipyridylketone **18** ($CDCl_3$, 25 °C) showed a single peak at δ 213.0. Unfortunately, complexes of compound **18** with $TiCl_4$ were not soluble enough in CD_2Cl_2 to allow their ^1H and ^{13}C NMR



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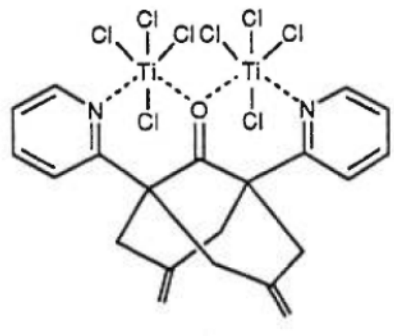

19

spectra to be recorded conveniently at low temperatures. However, in the ^{13}C NMR spectrum of a solution prepared by mixing bicyclic dipyridylketone **18** and $TiCl_4$ in a 1:2 ratio (0.17 M in $CDCl_3$, 25 °C), the carbonyl peak appeared at δ 225.9, which corresponds to a downfield shift of $\Delta\delta$ 12.9. Because our previous experiments show that similar shifts are characteristic of single chelates, we conclude that bicyclic dipyridylketone **18** resembles ketodiesters **3**, **9**, and **15** and does not yield significant amounts of a symmetric double chelate with $TiCl_4$.

Conclusions

In principle, compounds in which the carbonyl group of a simple ketone is flanked by two nearby sites of Lewis basicity are well designed to form symmetric double chelates **2**. In these hypothetical chelates, the oxygen atom of the central carbonyl group uses both of its lone pairs to bind two Lewis acids simultaneously. Unfortunately, persistent efforts to prepare such double chelates by treating ketodiesters and related compounds with two equivalents of $TiCl_4$ were unsuccessful. These instructive failures presumably result from the inherent reluctance of simple ketones to form complexes with multiple Lewis acids and from unfavorable Cl•••Cl interactions that are created in the hypothetical double chelates by the simultaneous attachment of two octahedrally coordinated atoms of titanium to a single carbonyl oxygen atom. We are optimistic that double chelates can be formed when these destabilizing interactions are not present, and we are now studying the complexation of ketodiesters and related compounds with strong Lewis acids that favor non-octahedral coordination.

Experimental Section

Ether and tetrahydrofuran (THF) were dried by distillation from the sodium ketyl of benzophenone, CH_2Cl_2 was dried by distillation from P_2O_5, *N*-isopropylcyclohexylamine was dried by distillation from CaH_2, ethylene oxide was dried by passage over anhydrous $CaSO_4$, and toluene was dried by distillation from sodium. $TiCl_4$ was purified by distillation, and 1,3-bis(2-pyridyl)-2-propanone[17], 2-methylene-1,3-propanediol diacetate[18], and $PdCl_2(PPh_3)_2$[19] were made by published procedures. Other reagents were commercial products that were used without further purification. Flash chromatography was performed in the normal way.[20]

Bis(2-phenylethyl) 4-Oxoheptanedioate (3). A solution of diethyl 4-oxoheptanedioate (2.00 g, 8.69 mmol) and excess 2-phenylethanol (6.34 g, 51.9 mmol) in toluene (15 mL) was treated with a catalytic amount of concentrated H_2SO_4 (85 mg, 0.87 mmol), and the mixture was heated at reflux for 5 h in an apparatus equipped with a Dean-Stark trap. Saturated aqueous $NaHCO_3$ (100 mL) was then added, and the mixture was extracted with ether. Volatiles were removed from the combined extracts by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, toluene (80%)/ether (20%)). This yielded colorless crystals of bis(2-phenylethyl) 4-oxoheptanedioate (**3**; 3.25 g, 8.50 mmol, 98%): mp 37-38 °C; IR (melt) 1735, 1714 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.59 (t, 4H, $^3J = 6.7$ Hz), 2.73 (t, 4H, $^3J = 6.7$ Hz), 2.95 (t, 4H, $^3J = 7.1$ Hz), 4.30 (t, 4H, $^3J = 7.1$ Hz), 7.21-7.32 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 27.9, 35.0, 36.9, 65.0, 126.5, 128.4, 128.8, 137.7, 172.4, 206.7; HRMS (FAB) calcd for $C_{23}H_{26}O_5 + H$ *m/e* 383.1859, found *m/e* 383.1840. Anal. Calcd for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85. Found: C, 72.52; H, 6.88.

2:4 Adduct 6a of Bis(2-phenylethyl) 4-Oxoheptanedioate (3) and $TiCl_4$. A solution of ketodiester **3** (37.5 mg, 0.0981 mmol) in CH_2Cl_2 was stirred at 25 °C under dry N_2 and treated dropwise with $TiCl_4$ (37.2 mg, 0.196 mmol). A supernatant layer of pentane (0.5 mL) was carefully added and allowed to diffuse slowly into the lower phase. This yielded yellow-orange crystals of adduct **6a** as a 1:1 CH_2Cl_2 solvate (67.2 mg, 0.0418 mmol, 85%).

X-ray Crystallographic Study of the CH_2Cl_2 solvate of the 2:4 Adduct 6a of Bis(2-phenylethyl) 4-Oxoheptanedioate (3) and $TiCl_4$.[21] Crystals of the CH_2Cl_2 solvate of the 2:4 adduct **6a** belong to the triclinic space group P1 with a = 7.982(2) Å, b = 9.264(4) Å, c = 22.362(11) Å, α = 86.26(4)°, β = 86.13(3)°, γ = 80.73(3)°, V = 1625.8(11) $Å^3$, D_{calcd} = 1.643 g cm^{-3}, and Z = 1. Data were collected at 205 K, and the structure was refined to $R1$ = 0.1136, $wR2$ = 0.2804 for 6164 reflections with $I > 2.00\ \sigma(I)$.

4-(1,1-Dimethylethyl)benzeneethanol (10). A solution of 1-bromo-4-(1,1-dimethylethyl)benzene (2.46 g, 11.5 mmol) in ether (40 mL) was stirred at 0 °C under dry N_2 and treated dropwise with a solution of BuLi (7.40 mL, 1.55 M in hexane, 11.5 mmol). The solution was kept at 0 °C for 1 h, and then a solution of ethylene oxide (3.6 g, 82 mmol) in ether (10 mL) was added dropwise. The resulting mixture was stirred at 0 °C for 2 h, treated with water, and extracted with ether. Volatiles were removed from the combined extracts by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (85%)/ethyl acetate (15%)). This yielded 4-(1,1-dimethylethyl)benzeneethanol (**10**; 1.57 g, 8.81 mmol, 77%) as a colorless oil: IR (liquid film) 3330 (br) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 9H), 1.43 (s, 1H), 2.85 (t, 2H, ^3J = 6.6 Hz), 3.87 (t, 2H, ^3J = 6.6 Hz), 7.18 (d, 2H, ^3J = 8.2 Hz), 7.35 (d, 2H, ^3J = 8.2 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 31.3, 34.4, 38.6, 63.6, 125.5, 128.7, 135.3, 149.3; HRMS (EI) calcd for $C_{12}H_{18}O$ m/e 173.1358, found m/e 173.1355.

2-[4-(1,1-Dimethylethyl)phenyl]ethyl 2-Methylpropanoate (11). A solution of 4-(1,1-dimethylethyl)benzeneethanol (10; 1.03 g, 5.78 mmol) and 2-methylpropanoic acid (0.52 g, 5.9 mmol) in benzene (10 mL) was treated with a catalytic amount of (1*S*)-10-camphorsulfonic acid (30 mg, 0.13 mmol), and the mixture was heated at reflux for 12 h in an apparatus equipped with a Dean-Stark trap. Saturated aqueous $NaHCO_3$ (10 mL) was then added, and the mixture was extracted with ether. Volatiles were removed from the combined extracts by evaporation under reduced pressure, and the residue was purified by distillation (100 °C/0.3 Torr) to give 2-[4-(1,1-dimethylethyl)phenyl]ethyl 2-methylpropanoate (**11**; 1.27 g, 5.11 mmol, 88%) as a colorless liquid: IR (film) 1731 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (d, 6H, ^3J = 7.0 Hz), 1.31 (s, 9H), 2.53 (septuplet, 1H, ^3J = 7.0 Hz), 2.91 (t, 2H, ^3J = 7.1 Hz), 4.27 (t, 2H, ^3J = 7.1 Hz), 7.16 (d, 2H, ^3J = 8.2 Hz), 7.33 (d, 2H, ^3J = 8.2 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 18.9, 31.3, 34.0, 34.4, 34.6, 64.7, 125.3, 128.6, 134.8, 149.3, 177.0; HRMS (EI) calcd for $C_{16}H_{24}O_2$ *m/e* 248.1776, found *m/e* 248.1756.

Bis[2-[4-(1,1-Dimethylethyl)phenyl]ethyl] 2,2,4,4-Tetramethyl-3-oxopentanedioate (9). A solution of *N*-isopropylcyclohexylamine (1.13 g, 8.00 mmol) in THF (10 mL) was stirred at -78 °C under dry N_2 and treated dropwise with a solution of BuLi (5.3 mL, 1.5 M in hexane, 8.0 mmol). The solution was kept at -78 °C for 40 min, and then a solution of 2-[4-(1,1-dimethylethyl)phenyl]ethyl 2-methylpropanoate (**11**; 1.98 g, 7.97 mmol) in THF (10 mL) was added dropwise. The resulting solution was kept at -78 °C for 30 min and was then added dropwise to a stirred solution of 1,1′-carbonyldiimidazole (0.630 g, 3.89 mmol) in THF (10 mL) at 25 °C. The mixture was kept at 25 °C for 12 h, treated with water, and extracted with ether. Volatiles were removed from the combined extracts by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (95%)/ethyl acetate (5%)) to give bis[2-[4-(1,1-dimethylethyl)phenyl]ethyl] 2,2,4,4-tetramethyl-3-oxopentanedioate (**9**; 0.882 g, 1.69 mmol, 43%) as a colorless solid. An analytically pure sample was prepared by recrystallization from hexane: mp 95-97 °C; IR (melt) 1740, 1730, 1710 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 12H), 1.29 (s, 18H), 2.87 (t, 4H, ^3J = 6.9 Hz), 4.25 (t, 4H, ^3J = 6.9 Hz), 7.11 (d, 4H, ^3J = 8.2 Hz), 7.31 (d, 4H, ^3J = 8.2 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 23.4, 31.3, 34.2, 34.3, 55.1, 65.8, 125.4, 128.5, 134.3, 149.4, 173.3, 205.1; HRMS (FAB) calcd for $C_{33}H_{46}O_5$ + H *m/e* 523.3423, found *m/e* 523.3465.

Diethyl 3,7-Dimethylene-9-oxobicyclo[3.3.1]nonane-1,5-dicarboxylate (15). A mixture of diethyl 3-ketoglutarate (5.04 g, 24.9 mmol), 3-chloro-2-(chloromethyl)-1-propene (6.91 g, 55.3 mmol), K_2CO_3 (15.2 g, 110 mmol), and $PdCl_2(PPh_3)_2$ (1.75 g, 2.49 mmol) in toluene (18 mL) was stirred at reflux for 36 h. The mixture was then cooled to 25 °C and filtered, and volatiles were removed from the filtrate by evaporation under reduced pressure. The residue was purified by flash chromatography (silica, hexane (85%)/ethyl acetate (15%)) to give colorless crystals of diethyl 3,7-dimethylene-9-oxobicyclo[3.3.1]nonane-1,5-dicarboxylate (**15**; 2.60 g, 8.49 mmol, 34%): mp 48-49 °C; IR (melt) 1735, 1713, 1652 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, 6H, ^3J = 7.1 Hz), 2.76 (d, 4H, ^2J = 15.4 Hz), 3.33 (d, 4H, ^2J = 15.4 Hz), 4.26 (q, 4H, ^3J = 7.1 Hz), 4.87 (t, 4H, ^4J = 2.2 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.1, 44.0, 56.9, 61.6, 115.0, 138.7, 170.5, 206.9; HRMS (FAB) calcd for $C_{17}H_{22}O_5$ + H *m/e* 307.1545, found *m/e* 307.1546. Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.35; H, 7.28.

3,7-Dimethylene-1,5-bis(2-pyridyl)bicyclo[3.3.1]nonan-9-one (18). A suspension of $Pd(OOCCH_3)_2$ (0.106 g, 0.472 mmol) and PPh_3 (0.493 g, 1.88 mmol) in toluene (25 mL) was stirred at 25 °C for 30 min, and then a solution of 2-methylene-1,3-propanediol diacetate (3.57 g, 20.7 mmol) in toluene (20 mL) was added, followed by a suspension of 1,3-bis(2-pyridyl)-2-propanone (2.00 g, 9.42 mmol) and K_2CO_3 (7.82 g, 56.6 mmol) in toluene (10 mL). The resulting mixture was stirred at reflux for 45 h, cooled to 25 °C, and filtered. Volatiles were removed from the filtrate by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (70%)/ethyl acetate (30%)) to give a mixture of 3,7-dimethylene-1,5-bis(2-pyridyl)bicyclo[3.3.1]nonan-9-one (**18**) and the corresponding hydrate. Dehydration was achieved by dissolving the crude product in chlorobenzene (60 mL) and removing water by azeotropic distillation.[22] This provided bicyclic dipyridylketone **18** (0.621 g, 1.96 mmol, 21%) as a tan solid. Recrystallization from hexane provided an analytically pure sample: mp 115-116 °C; IR (melt) 1712, 1646 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.11 (d, 4H, ^2J = 15.3 Hz), 3.46 (d, 4H, ^2J = 15.3 Hz), 4.96 (t, 4H, ^4J = 2.1 Hz), 7.16 (m, 2H), 7.37 (m, 2H), 7.65 (m, 2H), 8.60 (m, 2H); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 47.6, 55.4, 114.2, 121.7, 123.0, 135.6, 141.2, 148.3, 160.5, 213.0; HRMS (FAB) calcd for $C_{21}H_{20}N_2O$ + H *m/e* 317.1654, found *m/e* 317.1665. Anal. Calcd for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37. Found: C, 76.89; H, 6.38.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **9**, **10**, **11**, and **18** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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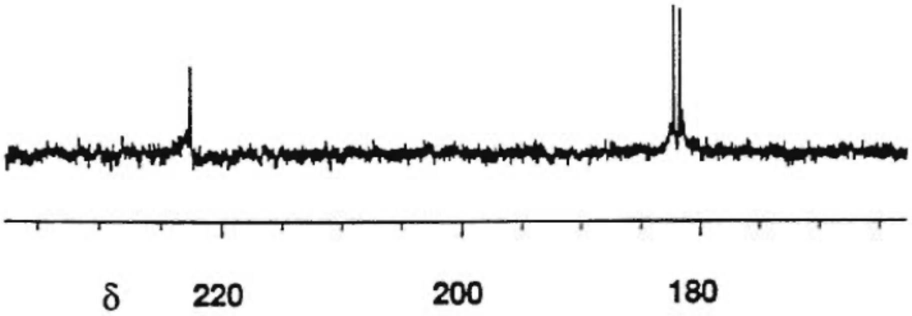


Figure 1. The carbonyl region of the low-temperature ^{13}C NMR spectrum of a solution prepared by mixing ketodiester **3** and $TiCl_4$ in a 1:2 ratio (0.060 M in CD_2Cl_2, -65 °C).

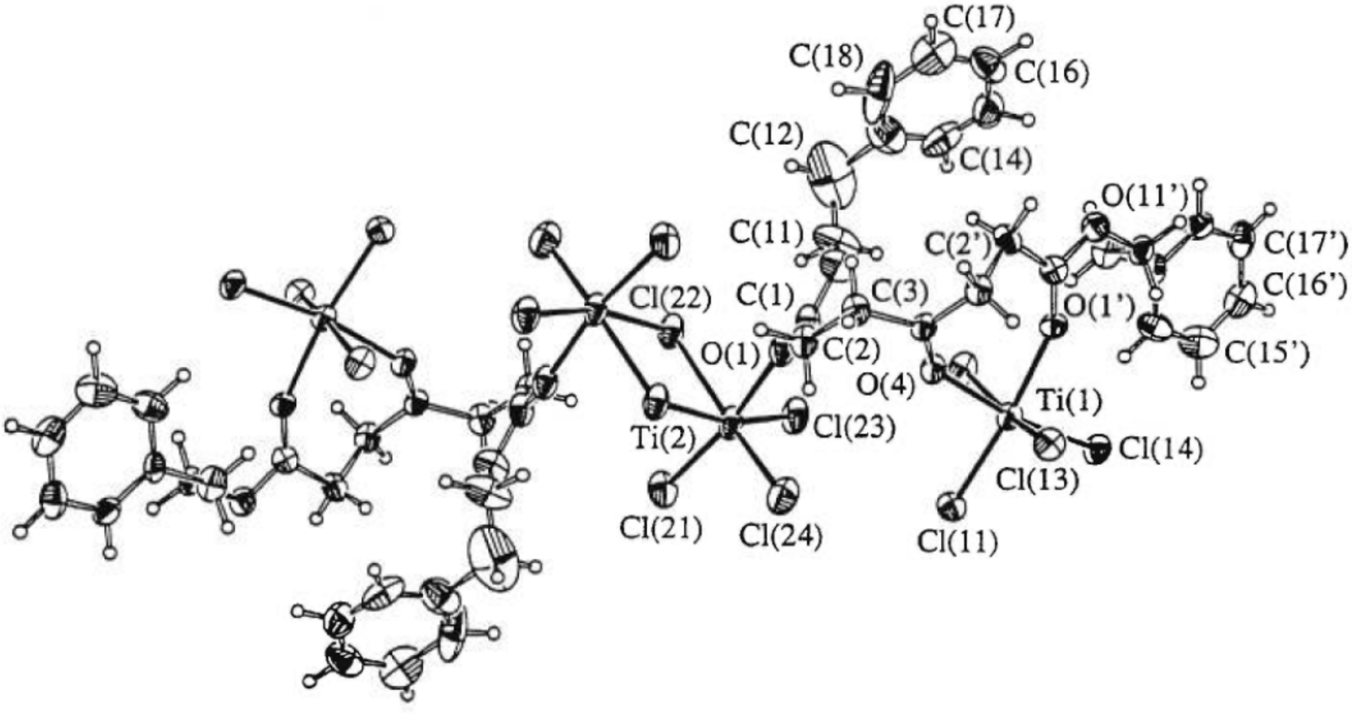


Figure 2. ORTEP view of the structure of complex **6a**, which is obtained when ketodiester **3** and $TiCl_4$ are mixed in CH_2Cl_2 in a 1:2 ratio. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, and hydrogen atoms are shown as spheres of arbitrary size. All bonds to titanium are drawn using solid lines. Included CH_2Cl_2 is not shown.

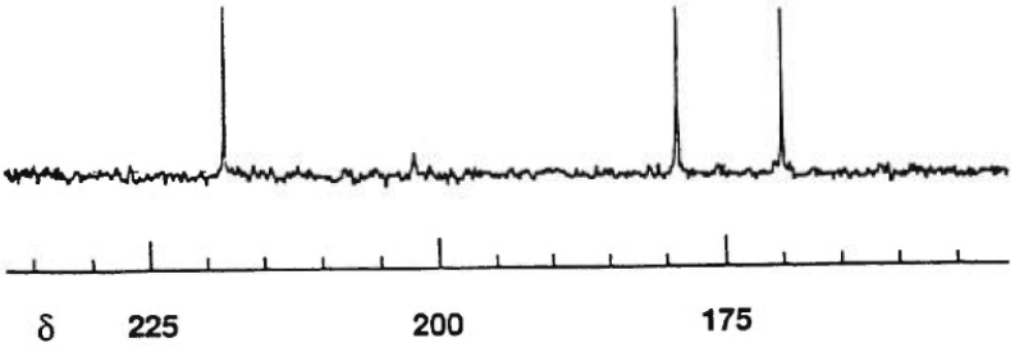


Figure 3. The carbonyl region of the low-temperature ^{13}C NMR spectrum of a solution prepared by mixing ketodiester **9** and $TiCl_4$ in a 1:1 ratio (0.064 M in CD_2Cl_2, -85 °C).

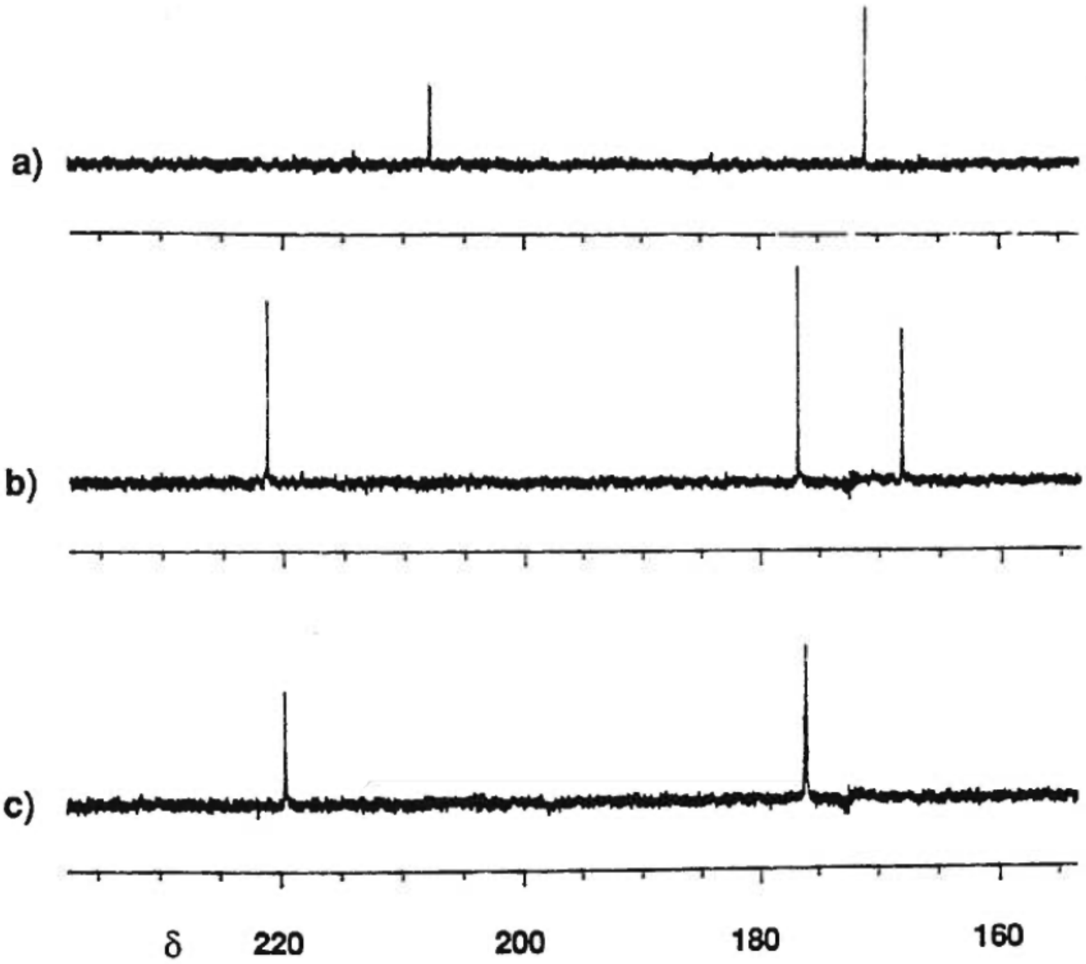
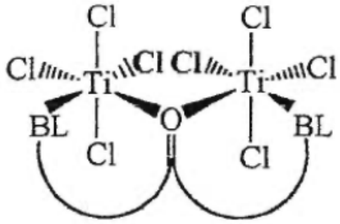


Figure 4. The carbonyl region of the ^{13}C NMR spectrum of a) a solution of pure bicyclic ketodiester **15** (CD_2Cl_2, 25 °C); b) a solution prepared by mixing ketodiester **15** with $TiCl_4$ in a 1:1 ratio (0.050 M in CD_2Cl_2, -85 °C); and c) a solution prepared by mixing ketodiester **15** with $TiCl_4$ in a 1:2 ratio (0.050 M in CD_2Cl_2, -85 °C).

3.4 CONCLUSION

Tous les efforts déployés dans notre étude visant à complexer simultanément l'oxygène d'une cétone simple par deux équivalents de $TiCl_4$ en utilisant la stratégie de la double chélation sont vains. Bien que nous ayons utilisé une diversité de systèmes flexibles ou rigides capables de former des doubles chélates incorporant des cycles à six ou sept chainons, nous n'avons pas réussi à atteindre notre objectif. Il semblerait que dans les doubles chélates hypothétiques **30**, l'interaction entre les atomes de chlore empêche sérieusement la formation de tels complexes.



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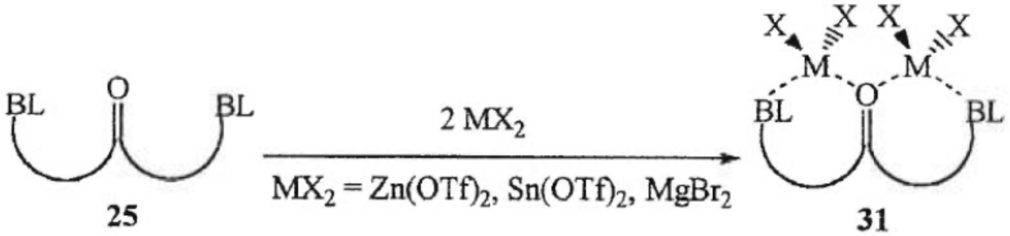
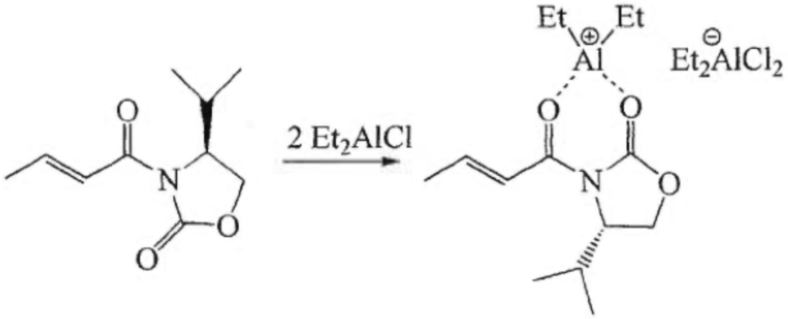
Nous avons essayé de surmonter ces contraintes attribuées à l'hexacoordination octaédrique préférentielle du $TiCl_4$[46] en choisissant d'autres acides de Lewis moins volumineux, divalents, et favorisant une géométrie de coordination tetraédrique afin d'éviter les interactions stérique et électrostatique entre les ligands des deux métaux (Schéma 9). Malheureusement, les très faibles solubilités des acides de Lewis divalents représentés au Schéma 9, dans les solvants appropriés pour ce genre d'étude, ne nous a pas permis de conclure si les double chélates **31** sont réalisables.

Schéma 9



Nous avons également tenté d'utiliser le Et_2AlCl, qui est capable de former des chélates cationiques avec des N-acyloxazolidinones α,β-insaturées et chirales, utilisées comme diènophiles dans des réactions de cycloaddition de Diels-Alder hautement stéréoselectives[47]. Par exemple, des investigations faites par la RMN à basse température ont indiqué que la réaction de la N-crotonoyloxazolidinone **32** avec deux équivalents de Et_2AlCl produit le chélate cationique **33** (Schéma 10)[48]. Nous avons aspiré à ce que la réaction d'un céto diester avec quatre équivalents de Et_2AlCl formerait un double chélate cationique. Malheureusement, le Et_2AlCl a réduit le groupe carbonyle de la fonction cétone.

Schéma 10



32 **33**

Malgré l'insuccès dans nos tentatives ambitieuses de former des doubles chélates, nous avons toutefois exploré certaines questions qui sont importantes. Nos résultats sont toujours compatibles avec l'hypothèse qu'une cétone simple est intrinsèquement assez basique pour être doublement complexée par deux sites acides de Lewis. Nous avons décidé d'atteindre notre objectif en utilisant des acides de Lewis bidentates possédant une structure rigide et bien organisée pour reconnaître, fixer et activer fortement un substrat.

CHAPITRE 4

ACIDES DE LEWIS BIDENTATES. SYNTHÈSE D'UN SQUELETTE ORGANIQUE CONÇU POUR FIXER DEUX SITES ACIDES DE LEWIS DANS UNE ORIENTATION CONVERGENTE

4.1 INTRODUCTION

N'étant pas parvenus à prouver que les céto diesters sont capables de former des doubles chélates avec les acides de Lewis, nous avons envisagé d'étudier la complexation simultanée intermoléculaire d'un groupe carbonyle par deux sites acides de Lewis en empruntant la voie des acides de Lewis bidentates. Jusqu'à présent, seuls les acides de Lewis bidentates dérivés du phénylènedimercure, élaborés par Wuest et collaborateurs,[22,24] sont capables de complexer simultanément l'oxygène d'un groupe carbonyle. Cependant, l'association de ces acides de Lewis du mercure avec les composés carbonylés est faible[49]. Ces résultats prouvent que la complexation conjointe de la fonction carbonyle par deux sites acides de Lewis est faisable et suggèrent que le choix d'autres acides de Lewis bidentates plus durs[36] que ceux du mercure permettrait une double complexation et une forte activation d'un substrat carbonylé.

Pour atteindre cet objectif, nous avons choisi de synthétiser des acides de Lewis bidentates d'aluminium et de titane et d'orienter les deux sites acides de Lewis sur un squelette rigide de façon convergente et de les rendre disponibles pour interagir simultanément avec l'oxygène d'un groupe carbonyle.

Ayant démontré que le diol **17** est un acide de Brønsted bidentate capable de coordiner doublement l'oxygène d'une fonction cétone simple, nous avons décidé d'utiliser le même squelette pour former un acide de Lewis bidentate. La transformation de ses deux groupes hydroxyles en aryloxydes d'aluminium ou de titane donnerait des acides de Lewis bidentates durs à condition que la distance qui sépare les deux oxygènes hydroxy soit convenable pour éviter toute alternative non désirée (Schéma 6).

Nous présentons dans l'article suivant la synthèse du diol **17**, qui a suscité de l'ingéniosité afin d'éviter toute cyclisation intramoléculaire causée par l'addition d'un groupe hydroxyle au triple lien adjacent[32]. Nous rapportons également nos efforts dans l'élaboration et la caractérisation par les études cristallographiques d'un acide de Lewis bidentate potentiel.

4.2 ARTICLE 3 : *Organometallics* **1996**, **15**, 2345.

MULTIDENTATE LEWIS ACIDS. SYNTHESIS OF AN ORGANIC FRAMEWORK DESIGNED TO HOLD TWO SITES OF LEWIS ACIDITY IN A CONVERGENT ORIENTATION.

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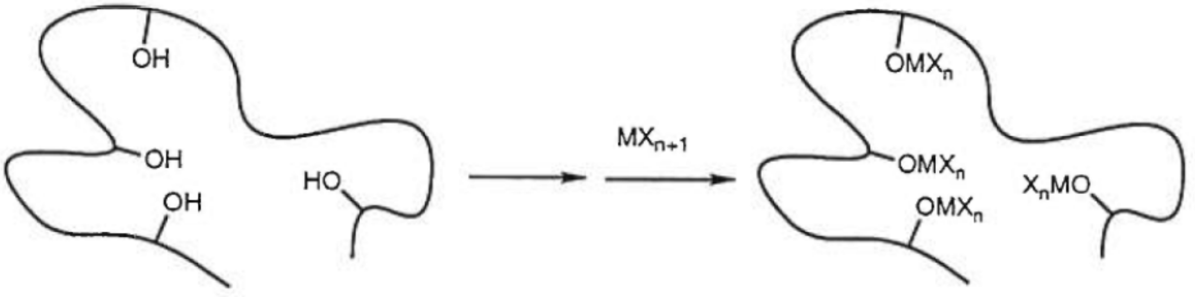
Abstract:

Treatment of 2,2'-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (2) with 2 equiv of $Al(i\text{-}Bu)_3$ converts the hydroxyl groups into potentially Lewis acidic $OAl(i\text{-}Bu)_2$ groups with a convergent orientation. Their intramolecular interaction produces the novel structure **11**, which incorporates an Al_2O_2 ring that is markedly distorted by constraints imposed by the diphenylacetylene framework. Unlike normal Al_2O_2 rings, which are planar and have trigonal planar oxygen atoms, the Al_2O_2 ring of compound **11** is puckered, and its oxygen atoms are distinctly pyramidalized. In addition, the average Al-O bond length in compound 11 (1.913(2) Å) is significantly longer than these found in related dimers of alkylaluminum alkoxides and aryloxides (1.840 - 1.895 Å).

Introduction

Multidentate Lewis acids interest chemists because they can be designed so that their multiple electrophilic sites are held in orientations favoring the recognition, binding, and chemical activation of molecules with complementary arrangements of basic sites.[2] We have shown that a convenient method for synthesizing multidentate Lewis acids is to add metal salts MX_{n+1} or related species to compounds containing hydroxyl groups or similar sites suitably oriented by an organic framework (eq. 1).[3] This yields metal alkoxides **1** with multiple Lewis acidic sites OMX_n. In this paper, we show that 2,2'-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**2**) provides a framework of potential value for the construction of bidentate Lewis acids with convergent electrophilic sites.[4, 5]



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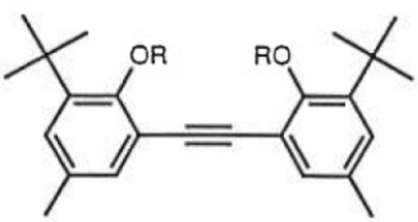
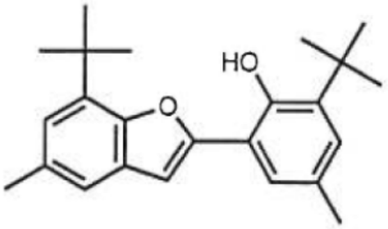


2 (R = H)
8 (R = Ac)



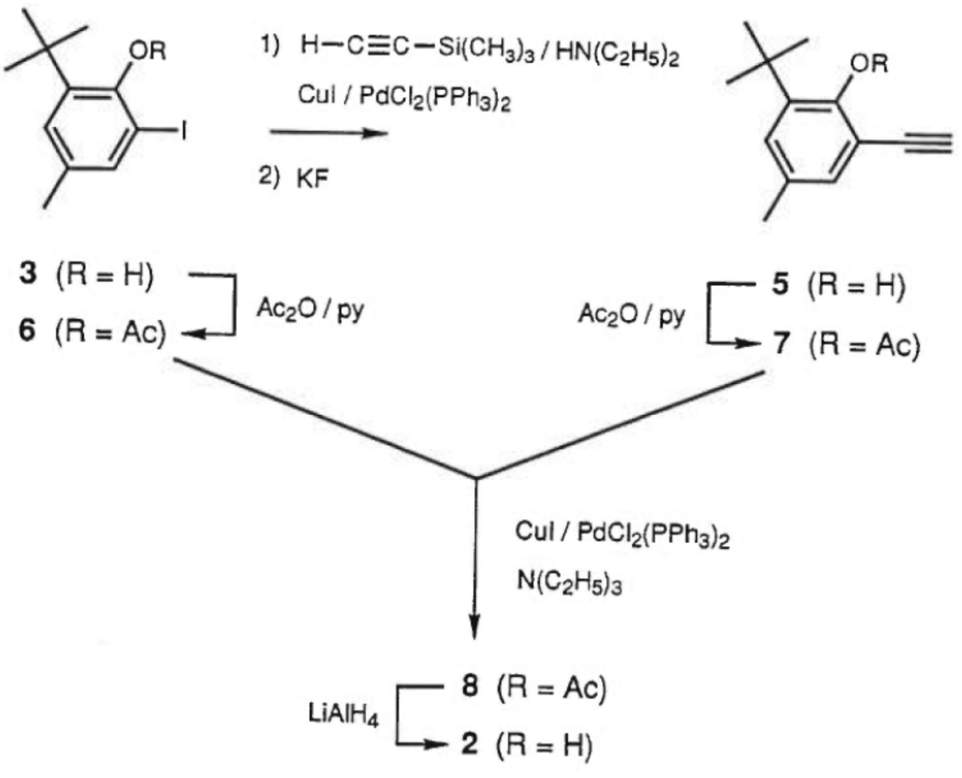
4

Results and Discussion

1) Synthesis of Diphenol 2

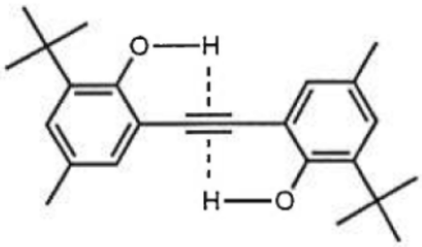
Derivatives of 2-ethynylphenol are known to form benzofurans by rapid intramolecular addition of the hydroxyl group to the adjacent triple bond,[6] so we were not certain that diphenol **2** could be prepared and characterized. In fact, attempts to prepare compound **2** in a single step by Pd(0)/Cu(I)-catalyzed coupling of 2-(1,1-dimethylethyl)-6-iodo-4-methylphenol (**3**)[7] with acetylene were unsuccessful and led to the formation of benzofuran **4** in 80% yield. However, the less direct route summarized in Scheme 1 allowed us to synthesize diphenol **2** from iodophenol **3** in six steps in 62% overall yield. Compound **3** was first converted into 2-(1,1-dimethylethyl)-6-

Scheme 1



ethynyl-4-methylphenol (**5**) in 95% overall yield by direct Pd(0)/Cu(I)-catalyzed coupling with (trimethylsilyl)acetylene followed by treatment with methanolic KF.[8] It is noteworthy that OH stretching in ethynylphenol **5** occurs at 3509 cm^{-1} (0.2 M in CH_2Cl_2), whereas the corresponding vibration in 2,6-bis(1,1-dimethylethyl)-4-methylphenol appears at 3638 cm^{-1}. This large difference indicates that compound **5** must incorporate a hydroxyl group intramolecularly π-bonded to the triple bond.[9]

Phenols **3** and **5** were then converted in high yields into the corresponding acetates **6** and **7**, which were coupled by a standard procedure to give the diacetate **8** of required diphenol **2** in 86% yield. Initial attempts to prepare compound **2** by using conventional methods to deprotect diacetate **8** yielded only benzofuran **4**, suggesting that diphenol **2** might in fact be too reactive to isolate. Finally, however, we discovered that reductive deprotection could be effected with $LiAlH_4$ to give compound **2** in 90% yield. The OH region of its IR spectrum (0.2 M in CH_2Cl_2) contains a single sharp band at 3504 cm^{-1}, showing that both hydroxyl groups are equivalent and doubly π-bonded to the central triple bond in an approximately symmetric manner.[10] Both in the solid state and solution, structure **9** is more stable than the unsymmetrically hydrogen-bonded alternative **10**, presumably because even the closest approach of oxygen atoms held at the ortho positions of an undistorted diphenylacetylene framework leaves them much too far apart (~4.1 Å) to permit strong hydrogen bonding.



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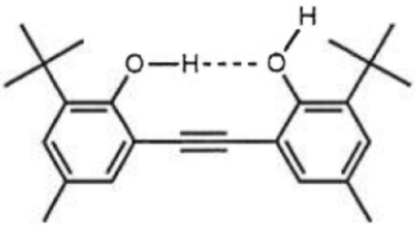
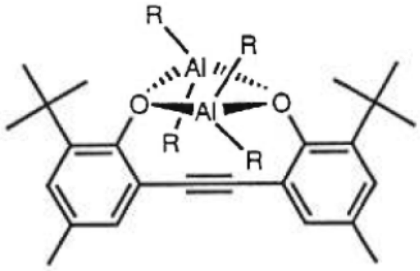


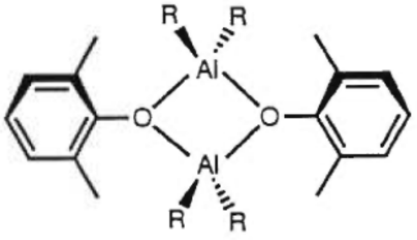
10

2) Reaction of Diphenol 2 with $Al(i\text{-}Bu)_3$

Diphenol **2** was treated with 2 equiv of $Al(i\text{-}Bu)_3$ in pentane in order to convert the hydroxyl groups into convergent Lewis acidic $OAl(i\text{-}Bu)_2$ groups.[11] Slow evaporation of solvent gave a 93% yield of crystalline product. The simplicity of its ^1H and ^{13}C NMR spectra provided evidence of high symmetry, but two distinct types of i-Bu group were nevertheless present in a 1:1 ratio. These data are inconsistent with simple structures in which the $OAl(i\text{-}Bu)_2$ groups are unassociated; however, they are fully compatible with structure **11**, in which the two $OAl(i\text{-}Bu)_2$ groups interact intramolecularly to form a four-membered Al_2O_2 ring characteristic of dimers of related dialkylaluminum alkoxides and aryloxides.[12-14] This surprised us for two reasons: The $OAl(i\text{-}Bu)_2$ groups are constrained by the relatively rigid diphenylacetylene framework of compound **11** to be too far apart for normal bonding, and dialkylaluminum aryloxides derived from similarly hindered phenols are typically monomeric.[11]



11 (R = i-Bu)



12 (R = i-Bu)

An X-ray crystallographic study confirmed that structure **11** is adopted in the solid state. The results of this study, summarized in Figure 1 and Tables 1-2, show that structure **11** incorporates several unusual features. To minimize the O···O distance, the aromatic rings are essentially coplanar. In addition, the bond angles at the acetylenic carbon atoms are distinctly bent within the molecular plane in the direction of the Al_2O_2 ring, and the average $C\text{-}C \equiv C$ angle is 167.0(2)°. This distortion further reduces the separation of the oxygen atoms to 2.542(2) Å, but they are still too far apart to allow the formation of an Al_2O_2 ring with normal geometric parameters, including an O···O distance no longer than 2.48 Å.[12-14] Previously observed Al_2O_2

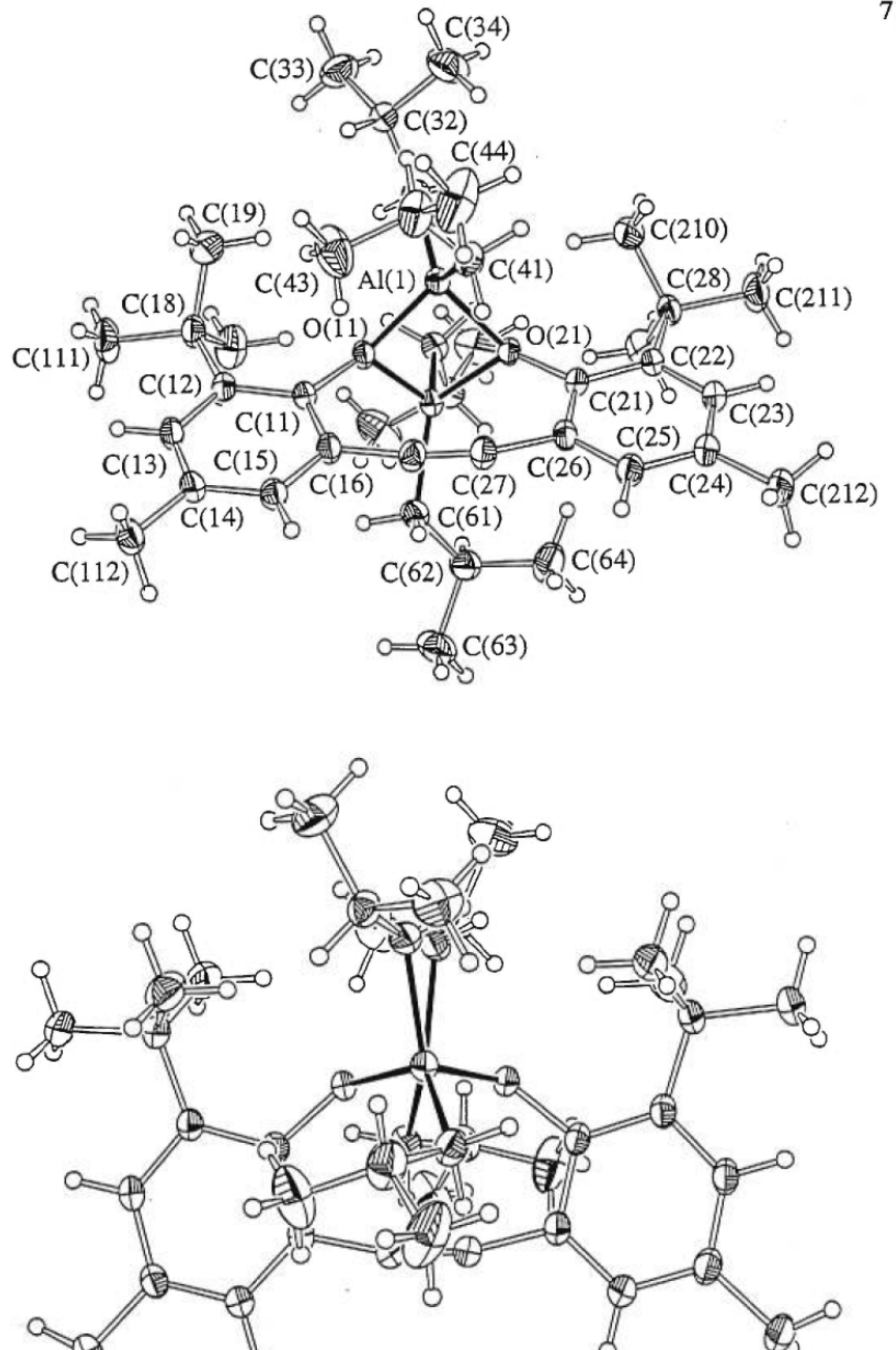


Figure 1. ORTEP drawings of two views of the structure of aluminum aryloxide **11**. Hydrogen atoms appear as spheres of arbitrary size, and other atoms are represented by ellipsoids corresponding to 40% probability. Bonds to aluminum are shown as solid lines. The upper figure shows the Al_2O_2 ring and the atomic numbering, and the lower figure highlights the puckering of the Al_2O_2 ring and the bending of angles at the acetylenic carbon atoms.

rings are rigorously or approximately planar, and the oxygen atoms are normally trigonal planar.[12-14] In sharp contrast, the Al_2O_2 ring of structure **11** is conspicuously puckered, and the average Al-O-Al-O dihedral angle is 16.64(6)°; in addition, the oxygen atoms are distinctly pyramidalized, and the sum of their average bond angles is 347.44(12)°. These notable distortions arise because the oxygen atoms are joined by a diphenylacetylene framework, thereby placing the Al_2O_2 ring in a strained bicyclo[6.1.1] skeleton that incorporates a triple bond. Puckering permits the bridgehead oxygen atoms to approach trigonal planar coordination and decreases repulsive interactions of the aluminum atoms and their i-Bu substituents with the bridging diphenylacetylene unit.

The unique constraints imposed on structure **11** make its average Al-O bond length (1.913(2) Å) markedly longer than those observed in previously studied dimers of alkylaluminum alkoxides and aryloxides (1.840-1.895 Å).[12-14] Distortions in structure **11** close the Al-O-Al angles to an average value of 94.29(6)° and open the O-Al-O angles to an average value of 83.27(6)°. Both values lie at or near the limits observed for comparable Al_2O_2 rings.[12-14] In particular, comparison of the average Al-O-Al and O-Al-O angles in structure **11** with those in the very closely related dimer **12** (101.5(1)° and 78.5(1)°, respectively)[14] clearly reveals the striking geometric effect of constraints imposed by the diphenylacetylene framework. All of these deformations suggest that $-\Delta H$ for intramolecular association of the $OAl(i\text{-}Bu)_2$ groups in structure **11** must be smaller than that for intermolecular associations of related alkylaluminum alkoxides and aryloxides.

Other geometric features of structure **11** are unexceptional. For example, the average Al-C bond length (1.968(2) Å), non-bonded Al···Al distance (2.805(1) Å), length of the triple bond (1.196(3) Å), and exocyclic C-Al-C Angle (120.00(10)°) resemble those found in related structures.[12-15] As expected, the aluminum atoms have highly distorted tetrahedral geometries, and the bond angles vary widely from 83.13(6) to 126.31(9)°.

Conclusions

Our observations suggest that derivatives of 2,2'-(1,2-ethynediyl)bis[phenol] can be used as frameworks for constructing bidentate Lewis acids with convergent electrophilic sites. In structure **11**, obtained by treating diphenol **2** with Al(i-Bu)$_3$, the convergence of two potentially Lewis acidic OAl(i-Bu)$_2$ groups permits their direct intramolecular association to form an Al_2O_2 ring. Constraints imposed by the diphenylacetylene framework cause novel geometric distortions of this ring, suggesting that $-\Delta H$ for intramolecular association is smaller than that for intermolecular associations of related alkylaluminum alkoxides and aryloxides. This may permit compound **11** or related derivatives to act as bidentate Lewis acids and to serve as effective receptors for bidentate Lewis bases with two complementary sites.

EXPERIMENTAL SECTION

Tetrahydrofuran (THF) was dried by distillation from the sodium ketyl of benzophenone, pentane was dried by distillation from CaH_2, acetic anhydride (Ac_2O) was purified by distillation from P_2O_5, pyridine was dried by distillation from NaOH, and dimethylformamide (DMF), $HN(C_2H_5)_2$, and $N(C_2H_5)_3$ were dried over anhydrous $MgSO_4$ and purified by distillation. Other commercial reagents were used without further purification. Flash chromatography was performed in the normal way.[16]

2-[7-(1,1-Dimethylethyl)-5-methylbenzofuran-2-yl]-6-(1,1-dimethylethyl)-4-methylphenol (4). A suspension of 2-(1,1-dimethylethyl)-6-iodo-4-methylphenol (**3**; 298 mg, 1.03 mmol),[7] $PdCl_2(PPh_3)_2$ (36 mg, 0.051 mmol), and CuI (19 mg, 0.10 mmol) in dry $HN(C_2H_5)_2$ (15 mL) was stirred at 25°C under dry Ar, and a stream of acetylene was passed through the mixture for 6 h. After filtration and removal of volatiles from the filtrate by evaporation under reduced pressure, H_2O was added and the mixture was extracted with $CHCl_3$. The combined extracts were dried with anhydrous $MgSO_4$, and solvent was removed by evaporation under reduced pressure. Flash chromatography (silica, hexane (93%) / ethyl acetate (7%)) of the residue yielded 2-[7-(1,1-dimethylethyl)-5-methylbenzofuran-2-yl]-6-(1,1-dimethylethyl)-4-methylphenol (**4**; 290 mg, 0.827 mmol, 80%) as a colorless solid, which was further purified by recrystallization from hexane: mp 146-147°C ; IR (KBr) 3489 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.49 (s, 9H), 1.56 (s, 9H), 2.35 (s, 3H), 2.46 (s, 3H), 6.91 (s, 1H), 7.04 (m, 1H), 7.13 (m, 1H), 7.26 (m, 1H), 7.31 (m, 1H), 7.45 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.8, 21.5, 29.6, 30.1, 34.1, 34.9, 102.8, 116.5, 118.6, 122.7, 125.6, 128.7, 128.8, 129.1, 132.7, 133.9, 137.3, 150.2, 150.7, 154.2; HRMS (FAB) calcd for $C_{24}H_{30}O_2$ 350.2246, found 350.2262.

2-(1,1-Dimethylethyl)-6-ethynyl-4-methylphenol (5). A suspension of 2-(1,1-dimethylethyl)-6-iodo-4-methylphenol (**3**; 4.32 g, 14.9 mmol),[7] $PdCl_2(PPh_3)_2$ (0.52 g, 0.74 mmol), and CuI (0.28 g, 1.5 mmol) in a mixture of dry $HN(C_2H_5)_2$ (16 mL) and dry DMF (4 mL) was stirred at 25°C under dry N_2 and treated with (trimethylsilyl)acetylene (2.19 g, 22.3 mmol). The mixture was kept at 25°C for 18 h, treated with 0.1 N aqueous HCl, and extracted with $CHCl_3$. The combined extracts were washed with saturated aqueous $NaHCO_3$ and H_2O, and then they were dried with anhydrous $MgSO_4$.

Evaporation of volatiles under reduced pressure left a residue that was treated with CH_3OH (60 mL) and $KF \cdot 2H_2O$ (4.21 g, 44.7 mmol). The resulting mixture was stirred at 25°C for 7 h, diluted with H_2O, and extracted with $CHCl_3$. Evaporation of volatiles under reduced pressure left a residue that was purified by flash chromatography (silica, hexane (95%) / ethyl acetate (5%)) to provide 2-(1,1-dimethylethyl)-6-ethynyl-4-methylphenol (**5**; 2.66 g, 14.1 mmol, 95%) as a colorless solid, which was further purified by recrystallization from pentane: mp 31-32°C; IR (CH_2Cl_2) 3509, 3299, 2099 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 9H), 2.25 (s, 3H), 3.45 (s, 1H), 6.00 (s, 1H), 7.06 (d, 1H, ^4J = 1.6 Hz), 7.07 (d, 1H, ^4J = 1.6 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.5, 29.3, 34.6, 79.0, 83.9, 108.4, 128.6, 129.2, 129.4, 135.4, 153.9; HRMS (EI) calcd for $C_{13}H_{16}O$ 188.1201, found 188.1201.

2-(1,1-Dimethylethyl)-6-iodo-4-methylphenol Acetate (6). A solution of 2-(1,1-dimethylethyl)-6-iodo-4-methylphenol (**3**; 3.33 g, 11.5 mmol)[7] in a mixture of dry pyridine (7 mL) and acetic anhydride (9 mL) was kept at 25° C for 36 h. Volatiles were then removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (80%) / ethyl acetate (20%)) to give pure 2-(1,1-dimethylethyl)-6-iodo-4-methylphenol acetate (**6**; 3.35 g, 10.1 mmol, 88%) as a colorless oil: bp 113°C / 0.3 Torr; IR (liquid film) 1767 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 9H), 2.31 (s, 3H), 2.39 (s, 3H), 7.19 (d, 1H, ^4J = 1.3 Hz), 7.56 (d, 1H, ^4J = 1.3 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.7, 22.3, 30.4, 35.0, 94.0, 128.6, 137.1, 138.0, 142.9, 147.4, 168.9; HRMS (FAB) calcd for $C_{13}H_{17}IO_2$+H 333.0352, found 333.0363.

2-(1,1-Dimethylethyl)-6-ethynyl-4-methylphenol Acetate (7). A solution of 2-(1,1-dimethylethyl)-6-ethynyl-4-methylphenol (**5**; 2.07 g, 11.0 mmol) in a mixture of dry pyridine (7 mL) and acetic anhydride (9 mL) was kept at 25°C for 24 h. Volatiles were then removed under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (90%) / ethyl acetate (10%)) to give 2-(1,1-dimethylethyl)-6-ethynyl-4-methylphenol acetate (**7**; 2.43 g, 10.6 mmol, 96%) as a colorless solid. Recrystallization from hexane provided an analytically pure sample in the form of colorless needles: mp 68-70°C; IR (melt) 2108, 1767 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 9H), 2.31 (s, 3H), 2.36 (s, 3H), 3.19 (s, 1H), 7.20 (d, 1H, ^4J = 1.6 Hz), 7.22 (d, 1H, ^4J = 1.6 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.9, 21.5, 30.2, 34.4, 79.7, 81.0, 117.2, 129.0, 131.8, 135.0, 141.5, 148.8, 169.0; HRMS (FAB) calcd for $C_{15}H_{18}O_2$+H 231.1385, found 231.1395. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.36; H, 8.14.

2,2'-(1,2-Ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] Diacetate (8). A suspension of 2-(1,1-dimethylethyl-6-iodo-4-methylphenol acetate (**6**; 1.08 g, 3.25 mmol), $PdCl_2(PPh_3)_2$ (0.11 g, 0.16 mmol), and CuI (0.060 g, 0.32 mmol) in dry $N(C_2H_5)_3$ (5 mL) was stirred at 25°C under dry Ar, and a solution of 2-(1,1-dimethylethyl)-6-ethynyl-4-methylphenol acetate (7; 1.12 g, 4.86 mmol) in dry $N(C_2H_5)_3$ (7 mL) was added dropwise. The resulting mixture was kept at 25°C for 1 h, treated with 0.1 N aqueous HCl, and extracted with $CHCl_3$. The combined extracts were washed with water and dried with anhydrous $MgSO_4$, and volatiles were then removed by evaporation under reduced pressure. Purification of the residue by flash chromatography (silica, hexane (90%) / ethyl acetate (10%)) provided 2,2'-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] diacetate (**8**; 1.22 g, 2.81 mmol, 86%) as a colorless solid, which was further purified by recrystallization from $CHCl_3$: mp 158-161°C; IR (KBr) 1763 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 18H), 2.32 (s, 6H), 2.36 (s, 6H), 7.18 (d, 2H, $^4J = 1.6$ Hz), 7.21 (d, 2H, $^4J = 1.6$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.9, 21.3, 30.2, 34.4, 89.0, 118.2, 128.6, 131.2, 134.9, 141.5, 148.2, 169.2; HRMS (FAB) calcd for $C_{28}H_{34}O_4$+H 435.2535, found 435.2521.

2,2'-(1,2-Ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (2). A suspension of $LiAlH_4$ (0.23 g, 6.1 mmol) in dry THF (15 mL) was stirred at -78°C under dry Ar and treated dropwise with a solution of 2,2'-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol diacetate (**8**; 1.08 g, 2.49 mmol) in dry THF (10 mL). The cooling bath was removed, and the mixture was kept at 25°C for 12 h. The mixture was then cooled to 0°C, treated dropwise with H_2O (10 mL), filtered through Celite, and extracted with $CHCl_3$. The combined extracts were washed with H_2O and dried with anhydrous $MgSO_4$, and volatiles were removed by evaporation under reduced pressure. Flash chromatography (silica, hexane (93%) / ethyl acetate (7%)) of the residue provided 2,2'-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (2; 0.78 g, 2.23 mmol, 90%) as a colorless solid. Recrystallization from hexane provided an analytically pure sample: mp 138-140°C; IR (CH_2Cl_2) 3504 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 18H), 2.30 (s, 6H), 6.00 (s, 2H), 7.14 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.6, 29.3, 34.6, 90.4, 109.1, 128.8, 129.2, 129.3, 135.5, 153.0; HRMS (FAB) calcd for $C_{24}H_{30}O_2$+H 351.2324, found 351.2311. Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.37; H, 9.14.

Reaction of Al(i-Bu)$_3$ with 2,2'-(1,2-Ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (2) and X-ray Crystallographic Study of the Product. A solution of 2,2'-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**2**; 0.15 g, 0.43 mmol) in dry pentane (6 mL) was stirred at 25°C under dry N_2 and treated dropwise with neat Al(i-Bu)$_3$ (0.17 g, 0.86 mmol). Slow evaporation of the solvent yielded colorless crystals of aluminum aryloxide **11** (0.25 g, 0.40 mmol, 93%): mp 192-194°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ -0.04 (d, 4H, ^3J = 7.4 Hz), 0.48 (d, 4H, ^3J = 7.4 Hz), 0.49 (d, 12H, ^3J = 6.5 Hz), 0.92 (d, 12H, ^3J = 6.5 Hz), 1.50 (s, 18H), 1.58 (m, 2H), 1.83 (m, 2H), 2.33 (s, 6H), 7.11 (m, 2H), 7.19 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.7, 22.5, 24.9, 25.4, 25.9, 27.8, 27.9, 31.3, 34.8, 99.2, 118.1, 127.1, 129.3, 132.9, 140.9, 153.1. Anal. Calcd for $C_{40}H_{64}Al_2O_2$: C, 76.15; H, 10.23. Found: C, 74.77; H, 10.22.

Crystallographic data are summarized in Table 2. A single crystal of the aluminum aryloxide was mounted quickly in air and transferred under a stream of cold, dry N_2 to an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from 25 reflections in the range $20.0° \leq \theta \leq 22.5°$. No absorption correction was applied. The structure was solved by direct methods (SHELXS-86) and difference-Fourier calculations (SHELXL-93).[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated at idealized positions using a riding model with different C-H distances for different types of C-H bonds. Atomic scattering factors were taken from standard sources. Refinement converged to R1 = 0.056, wR2 = 0.151, and goodness-of-fit = 0.940 for 399 parameters refined.

Selected bond lengths and angles are listed in Table 1. Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and distances to weighted least-squares planes are included as Supporting Information.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada, the Ministère de l'Éducation du Québec, and Merck Frosst for financial support. In addition, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and distances to weighted least-squares planes for aluminum aryloxide **11** (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any masthead page for ordering information.

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Table 1. Selected Bond Lengths and Angles for Aluminum Aryloxide 11

Bond Lengths (Å)

Al(1)-O(11)	1.915(2)	Al(2)-O(21)	1.909(2)
Al(l)-O(21)	1.917(2)	Al(2)-O(11)	1.912(2)
Al(1)-C(41)	1.955(2)	Al(2)-C(61)	1.958(2)
Al(1)-C(31)	1.977(2)	Al(2)-C(51)	1.983(2)
Al(1)-Al(2)	2.805(1)	O(11)-O(21)	2.542(2)
C(17)-C(27)	1.196(3)		

Bond Angles (deg)

O(11)-Al(1)-O(21)	83.13(6)	O(21)-Al(2)-O(11)	83.41(6)
O(11)-Al(1)-C(41)	126.31(9)	O(21)-Al(2)-C(61)	124.35(9)
O(21)-Al(1)-C(41)	109.84(8)	O(11)-Al(2)-C(61)	110.20(8)
O(11)-Al(l)-C(31)	101.11(8)	O(21)-Al(2)-C(51)	101.75(8)
O(21)-Al(1)-C(31)	110.83(8)	O(11)-Al(2)-C(51)	110.83(8)
C(41)-Al(1)-C(31)	119.69(10)	C(61)-Al(2)-C(51)	120.30(10)

C(11)-O(11)-Al(1)	129.69(12)	C(21)-O(21)-Al(2)	129.38(12)
C(11)-O(11)-Al(2)	123.48(12)	C(21)-O(21)-Al(1)	123.74(12)
Al(2)-O(11)-Al(1)	94.29(6)	Al(2)-O(21)-Al(1)	94.29(6)

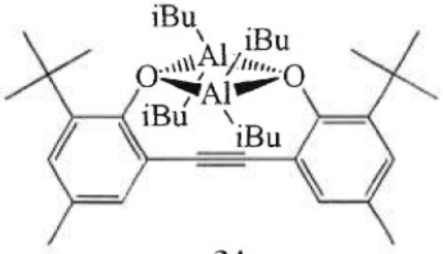
O(21)-Al(1)-O(11)-Al(2)	−16.62(6)	O(11)-Al(2)-O(21)-Al(1)	−16.66(6)

Table 2. **Crystallographic Data for Aluminum Aryloxide 11**

formula	$C_{40}H_{64}Al_2O_2$
fw	630.87
system	monoclinic
space group	$P2_1/n$
cell consts	
a, Å	10.645(3)
b, Å	17.975(5)
c, Å	20.812(5)
β, deg	98.88(2)
cell vol., $Å^3$	3935(2)
Z	4
T,K	220
D_{calcd}, g cm^{-3}	1.065
μ_{calcd}, mm^{-1}	0.86
radiation (λ, Å)	graphite-monochromated CuK α (1.54056)
cryst dimens, mm	0.53 x 0.45 x 0.45
scan width	0.80 ± 0.14 tan θ
$2\theta_{max}$, deg	140
data collcn range	± h, ± k, ± l
no. of reflcns collcd	27503
no. of reflcns retained	7461
no. of params refined	399
goodness-of-fit	0.940
R	0.056
R_w	0.077
$\Delta\rho_{max}$ (e $Å^{-3}$)	0.843
$\Delta\rho_{min}$ (e $Å^{-3}$)	-0.395

4.3 CONCLUSION

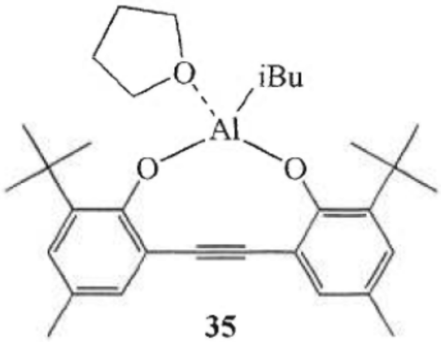
En traitant l'éthynediylbisphénol **17** par deux équivalents de Al(i-Bu)$_3$, nous avons confirmé la faisabilité de transformer un diol approprié en un acide de Lewis bidentate potentiel ayant deux sites acides de Lewis convergents. Nous avons formé le composé **34** où les deux groupes OAl(i-Bu)$_2$ interagissent intramoléculairement en formant un cycle Al$_2$O$_2$ remarquablement déformé par les contraintes imposées par le squelette diphénylacétylénique.



34

Bien qu'il soit rapporté dans la littérature que les aryloxydes de dialkylaluminium forment des complexes avec les composés carbonylés[50], nos essais de co-cristallisation des composés cétoniques simples et moins simples avec le composé **34** n'étaient pas profitables, vu que celui-ci réduit principalement le double lien carbonyle. Il est également connu que les alkoxydes d'aluminium sont des excellents réducteurs de composés carbonylés[51].

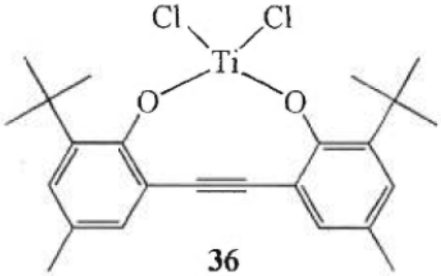
Pour tester l'acidité de Lewis du composé **34** , nous l'avons co-cristallisé avec du THF dans un mélange équimolaire. Le spectre RMN ^{1}H (CDCl$_3$, 25°C) des cristaux obtenus montre la formation d'un complexe 1:1 symétrique incorporant un seul groupe i-Bu. En plus, deux signaux à δ 4.48 et δ 2.26 attribuables aux groupes méthylènes du THF, déblindés de δ 0.9 et δ 0.5, respectivement, par rapport à ceux du THF libre, nous ont menés à conclure qu'il s'agissait du composé **35**. Il semblerait que le THF a ouvert le cycle Al$_2$O$_2$ du composé **34** en libérant une molécule de Al(i-Bu)$_3$[52]. Cette observation



35

est contraire aux conclusions d'Oliver et collaborateurs qui proposent que le THF n'est pas assez basique pour rompre des cycles Al_2O_2 similaires formés dans les dimères des aryloxydes de dialkylaluminium[52]. Il est à noter que dans les dimères des aryloxydes de dialkylaluminium étudiés par Oliver et collaborateurs, les cycles Al_2O_2 sont plans et nettement moins déformés que celui de la structure **34**. Il semblerait également que la tension dont souffre le composé **34** fait que l'association intramoléculaire des groupes $OAl(i\text{-}Bu)_2$ soit moins importante que dans le cas des associations intermoléculaires des alkoxydes et aryloxydes de dialkylaluminium[53].

Nous avons par ailleurs traité le diol **17** par le $TiCl_4$ et avons enregistré les spectres RMN ^1H ($CDCl_3$, 25°C) des mélanges 1:1 et 1:2. Les deux spectres sont identiques et montrent l'évidence d'un composé symétrique très compatible avec la structure **36**.



36

Il est ainsi clair que les inconvénients rencontrés jusque-là dans l'élaboration d'un acide de Lewis bidentate possédant deux sites acides de Lewis indépendants sont dus essentiellement à la proximité des deux oxygènes hydroxyles dans la structure du diol **17**. Il serait donc plus raisonnable d'envisager d'autres structures de diols qui espaceraient davantage les deux oxygènes hydroxyles afin de pouvoir former des acides de Lewis bidentates réels.

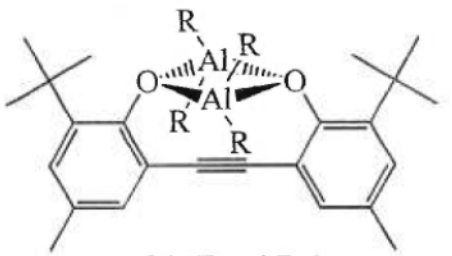
CHAPITRE 5

NOUVEAUX COMPLEXES DES ACIDES DE LEWIS BIDENTATES FORTS DÉRIVÉS DU (BUTADIYNE-1,3 DIYL-1,4)-2,2' BIS[PHÉNOL]

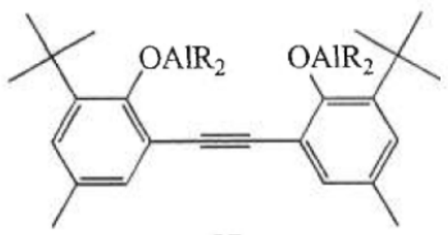
5.1 INTRODUCTION

Par des calculs[54], nous avons trouvé que la distance la plus courte séparant les deux oxygènes hydroxyles dans la structure de l'éthynyldiol **17** est de 4.1 Å. Cette distance est inconvenable pour générer des acides de Lewis bidentates d'aluminium sans que les groupes $OAlR_2$ interagissent entre eux et encore moins pour former des acides de Lewis bidentates de titane. Nous avons décidé d'introduire un deuxième espaceur éthynyle dans la même molécule afin d'espacer davantage les deux oxygènes hydroxyles. La nouvelle séparation de 6.5 Å entre les oxygènes hydroxyles du butadiynediol **18** nous paraît convenable pour générer des acides de Lewis bidentates ayant leurs deux sites acides de Lewis disponibles pour participer dans une double complexation d'un substrat carbonylé.

Les déformations importantes dans la structure **34** nous ont menés à espérer que cette structure pourrait être en équilibre en solution avec une faible quantité de l'acide de Lewis bidentate désiré **37**. Afin de tester cette faisabilité, nous avons étudié l'échange des groupes i-Bu du composé **34** par une étude RMN à température variable que nous présentons dans l'article suivant. Nous y présentons également les synthèses du diol **18** et des acides de Lewis bidentates d'aluminium et de titane qui en dérivent et nous rapportons les caractérisations de leurs complexes avec des composés carbonylés et d'autres bases de Lewis multidentates par la cristallographie et par la RMN à basse température.



34 (R = i-Bu)



37

5.2 ARTICLE 4 : *Organometallics* 1998,17, 1128.

Novel Complexes of Strong Bidentate Lewis Acids Derived from 2,2′-(1,3-Butadiyne-1,4-diyl)bis[phenol]

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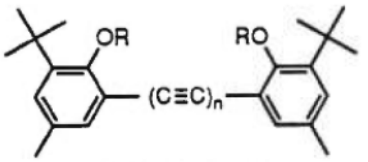
Abstract: Treatment of 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**) with two equivalents of $Al(i\text{-}Bu)_3$ converts the two hydroxyl groups into $OAl(i\text{-}Bu)_2$ groups, thereby transforming diphenol **1** into the corresponding bis(di-*i*-butylaluminum phenoxide) **8**, which holds two strongly Lewis acidic atoms of aluminum in a potentially convergent orientation. Bidentate Lewis acid **8** forms a crystalline 1:1 adduct with 1,2-dimethoxyethane (DME). An X-ray crystallographic study revealed that the adduct is a linear oligomer in which the two Lewis acidic sites of reagent **8** each bind a basic oxygen atom from different molecules of DME. However, low-temperature NMR studies indicated that in solution a discrete 1:1 adduct **9** is favored, in which the two Lewis acidic sites of reagent **8** each bind one of the two basic sites in a single molecule of DME. Formation of adduct **9** provides an example of the recognition and binding of a multidentate Lewis base by a complementary multidentate Lewis acid. Addition of two equivalents of $TiCl_4$ to diphenol **1** converts the hydroxyl groups into $OTiCl_3$ groups and produces the corresponding bis(trichlorotitanium phenoxide) **11**, which forms an unusual 1:2 complex with $CH_3COOC_2H_5$. An X-ray crystallographic study of this complex established that each Lewis acidic atom of titanium binds only one equivalent of $CH_3COOC_2H_5$ to form an unprecedented pentacoordinate adduct with a square pyramidal geometry. Formation of diverse reagents **8** and **11** from the same precursor demonstrates that the strategy of converting organic compounds with suitably oriented hydroxyl groups into the corresponding metal alkoxides is a versatile and effective way to make multidentate Lewis acids.

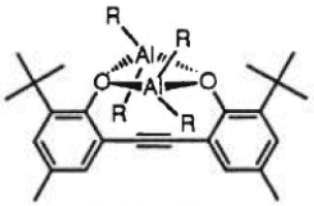
Introduction

The study of multidentate Lewis acids, which are complex reagents with multiple sites of Lewis acidity, is an increasingly active area of research.[2-5] Valuable applications of multidentate Lewis acids are likely to emerge as special features of their coordination chemistry become more fully understood, and as effective methods for making them are developed. We have shown that a particularly convenient way to make multidentate Lewis acids is to convert organic compounds with suitably oriented hydroxyl groups or similar sites into metal alkoxides or related derivatives with strong Lewis acidity.[3-4] For example, appropriate diols can be treated with two equivalents of $TiCl_4$ to produce the corresponding bis(trichlorotitanium alkoxides). By simple procedures of this type, hydroxyl groups can be transformed into various sites of strong Lewis acidity.

To allow useful multidentate Lewis acids to be created by this strategy, the hydroxyl groups must be held sufficiently close together that the resulting sites of Lewis acidity can operate in conjunction to recognize and bind basic substrates; however, the sites cannot be so close together that they interact directly in an unproductive way. In this paper, we show that our strategy can be used successfully to convert 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**) into reagents with two sites of strong Lewis acidity held in a potentially convergent orientation.[6]



1 (n = 2, R = H)
2 (n = 1, R = H)
3 (n = 1, R = Al(*i*-Bu)$_2$)
7 (n = 2, R = COCH$_3$)
8 (n = 2, R = Al(*i*-Bu)$_2$)
11 (n = 2, R = TiCl$_3$)

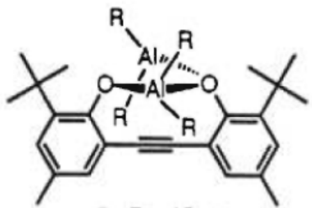


4 (R = *i*-Bu)

Results and Discussion

In earlier work,[4] we demonstrated that treatment of the closely analogous diphenol **2** with two equivalents of Al(*i*-Bu)$_3$ did not yield the desired product **3**, with two OAl(*i*-Bu)$_2$ groups containing potentially convergent Lewis acidic atoms of aluminum. Instead, we obtained an isomer **4** in which the OAl(*i*-Bu)$_2$ groups associate intramolecularly to form a four-membered Al$_2$O$_2$ ring characteristic of dimers of similar dialkylaluminum alkoxides and aryloxides.[4] The sites of Lewis acidity in hypothetical structure **3** are therefore too close together to prevent their direct interaction. However, an X-ray crystallographic study showed that isomer **4** incorporates significant strain, which is revealed by abnormal bending of the triple bond and notable deformations of the Al$_2$O$_2$ ring.[4] These observations encouraged us to hope that structure **4** might be in rapid equilibrium in solution with significant amounts of the desired bidentate Lewis acid **3**.

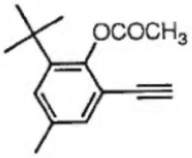
To study this possibility, we recorded variable-temperature NMR spectra of compound **4**. At 25 °C, its ^{13}C NMR spectrum (100 MHz, toluene-d$_8$) showed separate peaks for all three different carbon atoms in the two pairs of non-equivalent *i*-Bu groups. In particular, signals assigned to the CH$_3$ groups appeared at δ 28.39 and 28.53. As the temperature was increased, these signals broadened and finally coalesced at T_c = 55 °C, enabling us to estimate that $\Delta G^{\dagger}$ = 17.0±0.2 kcal mol^{-1} for exchange of the *i*-Bu groups.[7] In principle, this exchange can occur by two distinct processes: 1) Breaking two Al—O bonds in compound **4** and cleaving the Al$_2$O$_2$ ring, thereby producing the desired bidentate Lewis acid **3**; or 2) breaking only one Al—O bond and opening the Al$_2$O$_2$ ring to generate intermediate **5**, followed by rapid rotation of the



5 (R = *i*-Bu)

uncoordinated $Al(i\text{-}Bu)_2$ group around its single remaining Al—O bond. Breaking a single Al—O bond in the Al_2O_2 ring of $[Al(i\text{-}OPr)_3]_2$ is estimated to require at least 31.4 kcal mol^{-1}.[8] We suggest that exchange in compound **4** occurs by an analogous mechanism of single-bond cleavage, and that opening of the ring is accelerated because Al—O bonds in the Al_2O_2 rings of dimeric dialkylaluminum phenoxides are intrinsically weaker than those of dimeric aluminum trialkoxides. In addition, relief of strain in the Al_2O_2 ring of compound **4** may help lower $\Delta G^{\dagger}$. However, the observed value of $\Delta G^{\dagger}$ is still too large to imply that the desired bidentate Lewis acid **3** is readily accessible from isomer **4**.

To prevent loss of full bidentate Lewis acidity by inadvertent intramolecular association, the two $OAlR_2$ groups must be attached to a framework that holds them farther apart. Such a framework is provided by diphenol **1**, which was prepared in 80% overall yield by standard oxidative coupling[9] of the known acetylene **6**,[4] followed by mild reductive deprotection of the



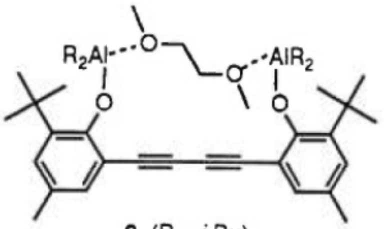
6

resulting diester **7**. Treatment of diphenol **1** in pentane with two equivalents of $Al(i\text{-}Bu)_3$ produced a homogeneous solution, and partial evaporation then gave crystals, presumably of the desired bidentate Lewis acid **8**. When the treatment of diphenol **1** with $Al(i\text{-}Bu)_3$ was followed by the addition of one equivalent of 1,2-dimethoxyethane (DME), we obtained an 86% yield of crystals of a 1:1 complex of bidentate Lewis acid **8** with DME. Similarly, 1:1 complexes were also formed when bidentate Lewis acid **8** was treated with other bidentate bases such as dioxane and pyridazine; in contrast, a representative monodentate base, tetrahydrofuran, gave a 1:2 complex.

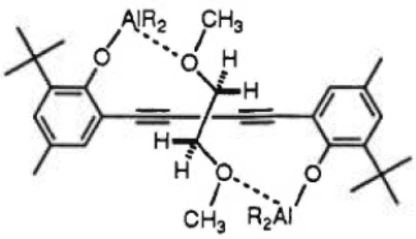
The structure of the 1:1 complex of bidentate Lewis acid **8** with DME was determined by an X-ray crystallographic study. The results of this study, summarized in Figure 1 and in Tables 1

— Figure 1, Table 1, and Table 2 —

and 2, established that in the solid state the two $OAl(i\text{-}Bu)_2$ groups of compound **8** do not associate intramolecularly and are therefore fully available for binding Lewis bases. However, the two Lewis acidic atoms of aluminum do not bind the two complementary basic atoms of oxygen in a single molecule of DME, thereby forming the discrete 1:1 adduct **9**; instead, the Lewis acidic sites each bind a basic site in two different molecules of DME, creating an oligomeric complex of 1:1 stoichiometry. The observed bond lengths and angles are similar to those found in related structures.[4,10] In particular, normal values are observed for the lengths of the covalent Al—O(1) bond (1.734(1) Å) and the dative Al•••O(22) bond (1.941(2) Å), as well as for the Al—O(1)—C(1) bond angle (156.6(1)°). Aluminum shows distorted tetrahedral coordination, and the bond angles at aluminum range from 99.0(1)° to 120.6(1)°. In addition, coordination of the bound oxygen atoms of DME is approximately trigonal planar, and the sum of the bond angles at O(22) is 359.3(1)°.



9 (R = *i*-Bu)



10 (R = *i*-Bu)

Even though the 1:1 adduct of bidentate Lewis acid **8** and DME proved to be a linear oligomer in the solid state, it is readily soluble in CH_2Cl_2. At 25 °C, the ^1H NMR spectrum of a 0.063 M solution prepared by dissolving the crystalline 1:1 adduct in CD_2Cl_2 showed two broad signals assigned to the CH_3 and CH_2 groups of DME at δ 3.75 (bs, 6H) and δ 4.28 (bs, 4H), respectively. The observed broadening indicates that DME must remain at least partly bound in solution. At the lowest accessible temperature (-100 °C), the signal corresponding to the CH_3 groups appeared as a sharp singlet at δ 3.66 (s, 6H), while the signal corresponding to the CH_2 groups had split into two widely separated and incompletely resolved multiplets ($\omega_{1/2}$ = 15 Hz) at δ 3.76 (m, 2H) and δ 5.02 (m, 2H). These observations support the hypothesis that the predominant species in solution is not a linear oligomer but rather the discrete 1:1 adduct **9**, in which both Lewis acidic sites in bidentate Lewis acid **8** operate conjointly to bind the two basic sites in a single molecule of DME.[11] In particular, if DME is bound in its extended conformation in the manner suggested by structure **10**, then the CH_3 groups are equivalent by symmetry, but the protons of each CH_2 group are diastereotopic and likely to have markedly different chemical shifts, as observed. In principle, exchange of the diastereotopic methylene protons can occur by 1) breaking a single dative Al•••O bond or 2) interconverting doubly bonded structure **10** and its enantiomer by simple rotations, without cleaving dative Al•••O bonds.

Our work establishes that diphenol **1** can easily be converted into bis(aluminum phenoxide) **8**, a strong multidentate Lewis acid; moreover, such reagents can recognize and bind complementary multidentate Lewis bases.[11] By similarly simple procedures, compound **1** can also be transformed into other strong bidentate Lewis acids with distinctly different properties. An important advantage of our basic strategy for making multidentate Lewis acids is that a wide variety can be made from a single organic precursor. For example, treatment of diphenol **1** with two equivalents of $TiCl_4$, followed by the addition of two equivalents of $CH_3COOC_2H_5$, produced red crystals of a 1:2 complex of bis(trichlorotitanium phenoxide) **11** with $CH_3COOC_2H_5$ in 63% yield. Because $TiCl_4$ and titanium(IV) chloroalkoxides normally form hexacoordinate octahedral 1:2 complexes with simple basic ligands,[12,13] the observed 1:2 stoichiometry of the complex of bidentate reagent **11** suggested that one Lewis acidic atom of titanium binds both equivalents of $CH_3COOC_2H_5$ while the other atom of titanium remains free, or that the two sites of Lewis acidity each bind one equivalent of $CH_3COOC_2H_5$, and hexacoordination is then achieved by using chloride or $CH_3COOC_2H_5$ itself to doubly bridge the two atoms of titanium.

The structure of the complex was determined by X-ray crystallography, and the results are summarized in Figure 2 and in Tables 3 and 4. These data reveal that the complex incorporates

— Figure 2, Table 3, and Table 4 —

several unusual features. In particular, the structure is symmetric, and the two atoms of titanium each bind a single molecule of $CH_3COOC_2H_5$ to form pentacoordinate adducts with approximate square pyramidal geometries. Cl(3) is oriented apically, while Cl(1), Cl(2), O(1), and O(21) define the basal plane. Bond angles at Ti in the basal plane range from 82.8(1)° to 91.2(1)°, while those defined by apical Cl(3), Ti, and the basal ligands vary from 96.3(1)° to 105.6(1)°. The observed structure is noteworthy because 1) no other pentacoordinate 1:1 adducts of $TiCl_4$ or titanium(IV) chloroalkoxides with basic organic ligands are known, and 2) calculations have predicted that the favored geometry of the hypothetical 1:1 complex of $TiCl_4$ with formaldehyde is trigonal bipyramidal, not square pyramidal.[12] The unusual preference of bis(trichlorotitanium phenoxide) **11** for pentacoordination is presumably due to steric hindrance created by substituents adjacent to the sites of Lewis acidity.

The C(7)—C(8) triple bond in the 1:2 complex of bis(trichlorotitanium phenoxide) **11** with $CH_3COOC_2H_5$ is oriented in such a way that its interaction with Ti trans to Cl(3) would produce a normal hexacoordinate complex with approximate octahedral geometry. However, complexes of Ti(IV) with olefins or acetylenes are very rare,[14] and the observed Ti•••C(7) and Ti•••C(8) distances (3.231(3) Å and 3.416(3) Å, respectively) are extremely long. We conclude that bis(trichlorotitanium phenoxide) **11** forms true pentacoordinate complexes.

When $TiCl_4$ reacts with two equivalents of a simple carbonyl compound in a stepwise manner, binding of the first equivalent to form a pentacoordinate 1:1 intermediate is calculated to be normally less exothermic than binding of the second equivalent to form the final hexacoordinate 1:2 adduct.[12] If so, binding of $CH_3COOC_2H_5$ in the novel pentacoordinate complex of bidentate Lewis acid **11** should be somewhat weaker than in related hexacoordinate complexes, and the dative Ti•••O(21) bond length should be abnormally long. In fact, the observed distance (2.078(2) Å) is similar to those previously found in hexacoordinate complexes of esters with $TiCl_4$ and titanium trichloroalkoxides.[13] In addition, the average length of the two basal Ti—Cl bonds (2.268(1) Å) is normal, and the Ti—O(1) bond length (1.782(2) Å) is similar to those found in other titanium(IV) chlorophenoxides and their complexes,[15] which exhibit strong oxygen-p titanium-d π-bonding.[16] Further evidence of strong Ti—O(1) π-bonding in the 1:2 complex of bidentate Lewis acid **11** with $CH_3COOC_2H_5$ is the observed opening of the Ti—O(1)—C(1) bond angle to 152.6(2)°. Curiously, the Ti—O(1) bond shows normal strength even though O(1) is trans to Cl(1) rather than to the more weakly π-donating ester ligand. The only evidence that pentacoordination has any special effects on bond lengths is provided by unusual shortening of the apical Ti—Cl(3) bond (2.204(1) Å). Such shortening is typical of bonds to apical ligands in square pyramidal complexes.[17] Although titanium has an unusual geometry and stoichiometry of coordination, $CH_3COOC_2H_5$ is bound in the normal $\eta^1(\sigma)$ manner,[18] with a Ti•••O(21)—C(22) bond angle of 149.0(2)° and a Ti•••O(21)—C(22)—C(21) dihedral angle of 1.9(6)°.

Conclusions

Our results show that the conversion of hydroxyl groups into metal alkoxides can serve as the basis of an effective strategy for constructing strong multidentate Lewis acids from simple organic precursors. Multidentate Lewis acids made by this strategy can be designed to have useful properties, such as the ability to recognize and bind complementary multidentate Lewis bases. Moreover, this strategy allows multidentate Lewis acids with markedly different properties to be made from the same precursor. We expect that our strategy for making multidentate Lewis acids will make them more readily available and will help promote further study of their unique coordination chemistry.

Experimental Section

Toluene and pentane were dried by distillation from sodium, and CH_2Cl_2 was dried by distillation from P_2O_5. $TiCl_4$ was purified by distillation; all other reagents were commercial products that were used without further purification. Flash chromatography was performed in the normal way.[19]

2,2′-(1,3-Butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] Diacetate (7). A mixture of CuCl (0.845 g, 8.54 mmol) and N,N,N′,N′-tetramethylethylenediamine (0.373 g, 3.21 mmol) in acetone (15 mL) was stirred at 25 °C for 1 h. The suspension was filtered, and the filtrate was added to a solution of 2-(1,1-dimethylethyl)-6-

ethynyl-4-methylphenol acetate (**6**; 0.740 g, 3.21 mmol)[4] in acetone (30 mL). The resulting mixture was stirred at 60 °C for 2 h under an atmosphere of O_2. Then 2 N aqueous HCl was added, the mixture was extracted with $CHCl_3$, and the combined extracts were washed with H_2O and dried with anhydrous $MgSO_4$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (95%)/ethyl acetate (5%)) to give 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] diacetate (**7**; 0.717 g, 1.56 mmol, 97%) as a colorless solid. An analytically pure sample was prepared by recrystallization from $CHCl_3$: mp 126-128 °C; IR (melt) 1769 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 18H), 2.34 (s, 6H), 2.44 (s, 6H), 7.26 (s, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.7, 21.1, 30.0, 34.3, 77.2, 78.2, 116.7, 129.4, 131.6, 134.9, 141.6, 149.5, 168.7; HRMS (FAB) calcd for $C_{30}H_{34}O_4$ + H *m/e* 459.2535, found *m/e* 459.2553.

2,2′-(1,3-Butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (1). A solution of 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] diacetate (**7**; 4.51 g, 9.83 mmol) in toluene (60 mL) was stirred at -78 °C under dry Ar and was treated dropwise with a solution of $(i\text{-Bu})_2AlH$ (52 mL, 1.5 M in toluene, 78 mmol). The cold mixture was treated with H_2O (80 mL), warmed to 25 °C, and filtered through Celite. The filtrate was extracted with $CHCl_3$, and the combined extracts were dried with anhydrous $MgSO_4$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (90%)/ethyl acetate (10%)) to give 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**; 3.31 g, 8.84 mmol, 90%) as a colorless solid. An analytically pure sample was prepared by recrystallization from $CHCl_3$: mp 142-144 °C; IR (melt) 3517, 2128 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 18H), 2.26 (s, 6H), 5.91 (s, 2H), 7.09 (s, 2H), 7.11 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.3, 29.0, 34.4, 78.1, 79.7, 107.9, 128.8, 129.7, 129.9, 135.6, 154.6; HRMS (FAB) calcd for $C_{26}H_{30}O_2$ *m/e* 374.2246, found *m/e* 374.2230.

1:1 Adduct of Bidentate Lewis Acid 8 and DME. A solution of 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**; 20.6 mg, 0.0550 mmol) in pentane (0.8 mL) was stirred at 25 °C under dry Ar and treated dropwise with neat $Al(i\text{-}Bu)_3$ (21.8 mg, 0.110 mmol). After 10 min, neat DME (5.0 mg, 0.055 mmol) was added. Partial evaporation of solvent yielded colorless crystals of the 1:1 adduct of bidentate Lewis acid **8** and DME (35.4 mg, 0.0475 mmol, 86%): IR (Nujol) 2130 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.20 (d, 8H, ^3J = 6.4 Hz), 0.90 (d, 24H, ^3J = 6.5 Hz), 1.38 (s, 18H), 1.81 (m, 4H), 2.23 (s, 6H), 3.75 (bs, 6H), 4.28 (bs, 4H), 7.06 (s, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.6, 22.8, 25.7, 28.2, 29.6, 34.8, 59.7 (b), 69.0 (b), 78.0, 82.9, 112.6, 126.6, 129.5, 131.4, 139.1, 158.7.

1:2 Complex of Bidentate Lewis Acid 11 with $CH_3COOC_2H_5$. A solution of 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**; 15.0 mg, 0.0400 mmol) in pentane (0.8 mL) was stirred at 25 °C under dry Ar and treated dropwise with neat $TiCl_4$ (15.6 mg, 0.0822 mmol). The resulting red suspension was then treated with $CH_3COOC_2H_5$ (7.2 mg, 0.082 mmol) and CH_2Cl_2 (0.4 mL). Partial evaporation of solvent yielded red crystals of the 1:2 complex of bidentate Lewis acid **11** with $CH_3COOC_2H_5$ (21.6 mg, 0.0252 mmol, 63%): IR (Nujol) 1644 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.31 (t, 6H, ^3J = 7.2 Hz), 1.52 (s, 18H), 2.34 (s, 6H), 2.41 (s, 6H), 4.37 (q, 4H, ^3J = 7.2 Hz), 7.13 (m, 2H), 7.22 (m, 2H); ^{13}C NMR (75.4 MHz, CD_2Cl_2) δ 14.3, 21.3, 21.5, 30.3, 35.6, 63.4, 83.3, 83.4, 119.1, 129.6, 132.7, 135.7, 138.4, 170.7, 176.0.

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes for the 1:1 complex of bidentate Lewis acid **8** with DME (16 pages) and the 1:2 complex of bidentate Lewis acid **11** with $CH_3COOC_2H_5$ (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any masthead page for ordering information.

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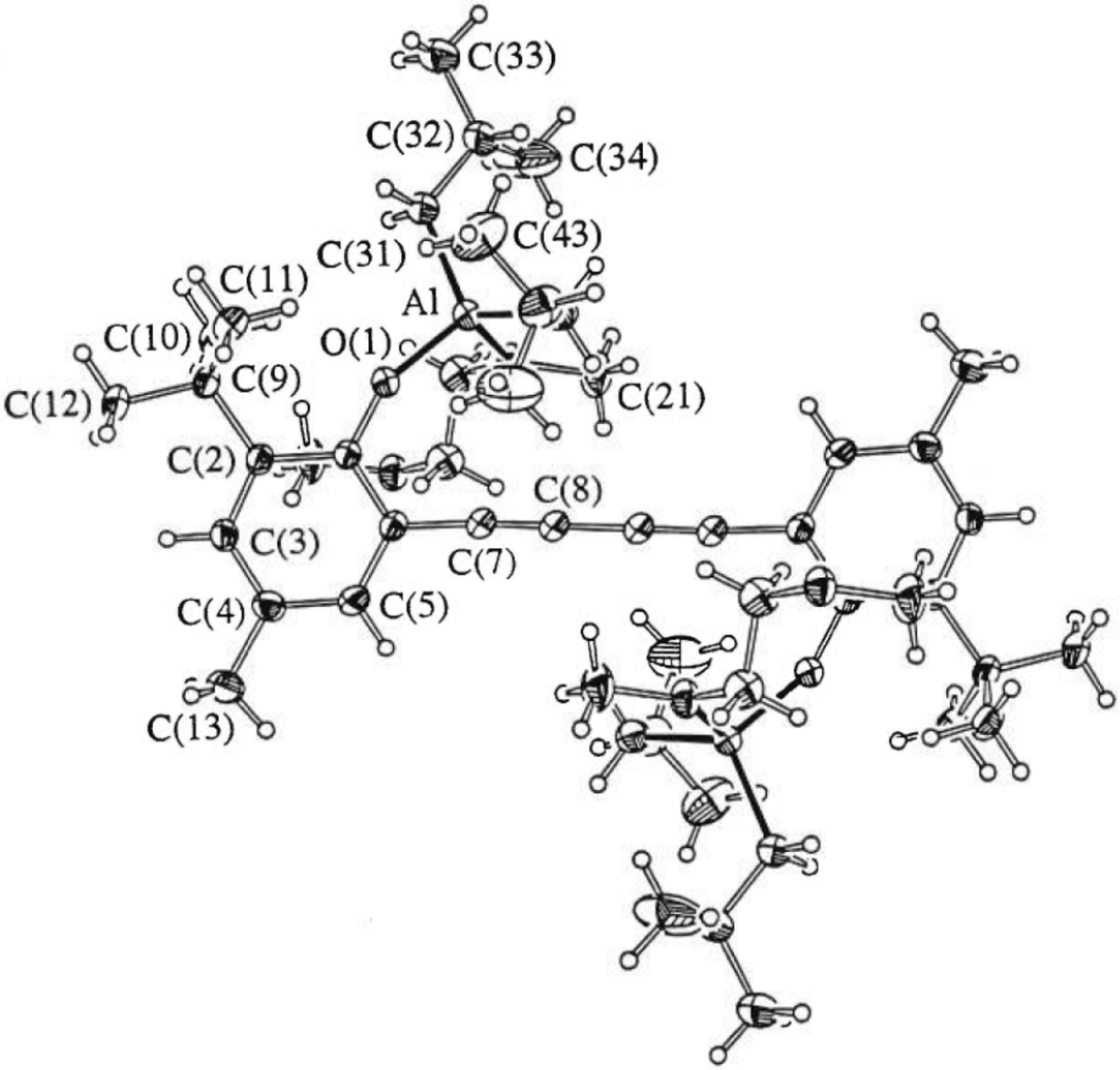


Figure 1. ORTEP view of the structure of the 1:1 complex of bidentate Lewis acid **8** with DME. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, and bonds to aluminum are drawn using solid lines.

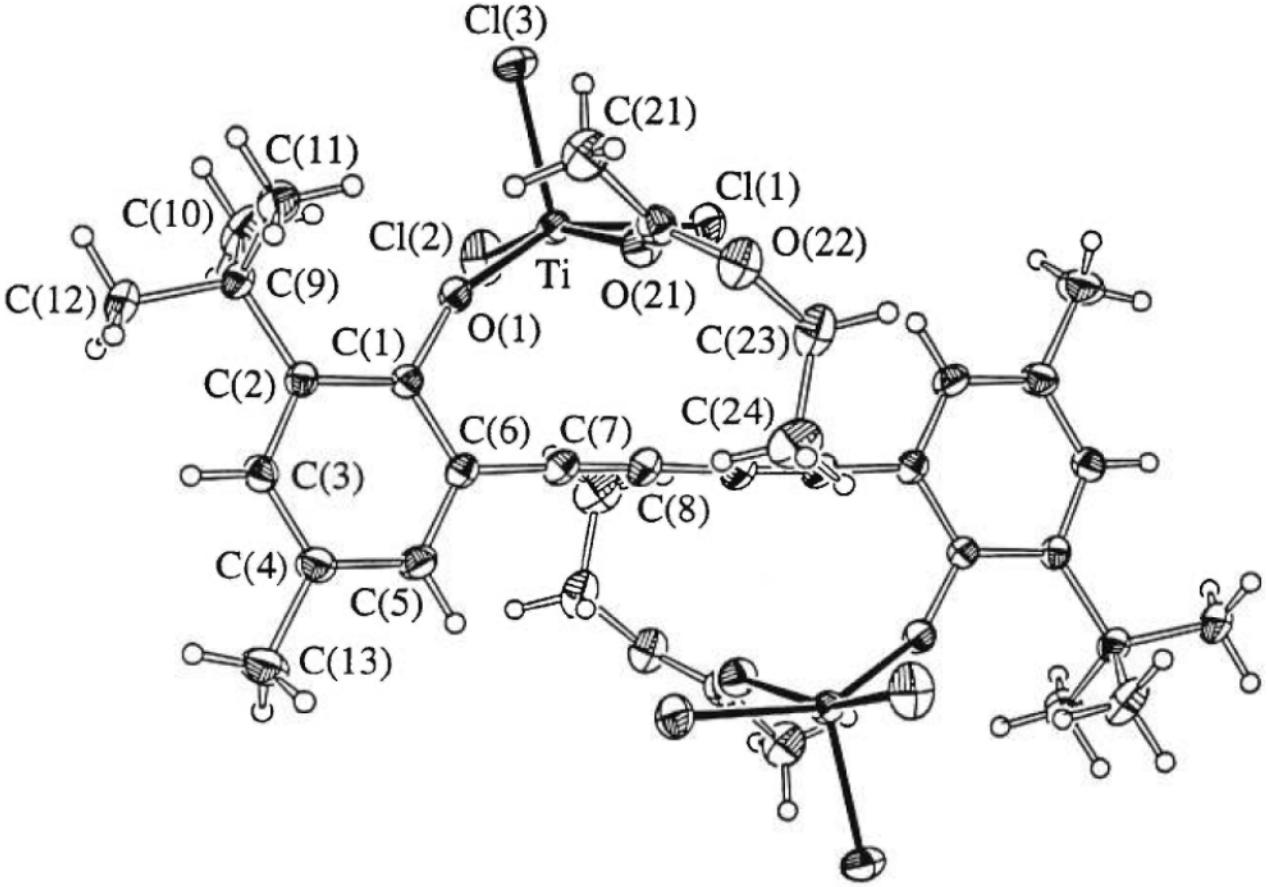


Figure 2. ORTEP view of the structure of the 1:2 complex of bidentate Lewis acid **11** with $CH_3COOC_2H_5$. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, and bonds to titanium are drawn using solid lines.

Table 1. Selected Bond Lengths and Angles for the 1:1 Complex of Bidentate Lewis Acid 8 with DME

Bond Lengths (Å)

Al—O(1)	1.734(1)
Al—O(22)	1.941(2)
Al—C(31)	1.971(2)
Al—C(41)	1.967(2)
O(1)—C(1)	1.336(2)
C(7)—C(8)	1.197(3)

Bond Angles (deg)

O(1)—Al—O(22)	99.0(1)
O(1)—Al—C(31)	107.7(1)
O(1)—Al—C(41)	120.6(1)
O(22)—Al—C(31)	104.0(1)
O(22)—Al—C(41)	104.8(1)
C(31)—Al—C(41)	117.6(1)
C(1)—O(1)—Al	156.6(1)
C(6)—C(7)—C(8)	175.9(2)
Al—O(22)—C(21)	127.0(1)
Al—O(22)—C(23)	118.3(1)
C(21)—O(22)—C(23)	114.0(2)

Table 2. Crystallographic Data for the 1:1 Complex of Bidentate Lewis Acid 8 with DME

formula	$C_{46}H_{74}Al_2O_4$
fw	745.01
system	triclinic
space group	P -1
cell constants	
a, Å	8.967(3)
b, Å	11.816(4)
c, Å	12.551(4)
α, deg	67.11(3)
β, deg	73.45(2)
γ, deg	78.23(2)
cell volume, $Å^3$	1167.8(7)
Z	1
T, K	210
D_{calcd}, g cm^{-3}	1.059
μ_{calcd}, mm^{-1}	0.843
radiation (λ, Å)	graphite-monochromated Cu Kα (1.54056)
cryst dimens, mm	0.38 x 0.19 x 0.17
data collcn range	±*h*, ±*k*, ±*l*
no. of reflcns collcd	29061

no. of reflcns refined	4418
goodness-of-fit	0.982
$R1$	0.0495
$wR2$	0.1364
$\Delta\rho_{max}$, e Å^{-3}	0.296
$\Delta\rho_{min}$, e Å^{-3}	-0.481

Table 3. Selected Bond Lengths and Angles for the 1:2 Complex of Bidentate Lewis Acid 11 with $CH_3COOC_2H_5$

Bond Lengths (Å)

Ti—O(1)	1.782(2)
Ti—O(21)	2.078(2)
Ti—Cl(1)	2.273(1)
Ti—Cl(2)	2.264(1)
Ti—Cl(3)	2.204(1)
O(1)—C(1)	1.348(3)
O(21)—C(22)	1.222(4)
C(7)—C(8)	1.198(4)

Bond Angles (deg)

O(1)—Ti—O(21)	86.2(1)
O(1)—Ti—Cl(1)	150.3(1)
O(1)—Ti—Cl(2)	91.2(1)
O(1)—Ti—Cl(3)	103.0(1)
O(21)—Ti—Cl(1)	82.8(1)
O(21)—Ti—Cl(2)	161.5(1)
O(21)—Ti—Cl(3)	96.3(1)
Cl(1)—Ti—Cl(2)	90.7(1)
Cl(1)—Ti—Cl(3)	105.6(1)
Cl(2)—Ti—Cl(3)	102.0(1)
Ti—O(1)—C(1)	152.6(2)

Ti—O(21)—C(22)	149.0(2)
C(6)—C(7)—C(8)	178.1(3)

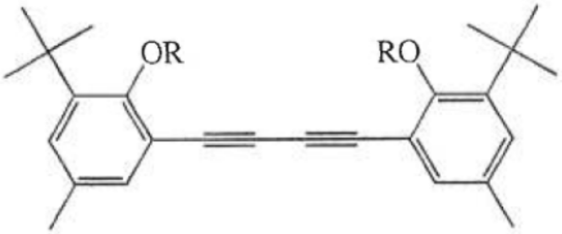
Table 4. Crystallographic Data for the 1:2 Complex of Bidentate Lewis Acid 11 with $CH_3COOC_2H_5$

formula	$C_{34}H_{44}Cl_6O_6Ti_2$
fw	857.19
system	triclinic
space group	P -1
cell constants	
a, Å	8.691(2)
b, Å	9.644(4)
c, Å	12.540(4)
α, deg	90.29(3)
β, deg	98.83(2)
γ, deg	105.68(3)
cell volume, Å^3	998.7(6)
Z	1
T, K	210
D_{calcd}, g cm^{-3}	1.425
μ_{calcd}, mm^{-1}	4.281
radiation (λ, Å)	graphite-monochromated Cu Kα (1.54056)
cryst dimens, mm	0.40 x 0.30 x 0.06
data collcn range	$\pm h$, $\pm k$, $\pm l$
no. of reflcns collcd	22669

no. of reflcns refined	3710
goodness-of-fit	0.986
$R1$	0.0473
w$R2$	0.1204
$\Delta\rho_{\text{max}}$, e Å^{-3}	0.724
$\Delta\rho_{\text{min}}$, e Å^{-3}	-0.762

5.3 CONCLUSION

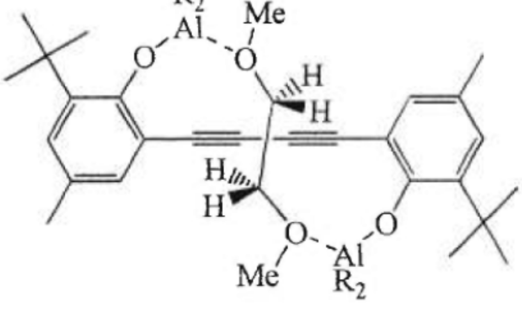
Nous avons réussi à espacer davantage les deux oxygènes hydroxyles en synthétisant le diol **18** qui nous a effectivement permis d'obtenir les acides de Lewis bidentates réels **38** et **39**.



38 (R = $Al(i\text{-}Bu)_2$)

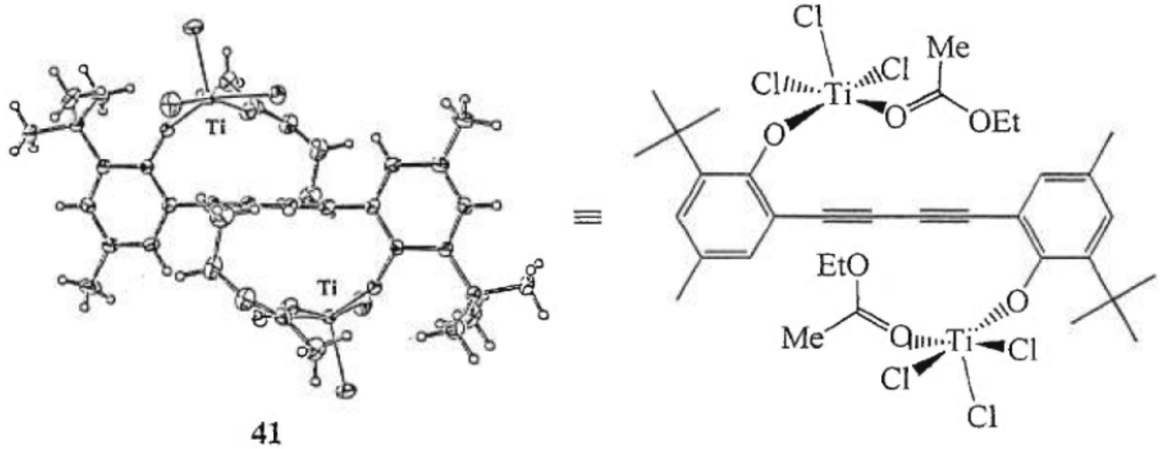
39 (R = $TiCl_3$)

L'étude cristallographique du complexe 1:1 formé par l'acide de Lewis bidentate **38** et le diméthoxy-1,2 éthane (DME) a montré que les deux groupes $OAl(i\text{-}Bu)_2$ ne sont pas associés intramoléculairement mais que chaque groupe coordonne un atome d'oxygène de deux molécules de DME différentes, créant un complexe oligomérique de stoechiométrie 1:1. Une étude RMN ^1H à basse température du même complexe supporte l'hypothèse que c'est plutôt la forme monomérique **40** qui prédomine en solution.



40 (R = i-Bu)

Nous avons également caractérisé par la cristallographie le complexe 1:2 **41** formé par l'acide de Lewis bidentate **39** et l'acétate d'éthyle dans lequel chaque groupe $OTiCl_3$ est lié à une seule molécule d'ester.



41

Il est donc possible d'obtenir des acides de Lewis bidentates réels et de propriétés différentes à partir d'un même diol mais il est également évident, d'après les observations énoncées ci-dessus, que les deux groupes hydroxyles du diol doivent être orientés de façon plus rigide et séparés d'une distance intermédiaire à celles des diols **17** et **18** pour que les deux sites acides de Lewis fixés sur les deux atomes d'oxygène puissent participer dans une double complexation d'un composé carbonylé.

CHAPITRE 6

NOUVEAUX COMPLEXES DES ACIDES DE LEWIS BIDENTATES FORTS DÉRIVÉS DU BIS(DIMÉTHYL-1,1 ÉTHYL)-2,7 FLUORÈNEDIOL-1,8

6.1 ARTICLE 5 : *Inorg. Chem.* Accepté le 27/02/98

Novel Complexes of Strong Bidentate Lewis Acids Derived from 2,7-Bis(1,1-dimethylethyl)fluorene-1,8-diol

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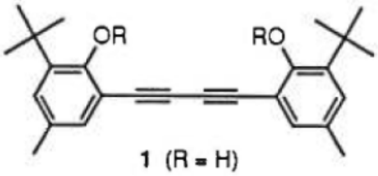
Abstract: Treatment of 2,7-bis(1,1-dimethylethyl)fluorene-1,8-diol (3) with two equivalents of $TiCl_4$ converts the two OH groups into $OTiCl_3$ groups and thereby yields bis(trichlorotitanium phenoxide) 7, a structurally well-defined reagent that holds two sites of strong Lewis acidity in close proximity. Bidentate Lewis acid 7 forms a crystalline 1:2 complex with 4,4'-dimethylbenzophenone. An X-ray crystallographic study revealed that each atom of titanium binds only one molecule of ketone to form an unusual pentacoordinate adduct with an approximately trigonal bipyramidal geometry. Treatment of fluorenediol 3 with two equivalents of $Al(CH_2CH_3)_3$ does not yield the expected bis(diethylaluminum phenoxide) 8, but rather its dimer 9. Formation of diverse reagents 7 and 9 from the same precursor demonstrates that the strategy of converting organic compounds with suitably oriented hydroxyl groups into the corresponding metal alkoxides is a particularly versatile and effective way to make strong, structurally well-defined multidentate Lewis acids.

Introduction

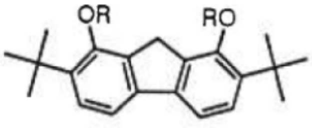
An increasingly active area of research in coordination chemistry is the study of multidentate Lewis acids, which are reagents with multiple sites of Lewis acidity available for the complexation of complementary Lewis bases.[2-7] Complexes of multidentate Lewis acids are chemically important because they promise to be stronger than analogous complexes of simple monodentate Lewis acids.[7] In addition, the recognition of bases by multidentate Lewis acids should be more selective, and the reactivity of bound substrates should be modified more dramatically.[7] As a result, multidentate Lewis acids are likely to become increasingly useful to chemists as the special features of their coordination chemistry are revealed, and as simple ways to make them are devised.

Our earlier work has shown that a particularly convenient strategy for making strong multidentate Lewis acids is to convert organic compounds with multiple hydroxyl groups or similar sites into the corresponding metal alkoxides or related derivatives.[3-5] For example, treatment of diphenol **1** with two equivalents of $TiCl_4$ can be used to make complexes of bis(trichlorotitanium phenoxide) **2**, which is a strong bidentate Lewis acid.[5] Unfortunately, rotation of the aryl groups around the diyne linker in compound **2** is expected to occur readily, and no conformational constraints ensure that the two sites of Lewis acidity are held in the closest possible proximity in a potentially convergent manner.[8] As a result, they are free to operate independently.

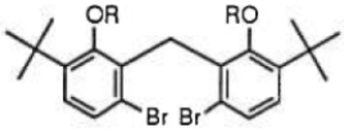


1 (R = H)
2 (R = $TiCl_3$)

To allow structurally well-defined multidentate Lewis acids to be created by our strategy, the hydroxyl groups should be oriented more rigidly, in positions close enough together to ensure that the resulting sites of Lewis acidity can act in conjunction, but far enough apart to prevent the sites from interacting directly in unproductive ways. In this paper, we show that our strategy can be used successfully to convert 2,7-bis(1,1-dimethylethyl)fluorene-1,8-diol (**3**) into reagents with well-defined structures that hold two sites of strong Lewis acidity in close proximity.



3 (R = H)
4 (R = CH_3)
7 (R = $TiCl_3$)
8 (R = $Al(CH_2CH_3)_2$)



5 (R = H)
6 (R = CH_3)

Results and Discussion

Fluorenediol **3** was prepared in 86% yield from the known dimethyl ether **4**[8] by adding BBr_3 and then water. Dimethyl ether **4** was synthesized in four steps by a modification of the published method, which requires six steps.[9] The modification involves direct *t*-butylation of 3-bromophenol, condensation of the resulting 5-bromo-2-(1,1-dimethylethyl)phenol[9] with formaldehyde to produce diphenol **5**,[9] methylation to give protected intermediate **6**,[9] and subsequent Ni(0)-catalyzed intramolecular aryl-aryl coupling. Our modifications increased the overall yield of dimethyl ether **4** from 3-bromophenol from 11% to 28%. Moreover, we found that fluorenediol **3** could be made from 3-bromophenol in only three steps by direct aryl-aryl coupling of unprotected diphenol **5**, but the overall yield was somewhat lower.

To test our general strategy for making multidentate Lewis acids from organic compounds with suitably oriented hydroxyl groups, we attempted to convert fluorenediol **3** into the corresponding bis(trichlorotitanium phenoxide) **7**, a strong bidentate Lewis acid, by adding two equivalents of $TiCl_4$ to a solution of compound **3** in CH_2Cl_2. Slow evaporation then provided a 90% yield of red crystals of a compound assigned structure **7**. This assignment was confirmed by X-ray crystallography, which provided the structural data summarized in Figure 1 and in Tables 1

— Figure 1, Table 1, and Table 2 —

and 2. These data reveal that compound **7** is a true bidentate Lewis acid, with two free $OTiCl_3$ groups held in close proximity. The average lengths of the Ti—Cl bonds (2.174(2) Å) and the Ti—O bonds (1.727(3) Å) are similar to those found in other uncomplexed titanium trichlorophenoxides.[10] In addition, the average Ti—O—C bond angle has a large value (163.6(3)°) that is close to those found in related compounds with strong oxygen-p titanium-d π-bonding.[10,11] As expected, each atom of titanium adopts an approximately tetrahedral geometry, and the bond angles at titanium vary only from 107.9(1)° to 111.0(1)°.

Treatment of a solution of bis(trichlorotitanium phenoxide) **7** in CH_2Cl_2 with two equivalents of 4,4´-dimethylbenzophenone, followed by partial evaporation of the solvent, provided red crystals of a 1:2 complex, which was isolated as a CH_2Cl_2 solvate in 81% yield. Because $TiCl_4$ and titanium(IV) chloroalkoxides normally form hexacoordinate octahedral 1:2 complexes with simple basic ligands,[12] the observed 1:2 stoichiometry of the complex of bidentate reagent **7** was unexpected. It suggested that one Lewis acidic atom of titanium binds both equivalents of ketone while the other atom of titanium remains free, or that the two sites of Lewis acidity each bind one equivalent of ketone, and hexacoordination is then achieved by using chloride or the carbonyl oxygen atoms of the ketones to doubly bridge the two atoms of titanium.

The structure of the solvated 1:2 complex of bis(trichlorotitanium phenoxide) **7** with 4,4′-dimethylbenzophenone was determined by X-ray crystallography, and the results are summarized in Figure 2 and in Tables 3 and 4. These data reveal that the complex incorporates several unusual features. In particular, the two atoms of titanium each bind a single molecule of 4,4′-dimethylbenzophenone to form pentacoordinate adducts with approximately trigonal bipyramidal geometries. All Ti—O bonds are oriented apically, and all Ti—Cl bonds are equatorial. The Cl—Ti—Cl bond angles range from 111.4(1)° to 133.8(1)° and average 119.5(1)°, the Cl—Ti—O bond angles involving the phenoxide oxygen atoms range from 87.8(1)° to 99.9(1)° and average 94.4(1)°, the Cl—Ti—O bond angles involving the carbonyl oxygen atoms of the bound ketones range from 82.6(1)° to 91.2(1)° and average 86.1(1)°, and the O—Ti—O bond angles average 170.8(1)°. The observed structure is noteworthy because the 1:2 adduct of bis(trichlorotitanium phenoxide) **2** with $CH_3COOCH_2CH_3$ is the only other related complex known to incorporate pentacoordinate Ti(IV), and in this case an approximately square pyramidal geometry is favored.[5] Calculations have predicted that the preferred geometry of the hypothetical

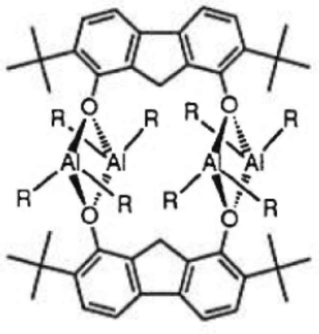
— Figure 2, Table 3, and Table 4 —

1:1 complex of $TiCl_4$ with formaldehyde is trigonal bipyramidal, not square pyramidal,[12] but our observations suggest that both structures are accessible. The unusual preferences of bis(trichlorotitanium phenoxides) **2** and **7** for pentacoordination are presumably due to steric hindrance created by substituents adjacent to the sites of Lewis acidity.

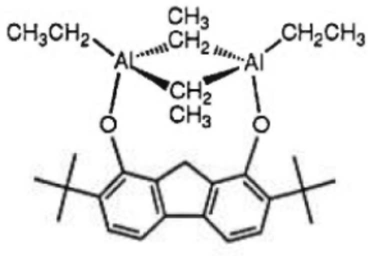
Other geometric parameters in the structure of the 1:2 complex of bis(trichlorotitanium phenoxide) **7** with 4,4´-dimethylbenzophenone have normal values. For example, the average dative Ti•••O bond length involving the carbonyl oxygen atoms (2.062(3) Å) and the average Ti—O bond length involving the phenoxide oxygen atoms (1.770(3) Å) are closely similar to those found in the related 1:2 complex of bis(trichlorotitanium phenoxide) **2** with $CH_3COOCH_2CH_3$.[5] The Ti—Cl bond lengths also have a normal average value (2.248(2) Å), and the average phenoxy Ti—O—C bond angles are expectedly large (155.3(2)°), which confirms the presence of strong Ti—O π-bonding. Although $CH_3COOCH_2CH_3$ is bound by bis(trichlorotitanium phenoxide) **2** in the normal $\eta^1(\sigma)$ manner,[13] with Ti close to the carbonyl plane, 4,4´-dimethylbenzophenone is bound by bis(trichlorotitanium phenoxide) **7** with an average Ti•••O=C bond angle of 161.7(3)° and an average Ti•••O=C—C dihedral angle of 33.0(10)°. This reveals that Ti lies far from the carbonyl plane and that the interaction must therefore have important π character.

Our work establishes that fluorenediol **3** can easily be converted into bis(trichlorotitanium phenoxide) **7**, a bidentate Lewis acid that is strong and structurally well-defined. In principle, equally simple procedures should transform compound **3** into many other bidentate Lewis acids. This versatility is an important advantage of our basic strategy for making multidentate Lewis acids, because it allows a wide variety of reagents to be made from a single organic precursor. To test the generality of our strategy, we attempted to make a new bidentate Lewis acid **8** by treating a solution of fluorenediol **3** in toluene with two equivalents of $Al(CH_2CH_3)_3$. Partial evaporation of solvent yielded colorless crystals of a bis(diethylaluminum phenoxide) in 62% yield. The aromatic region of its ^{1}H NMR spectrum, recorded at 25 °C, showed that the fluorene ring was symmetrically substituted but that two different ethyl groups were present, thereby excluding the expected structure **8**.

Two closely related alternative structures that are consistent with the observed NMR spectrum are the dimer **9** and the ethyl-bridged monomer **10**. To distinguish these alternatives, we



9 (R = CH_2CH_3)



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recorded variable-temperature ^{1}H NMR spectra (400 MHz, toluene-d_8) and analyzed the exchange of the non-equivalent ethyl groups. At 25 °C, the spectrum showed separate ethyl quartets centered at δ 0.51 and 0.62. As the temperature was increased, these signals broadened and finally coalesced at $T_c = 92$ °C, enabling us to estimate that $\Delta G^\dagger = 18.2 \pm 0.2$ kcal mol^{-1} for exchange of the ethyl groups.[14] In principle, this exchange can occur in hypothetical dimer **9** by breaking individual Al—O bonds and opening the Al_2O_2 rings, or simply by rotating the rings around axes defined by their O•••O diagonals. Exchange can occur in hypothetical ethyl-bridged structure **10** by breaking at least one three-center two-electron bond and opening the Al_2C_2 ring. The observed $\Delta G^\dagger$ is similar to those measured for processes in which analogous Al_2O_2 rings are opened,[5] and it is much larger than the $\Delta G^\dagger$ observed for exchange of the terminal and bridging ethyl groups in $[Al(CH_2CH_3)_3]_2$, which is only 10.2±0.3 kcal mol^{-1} in toluene at 25 °C.[15] As a result, we conclude that the structure favored in solution must be dimer **9** or a higher cyclic oligomer, and we suggest that this exchange occurs by breaking individual Al—O bonds and opening the Al_2O_2 rings.

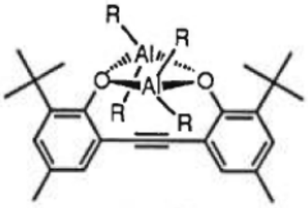
An X-ray crystallographic study subsequently confirmed that dimer **9** is formed in the solid state. The results of this study, summarized in Figure 3 and in Tables 5 and 6, show that dimer **9** incorporates several interesting features. Normal Al_2O_2 rings are rigorously or approximately planar,[3] but those of dimer **9** are distinctly puckered, and the average of the absolute values of the Al—O—Al—O dihedral angles is 12.8(1)°. However, the oxygen atoms are nearly trigonal planar, and the average value of the sums of their bond angles is 358.8(1)°, so the amount of strain is small. This is confirmed by the average Al—O bond length (1.884(2) Å), which is rather long but still within the range of distances normally observed in the Al_2O_2 rings of dimeric alkylaluminum alkoxides and aryloxides (1.840-1.895 Å).[3] In addition, the average values of the Al—O—Al angles (99.1(1)°), O—Al—O angles (79.6(1)°), Al—C bond lengths (1.956(3) Å), non-bonded Al•••Al distances (2.866(2) Å), non-bonded O•••O distances (2.411(2) Å), and C—Al—C angles (112.0(1)°) are similar to those found in other Al_2O_2 rings.[3]

— Figure 3, Table 5, and Table 6 —

The Al_2O_2 rings of dimer **9** are approximately orthogonal to the aryl groups to which they are connected, and the average of the absolute values of the C(*t*-Bu)—C—O—Al dihedral angles is

97.8(3)°. This conformational preference separates the ethyl groups in dimer **9** into two diastereotopic sets, one oriented toward the interior of the dimer and the other toward the exterior, and each aluminum atom is bonded to one ethyl group of each type. Exchange of the ethyl groups by simple rotations of intact Al_2O_2 rings around axes defined by their O•••O diagonals is presumably disfavored because this would create highly unfavorable interactions with adjacent substituents on the aryl rings.

It is instructive to compare ΔG† for exchange in dimer **9** (18.2±0.2 kcal mol^{-1} at 92 °C) with that observed for the closely related exchange of *i*-butyl groups in structure **11** (17.0±0.2 kcal mol^{-1} at 55 °C).[5] Even though the Al_2O_2 ring of structure **11** is much more highly distorted than that of dimer **9**, its opening is only slightly faster. This suggests that the observed deformations are not enthalpically costly.



11 (R = *i*-Bu)

Conclusions

Our results confirm that the conversion of hydroxyl groups into metal alkoxides can serve as the basis of an effective strategy for constructing strong multidentate Lewis acids from simple organic precursors. Precursors with rigidly oriented hydroxyl groups give rise to multidentate Lewis acids that are structurally well-defined, in which the sites of Lewis acidity are held close enough together to be able to act in conjunction, but far enough apart to avoid interacting directly in unproductive ways. In principle, multidentate Lewis acids made by this strategy can be designed to have useful properties, such as the ability to recognize and bind complementary Lewis bases. Moreover, this strategy allows multidentate Lewis acids with markedly different properties to be made from the same precursor. We expect that our strategy for synthesizing structurally well-defined multidentate Lewis acids will make them more readily available and will help promote further study of their unique coordination chemistry.

Experimental Section

Pentane was dried by distillation from sodium, CH_2Cl_2 was dried by distillation from P_2O_5, and $TiCl_4$ was purified by distillation. All other reagents were commercial products that were used without further purification. Flash chromatography was performed in the normal way.[16]

5-Bromo-2-(1,1-dimethylethyl)phenol.[9,17] A suspension prepared by adding SiO_2 (14.4 g, 240 mmol)[18] and Na_2CO_3 (5.05 g, 47.6 mmol) to 3-bromophenol (5.00 g, 28.9 mmol) in CCl_4 (40 mL) was stirred at 25 °C and treated dropwise with 2-bromo-2-methylpropane (4.76 g, 34.7 mmol). The mixture was then heated at reflux for 18 h, cooled to 25 °C, and filtered. The filtered solid was washed with $CHCl_3$, and the washings were added to the original filtrate. The combined organic phases were washed with H_2O and saturated aqueous NaCl, and then they were dried with anhydrous $MgSO_4$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (93%)/ethyl acetate (7%)) to give 5-bromo-2-(1,1-dimethylethyl)phenol (5.75 g, 25.1 mmol, 87%) as a colorless oil.[9]

2,2´-Methylenebis[3-bromo-6-(1,1-dimethylethyl)phenol] (5).[9] Diphenol **5** was prepared from 5-bromo-2-(1,1-dimethylethyl)phenol by the published method.[9]

1,1´-Methylenebis[6-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (6).[9] A suspension prepared by adding K_2CO_3 (2.70 g, 19.5 mmol) to 2,2´-methylenebis[3-bromo-6-(1,1-dimethylethyl)phenol] (**5**; 0.917 g, 1.95 mmol) in acetone (20 mL) was stirred at 25 °C and treated with iodomethane (5.70 g, 40.2 mmol). The mixture was then heated at reflux for 36 h, cooled to 25 °C, and filtered. The filtered solid was washed with $CHCl_3$, and the washings were added to the original filtrate. Volatiles were removed by evaporation under reduced pressure, the residue was treated with saturated aqueous NH_4Cl, and the resulting mixture was extracted with $CHCl_3$. The combined extracts were washed with saturated aqueous NaCl and dried with anhydrous $MgSO_4$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (100%)) to give 1,1´-methylenebis[6-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (**6**; 0.923 g, 1.85 mmol, 95%) as a colorless solid. An analytically pure sample was prepared by recrystallization from hexane: mp 165-167 °C (lit.[9] 164-166 °C).

2,7-Bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluorene (4).[9] Dimethyl ether **4** was prepared from 1,1´-methylenebis[6-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (**6**) by the published procedure.[9]

2,7-Bis(1,1-dimethylethyl)-9*H*-fluorene-1,8-diol (3). A solution of 2,7-bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluorene (**4**; 225 mg, 0.665 mmol) in CH_2Cl_2 (10 mL) was stirred at -78 °C under dry Ar and treated dropwise with a solution of BBr_3 (666 mg, 2.66 mmol) in CH_2Cl_2 (2.6 mL). The cooling bath was removed, and the temperature was allowed to rise to 25 °C. After 18 h, the resulting mixture was recooled to 0 °C, treated with H_2O (15 mL), and extracted with $CHCl_3$. The combined extracts were washed with saturated aqueous NaCl and dried with anhydrous $MgSO_4$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (93%)/ethyl acetate (7%)) to give 2,7-bis(1,1-dimethylethyl)-9*H*-fluorene-1,8-diol (**3**; 178 mg, 0.573 mmol, 86%) as a colorless solid. An analytically pure sample was prepared by recrystallization from $CHCl_3$: mp 176-178 °C; IR (melt) 3548 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (s, 18H), 3.64 (s, 2H), 4.80 (s, 2H), 7.27 (d, 2H, ^3J = 8.0 Hz), 7.32 (d, 2H, ^3J = 8.0 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.5, 30.0, 34.5, 112.4, 126.3, 128.1, 134.4, 141.4, 150.8; HRMS (EI) calcd for $C_{21}H_{26}O_2$ *m/e* 310.1933, found *m/e* 310.1925.

Bis(trichlorotitanium phenoxide) 7. A solution of 2,7-bis(1,1-dimethylethyl)-9*H*-fluorene-1,8-diol (**3**; 10.6 mg, 0.0341 mmol) in CH_2Cl_2 (0.5 mL) was stirred at 25 °C under dry Ar and treated dropwise with neat $TiCl_4$ (13.8 mg, 0.0727 mmol). After the addition was complete, the resulting red mixture was kept at 25 °C for 20 min. Partial evaporation of solvent then yielded red crystals of bis(trichlorotitanium phenoxide) **7** (19.0 mg, 0.0308 mmol, 90%): mp 172-176 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 18H), 4.60 (s, 2H), 7.42 (d, 2H, ^3J = 8.0 Hz), 7.53 (d, 2H, ^3J = 8.0 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 30.5, 33.6, 35.2, 118.2, 126.4, 135.7, 137.0, 140.9, 168.9.

X-ray Crystallographic Study of Bis(trichlorotitanium phenoxide) 7. Data were collected on an Enraf-Nonius CAD-4 diffractometer. Cell constants were obtained using 25 well-centered reflections ($40° \leq 2\theta \leq 50°$). Five standard reflections were measured every 1 h of exposure time and showed only small fluctuations. The data were corrected for absorption by Gaussian integration. The structure was solved by direct methods using SHELXS-85.[19] Full-matrix least-squares refinement on F^2 was carried out with SHELXL-93.[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined using a riding model with isotropic thermal parameters 1.2 times those of their carrier atoms (1.5 times for methyl groups).

1:2 Complex of Bis(trichlorotitanium phenoxide) 7 with 4,4´-Dimethylbenzophenone. A solution of 2,7-bis(1,1-dimethylethyl)-9*H*-fluorene-1,8-diol (**3**; 27.0 mg, 0.0870 mmol) in CH_2Cl_2 (1.2 mL) was stirred at 25 °C under dry Ar and treated dropwise with neat $TiCl_4$ (32.9 mg, 0.173 mmol). After the addition was complete, the resulting red mixture was kept at 25 °C for 15 min and was then treated with a solution of 4,4´-dimethylbenzophenone (37.0 mg, 0.176 mmol) in CH_2Cl_2 (1.2 mL). Partial evaporation of solvent then yielded red crystals of the 1:2 complex of bis(trichlorotitanium phenoxide) **7** with 4,4´-dimethylbenzophenone as a solvate containing an equimolar amount of CH_2Cl_2 (79.0 mg, 0.0704 mmol, 81%): mp 102-110 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 18H), 2.45 (s, 12H), 4.77 (s, 2H), 5.30 (s, 2H), 7.31 (d, 8H, ^3J = 8.0 Hz), 7.39 (d, 2H, ^3J = 8.0 Hz), 7.48 (d, 2H, ^3J = 8.0 Hz), 7.90 (d, 8H, ^3J = 8.0 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.8, 30.6, 35.0, 35.2, 53.3, 117.2, 125.6, 129.1, 132.5, 133.4, 137.4, 141.2, 145.7, 145.7, 168.2, 201.4.

X-ray Crystallographic Study of the 1:2 Complex of Bis(trichlorotitanium phenoxide) 7 with 4,4´-Dimethylbenzophenone. Data were collected on an Enraf-Nonius CAD-4 diffractometer. Cell constants were obtained using 25 well-centered reflections ($40° \leq 2\,\theta \leq 45°$). Five standard reflections were measured every 1 h of exposure time and showed only small fluctuations. The data were corrected for absorption by Gaussian integration. The structure was solved by direct methods using SHELXS-96.[21] Full-matrix least-squares refinement on F^2 was carried out with SHELXL-96.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined using a riding model with isotropic thermal parameters 1.2 times those of their carrier atoms (1.5 times for methyl groups).

Dimer 9 of Bis(diethylaluminum phenoxide) 8. A solution of 2,7-bis(1,1-dimethylethyl)-9*H*-fluorene-1,8-diol (**3**; 14.8 mg, 0.0477 mmol) in a mixture of pentane (0.6 mL) and CH_2Cl_2 (0.2 mL) was stirred at 25 °C under dry Ar and treated dropwise with neat $Al(CH_2CH_3)_3$ (10.9 mg, 0.0955 mmol). After the addition was complete, the resulting brown mixture was kept at 25 °C for 20 min. Partial evaporation of solvent then yielded brown crystals of the dimer **9** of bis(diethylaluminum phenoxide) **8** (14.6 mg, 0.0153 mmol, 62%): ^1H NMR (400 MHz, $CDCl_3$) δ 0.28 (q, 8H, ^3J = 8.1 Hz), 0.35 (q, 8H, ^3J = 8.1 Hz), 0.65 (t, 12H, ^3J = 8.1 Hz), 0.87 (t, 12H, ^3J = 8.1 Hz), 1.55 (s, 36H), 4.75 (s, 4H), 7.52 (d, 4H, ^3J = 8.0 Hz), 7.55 (d, 4H, ^3J = 8.0 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 2.1, 5.2, 8.1, 8.7, 33.1, 36.4, 36.9, 115.7, 128.9, 134.5, 139.6, 141.7, 148.8.

X-ray Crystallographic Study of the Dimer 9 of Bis(diethylaluminum phenoxide) 8. Data were collected on an Enraf-Nonius CAD-4 diffractometer. Cell constants were obtained using 25 well-centered reflections ($40° \leq 2\theta \leq 42°$). Five standard reflections were measured every 1 h of exposure time and showed only small fluctuations. The data were corrected for absorption by Gaussian integration. The structure was solved by direct methods using SHELXS-96.[21] Full-matrix least-squares refinement on F^2 was carried out with SHELXL-96.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined using a riding model with isotropic thermal parameters 1.2 times those of their carrier atoms (1.5 times for methyl groups).

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes for bis(trichlorotitanium phenoxide) **7** (17 pages), the CH_2Cl_2 solvate of its 1:2 complex with 4,4′-dimethylbenzophenone (23 pages), and the dimer **9** of bis(diethylaluminum phenoxide) **8** (30 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any masthead page for ordering information.

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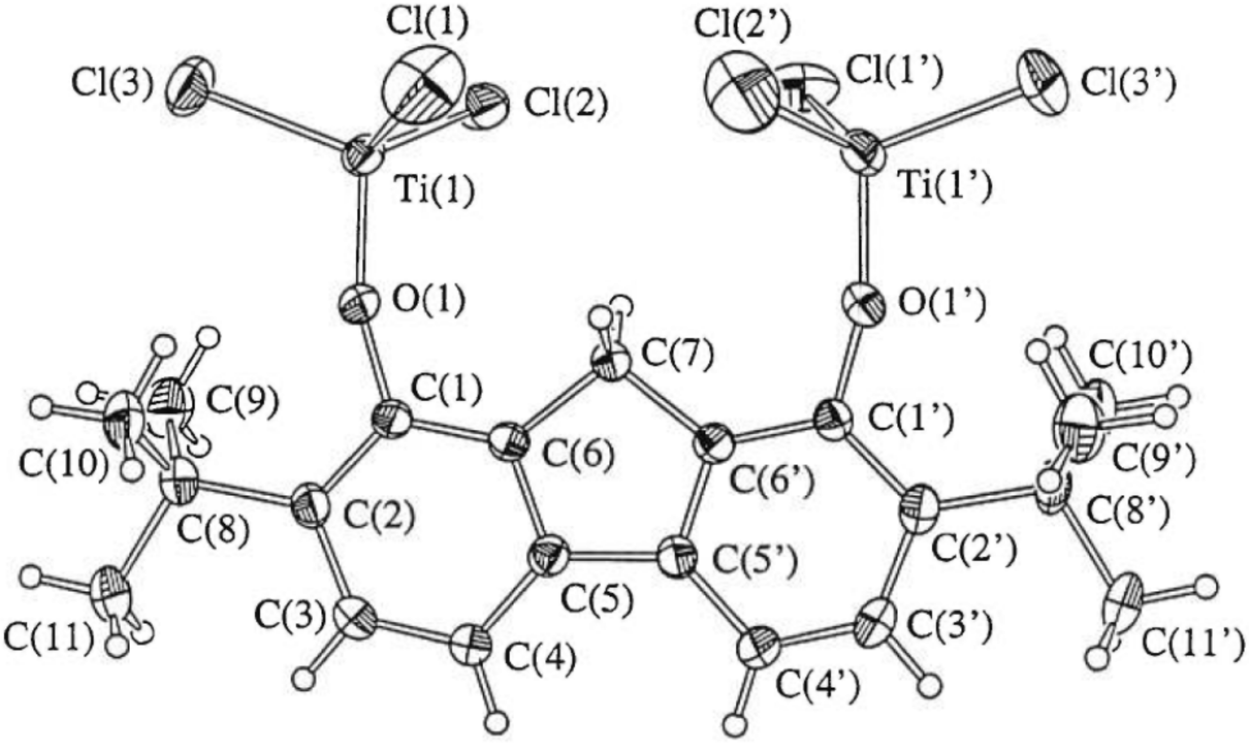


Figure 1. ORTEP view of the structure of bis(trichlorotitanium phenoxide) 7. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, and hydrogen atoms are shown as spheres of arbitrary size.

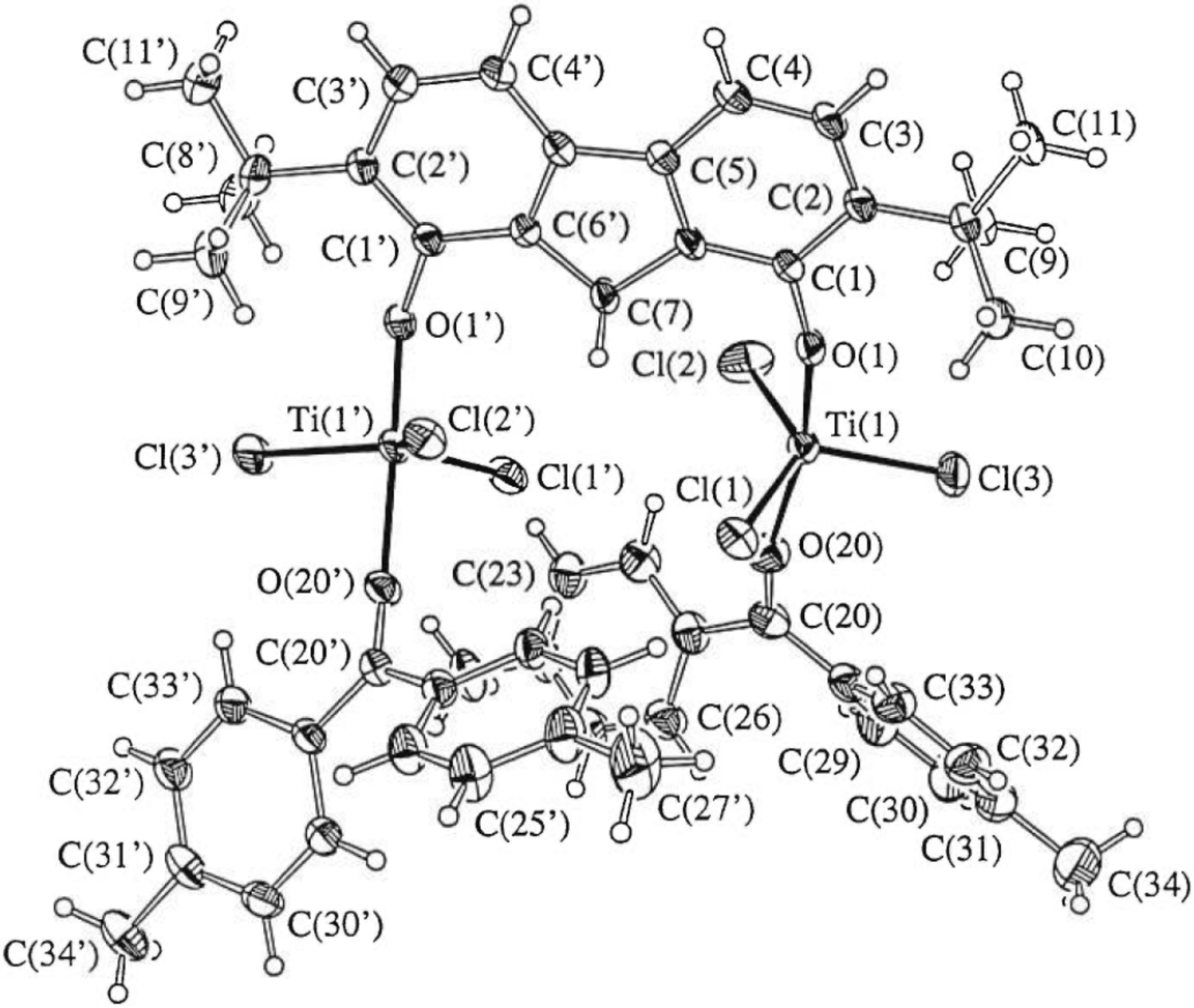


Figure 2. ORTEP view of the structure of the CH_2Cl_2 solvate of the 1:2 complex of bis(trichlorotitanium phenoxide) **7** with 4,4′-dimethylbenzophenone. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, bonds to titanium are drawn using solid lines, and CH_2Cl_2 is omitted for clarity.

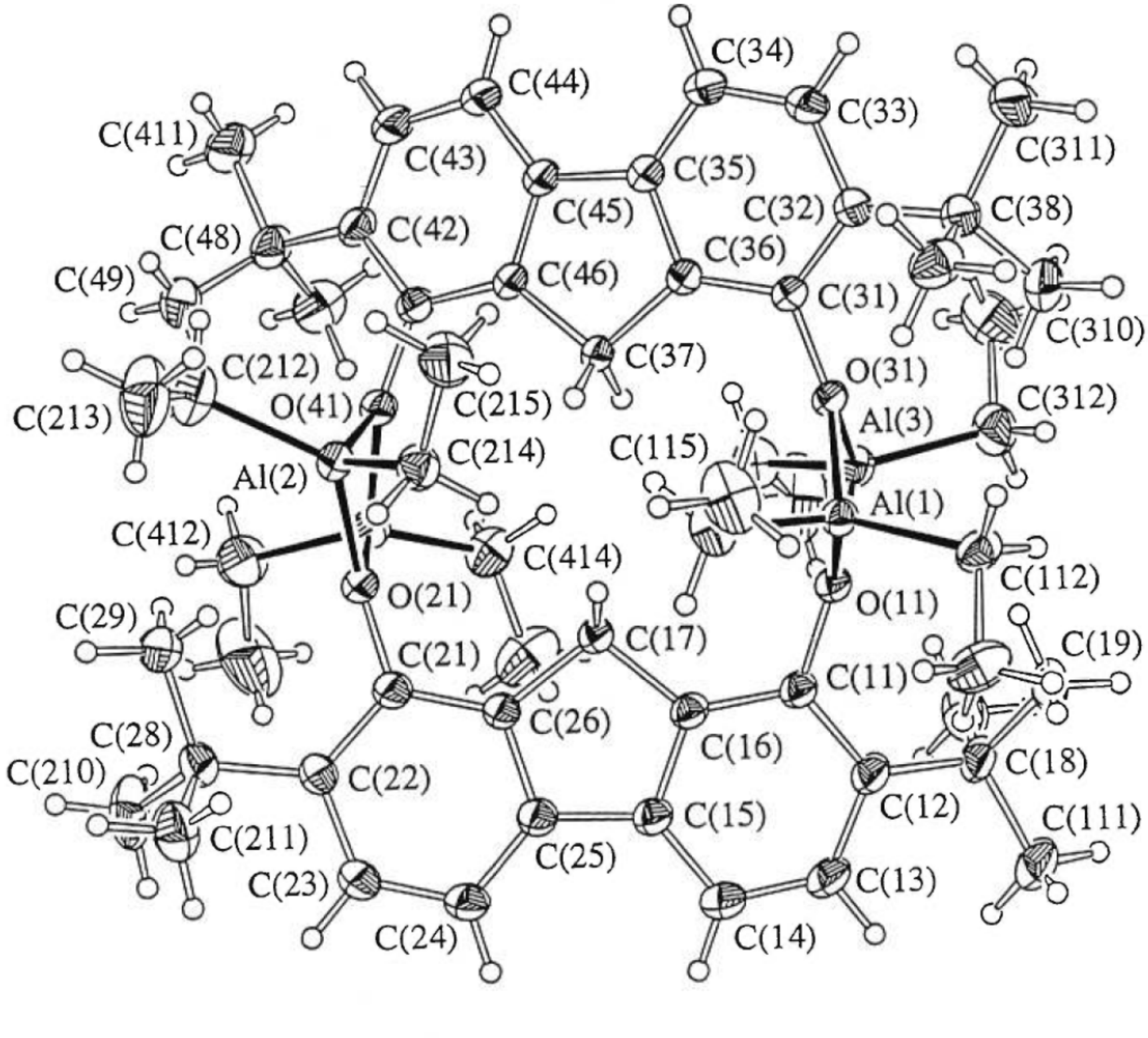


Figure 3. ORTEP view of the structure of the dimer **9** of bis(diethylaluminum phenoxide) **8**. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, and bonds to aluminum are drawn using solid lines.

Table 1. Selected Bond Lengths and Angles for Bis(trichlorotitanium phenoxide) 7

Bond Lengths (Å)

Ti(1)—O(1)	1.723(3)
Ti(1′)—O(1′)	1.731(3)
Ti(1)—Cl(1)	2.157(2)
Ti(1′)—Cl(1′)	2.192(2)
Ti(1)—Cl(2)	2.179(2)
Ti(1′)—Cl(2′)	2.159(2)
Ti(1)—Cl(3)	2.185(2)
Ti(1′)—Cl(3′)	2.170(2)

Bond Angles (deg)

Cl(1)—Ti(1)—O(1)	109.6(1)
Cl(1′)—Ti(1′)—O(1′)	108.4(1)
Cl(2)—Ti(1)—O(1)	107.9(1)
Cl(2′)—Ti(1′)—O(1′)	109.7(1)
Cl(3)—Ti(1)—O(1)	110.1(1)
Cl(3′)—Ti(1′)—O(1′)	111.0(1)
Cl(1)—Ti(1)—Cl(2)	109.5(1)
Cl(1′)—Ti(1′)—Cl(2′)	108.6(1)
Cl(1)—Ti(1)—Cl(3)	109.9(1)
Cl(1′)—Ti(1′)—Cl(3′)	109.6(1)
Cl(2)—Ti(1)—Cl(3)	109.8(1)

Cl(2′)—Ti(1′)—Cl(3′)	109.6(1)
C(1)—O(1)—Ti(1)	162.7(3)
C(1′)—O(1′)—Ti(1′)	164.6(3)

Table 2. Crystallographic Data for Bis(trichlorotitanium phenoxide) 7

formula	$C_{21}H_{24}Cl_6O_2Ti_2$
fw	616.90
system	monoclinic
space group	$P2_1/c$
cell constants	
a, Å	15.551(6)
b, Å	9.988(5)
c, Å	19.842(10)
α, deg	90
β, deg	113.96(4)
γ, deg	90
cell volume, $Å^3$	2816(2)
Z	4
T, K	225
D_{calcd}, g cm^{-3}	1.455
μ_{calcd}, mm^{-1}	10.39
radiation (λ, Å)	graphite-monochromated Cu Kα (1.54056)
cryst dimens, mm	0.64 x 0.28 x 0.18
data collcn range	$\pm h$, $+k$, $+l$
no. of reflcns collcd	19488
no. of reflcns refined	5338

goodness-of-fit	0.920
$R1$	0.0608
w$R2$	0.1512
$\Delta\rho_{\text{max}}$, e Å^{-3}	0.974
$\Delta\rho_{\text{min}}$, e Å^{-3}	-0.743

Table 3. Selected Bond Lengths and Angles for the CH_2Cl_2 Solvate of the 1:2 Complex of Bis(trichlorotitanium phenoxide) 7 with 4,4´-Dimethylbenzophenone.

Bond Lengths (Å)

Ti(1)—O(1)	1.764(3)
Ti(1´)—O(1´)	1.776(3)
Ti(1)—O(20)	2.066(3)
Ti(1´)—O(20´)	2.058(3)
Ti(1)—Cl(1)	2.257(2)
Ti(1´)—Cl(1´)	2.236(2)
Ti(1)—Cl(2)	2.265(2)
Ti(1´)—Cl(2´)	2.271(2)
Ti(1)—Cl(3)	2.223(1)
Ti(1´)—Cl(3´)	2.234(1)
O(20)—C(20)	1.248(5)
O(20´)—C(20´)	1.269(4)

Bond Angles (deg)

O(1)—Ti(1)—O(20)	168.8(1)
O(1´)—Ti(1´)—O(20´)	172.8(1)
O(1)—Ti(1)—Cl(1)	94.1(1)
O(1)—Ti(1)—Cl(2)	91.6(1)
O(1)—Ti(1)—Cl(3)	99.9(1)
O(1´)—Ti(1´)—Cl(1´)	98.1(1)
O(1´)—Ti(1´)—Cl(2´)	87.8(1)

O(1´)—Ti(1´)—Cl(3´)	95.1(1)
O(20)—Ti(1)—Cl(1)	82.6(1)
O(20)—Ti(1)—Cl(2)	83.0(1)
O(20)—Ti(1)—Cl(3)	91.2(1)
O(20´)—Ti(1´)—Cl(1´)	87.8(1)
O(20´)—Ti(1´)—Cl(2´)	85.6(1)
O(20´)—Ti(1´)—Cl(3´)	86.4(1)
Cl(1)—Ti(1)—Cl(2)	133.8(1)
Cl(1)—Ti(1)—Cl(3)	112.6(1)
Cl(2)—Ti(1)—Cl(3)	111.4(1)
Cl(1´)—Ti(1´)—Cl(2´)	121.3(1)
Cl(1´)—Ti(1´)—Cl(3´)	112.4(1)
Cl(2´)—Ti(1´)—Cl(3´)	125.2(1)
Ti(1)—O(1)—C(1)	162.9(2)
Ti(1´)—O(1´)—C(1´)	147.6(2)
Ti(1)—O(20)—C(20)	165.0(3)
Ti(1´)—O(20´)—C(20´)	158.4(3)

Dihedral Angles (deg)

Ti(1)—O(20)—C(20)—C(21)	-158.5(10)
Ti(1)—O(20)—C(20)—C(28)	21.8(15)
Ti(1´)—O(20´)—C(20´)—C(21´)	-44.9(9)
Ti(1´)—O(20´)—C(20´)—C(28´)	136.4(6)

Table 4. Crystallographic Data for the CH_2Cl_2 Solvate of the 1:2 Complex of Bis(trichlorotitanium phenoxide) 7 with 4,4´-Dimethylbenzophenone.

formula	$C_{51}H_{52}Cl_6O_4Ti_2 \cdot CH_2Cl_2$
fw	1122.35
system	monoclinic
space group	$P2_1/c$
cell constants	
a, Å	12.756(3)
b, Å	21.458(13)
c, Å	20.047(7)
α, deg	90
β, deg	101.28(2)
γ, deg	90
cell volume, $Å^3$	5381(4)
Z	4
T, K	210
D_{calcd}, g cm^{-3}	1.385
μ_{calcd}, mm^{-1}	4.181
radiation (λ, Å)	graphite-monochromated Cu Kα (1.54056)
cryst dimens, mm	0.70 x 0.43 x 0.11
data collcn range	$\pm h$, $\pm k$, $\pm l$
no. of reflcns collcd	38277

no. of reflcns refined	10208
goodness-of-fit	0.981
$R1$	0.0598
w$R2$	0.1715
$\Delta\rho_{\max}$, e Å^{-3}	0.639
$\Delta\rho_{\min}$, e Å^{-3}	-1.164

Table 5. Selected Bond Lengths and Angles for the Dimer 9 of Bis(diethylaluminum phenoxide) 8

Bond Lengths (Å)

Al(1)—O(11)	1.894(2)
Al(1)—O(31)	1.865(2)
Al(1)—C(112)	1.963(2)
Al(1)—C(114)	1.943(3)
Al(3)—O(11)	1.882(2)
Al(3)—O(31)	1.904(2)
Al(3)—C(312)	1.960(3)
Al(3)—C(314)	1.951(3)
Al(2)—O(21)	1.868(2)
Al(2)—O(41)	1.903(2)
Al(2)—C(212)	1.966(3)
Al(2)—C(214)	1.953(2)
Al(4)—O(21)	1.889(2)
Al(4)—O(41)	1.870(2)
Al(4)—C(412)	1.969(3)
Al(4)—C(414)	1.947(3)
Al(1)•••Al(3)	2.862(1)
Al(2)•••Al(4)	2.871(2)
O(11)•••O(31)	2.424(2)
O(21)•••O(41)	2.398(2)
O(11)—C(11)	1.415(2)
O(31)—C(31)	1.417(2)

O(21)—C(21)	1.409(2)
O(41)—C(41)	1.410(2)

Bond Angles (deg)

O(11)—Al(1)—O(31)	80.3(1)
O(11)—Al(1)—C(112)	109.3(1)
O(11)—Al(1)—C(114)	119.0(1)
C(112)—Al(1)—C(114)	113.7(1)
O(31)—Al(1)—C(112)	118.9(1)
O(31)—Al(1)—C(114)	111.8(1)
O(11)—Al(3)—O(31)	79.6(1)
O(11)—Al(3)—C(312)	120.6(1)
O(11)—Al(3)—C(314)	110.8(1)
C(312)—Al(3)—C(314)	112.6(1)
O(31)—Al(3)—C(312)	108.1(1)
O(31)—Al(3)—C(314)	121.9(1)
O(21)—Al(2)—O(41)	79.0(1)
O(21)—Al(2)—C(212)	126.2(1)
O(21)—Al(2)—C(214)	108.0(1)
C(212)—Al(2)—C(214)	109.8(1)
O(41)—Al(2)—C(212)	104.6(1)
O(41)—Al(2)—C(214)	128.4(1)
O(21)—Al(4)—O(41)	79.3(1)
O(21)—Al(4)—C(412)	107.6(1)
O(21)—Al(4)—C(414)	121.8(1)
C(412)—Al(4)—C(414)	112.1(1)

O(41)—Al(4)—C(412)	119.0(1)
O(41)—Al(4)—C(414)	113.7(1)
C(11)—O(11)—Al(1)	124.8(1)
C(11)—O(11)—Al(3)	135.4(1)
Al(1)—O(11)—Al(3)	98.6(1)
C(31)—O(31)—Al(1)	134.1(1)
C(31)—O(31)—Al(3)	125.4(1)
Al(1)—O(31)—Al(3)	98.8(1)
C(21)—O(21)—Al(2)	136.9(1)
C(21)—O(21)—Al(4)	121.7(1)
Al(2)—O(21)—Al(4)	99.7(1)
C(41)—O(41)—Al(2)	119.0(1)
C(41)—O(41)—Al(4)	141.5(1)
Al(2)—O(41)—Al(4)	99.1(1)

Dihedral Angles (deg)

O(11)—Al(1)—O(31)—Al(3)	-12.4(1)
O(11)—Al(3)—O(31)—Al(1)	12.5(1)
O(31)—Al(1)—O(11)—Al(3)	12.5(1)
O(31)—Al(3)—O(11)—Al(1)	-12.3(1)
O(21)—Al(2)—O(41)—Al(4)	13.3(1)
O(21)—Al(4)—O(41)—Al(2)	-13.1(1)
O(41)—Al(2)—O(21)—Al(4)	-13.2(1)
O(41)—Al(4)—O(21)—Al(2)	13.4(1)
C(12)—C(11)—O(11)—Al(1)	-104.8(2)
C(12)—C(11)—O(11)—Al(3)	90.9(2)

C(32)—C(31)—O(31)—Al(1)	87.6(2)
C(32)—C(31)—O(31)—Al(3)	-110.8(2)
C(22)—C(21)—O(21)—Al(2)	94.5(2)
C(22)—C(21)—O(21)—Al(4)	-103.6(2)
C(42)—C(41)—O(41)—Al(2)	-110.3(2)
C(42)—C(41)—O(41)—Al(4)	80.2(3)

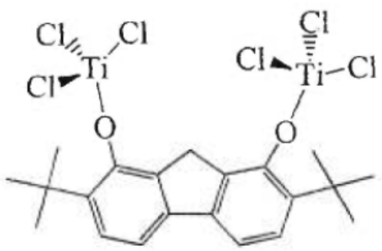
Table 6. Crystallographic Data for the Dimer 9 of Bis(diethylaluminum phenoxide) 7

formula	$C_{58}H_{88}Al_4O_4$
fw	957.264
system	triclinic
space group	P -1
cell constants	
a, Å	12.330(3)
b, Å	14.588(3)
c, Å	16.638(9)
α, deg	73.95(3)
β, deg	84.88(4)
γ, deg	79.97(2)
cell volume, $Å^3$	2829(2)
Z	2
T, K	225
D_{calcd}, g cm^{-3}	1.135
μ_{calcd}, mm^{-1}	1.186
radiation (*λ*, Å)	graphite-monochromated Cu Kα (1.54056)
cryst dimens, mm	0.58 x 0.46 x 0.38
data collcn range	±*h*, ±*k*, ±*l*
no. of reflcns collcd	45681

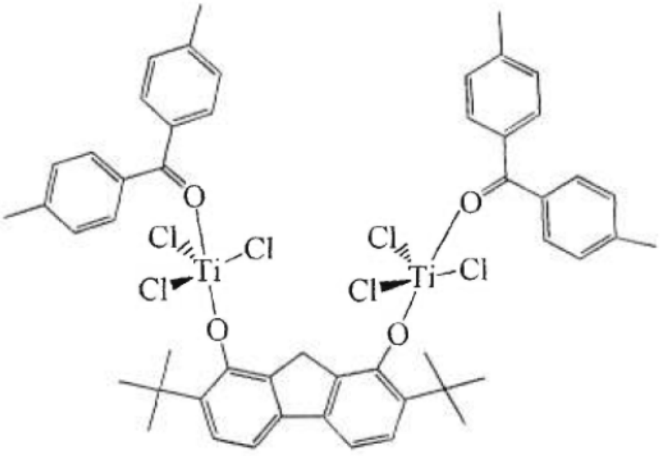
no. of reflcns refined	10709
goodness-of-fit	1.031
$R1$	0.0581
w$R2$	0.1662
$\Delta\rho_{\max}$, e Å^{-3}	0.686
$\Delta\rho_{\min}$, e Å^{-3}	-0.407

6.2 CONCLUSION

Dans la structure du fluorènediol **19**, les deux oxygènes hydroxyles sont orientés par un squelette organique rigide et sont espacés de 5.9 Å[54]. Nous avons réussi à le convertir en l'acide de Lewis bidentate **42** qui a été caractérisé par une étude cristallographique. Nous avons pareillement caractérisé le complexe 1:2 **43** formé par le composé **42** et la diméthyl-4,4' benzophénone. Dans ce complexe, malheureusement, chaque groupe OTiCl$_3$ est lié à une seule molécule de cétone. La géométrie bipyramidale à base triangulaire du titane pentacoordonné est moins congestionnée que celle de la structure **41**, qui favorise une géométrie pyramidale à base carrée.

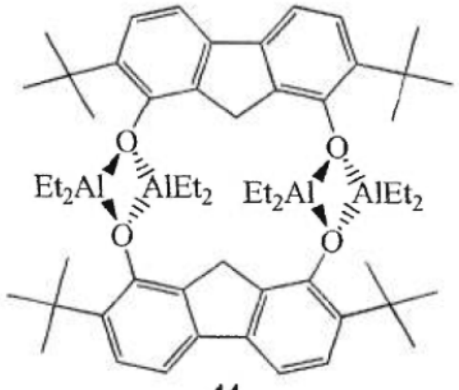


42



43

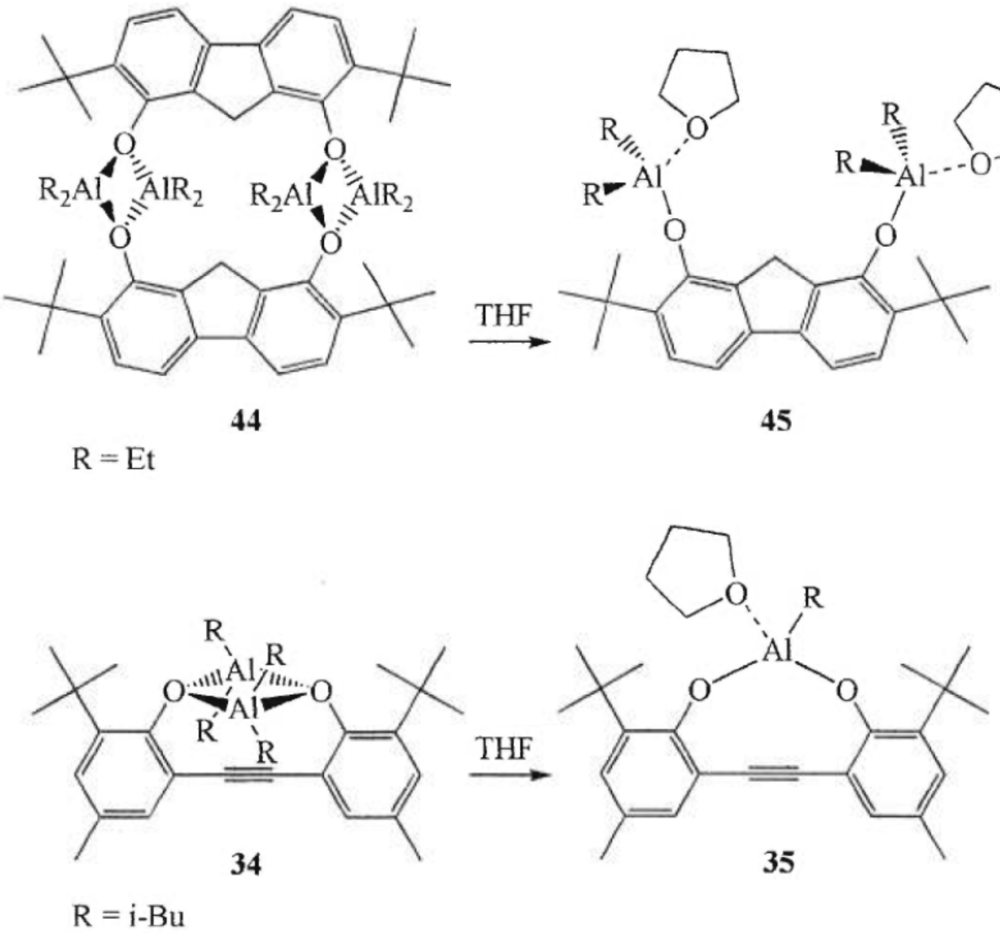
La réaction du diol **19** avec deux équivalents de AlEt$_3$ a fourni le complexe dimérique **44** dans lequel les deux groupes OAlEt$_2$ interagissent intermoléculairement en formant des cycles Al$_2$O$_2$ moins déformés que celui du composé **34** (Schéma 11).



44

Tous nos essais de co-cristallisation du composé **44** avec les composés carbonylés ont été infructueux. Nous avons testé l'acidité de Lewis du composé **44** en le co-cristallisant avec du THF dans un mélange équimolaire. Le spectre RMN ^{1}H ($CDCl_3$, 25°C) des cristaux obtenus montre la formation d'un complexe 1:2 symétrique très compatible avec la structure **45** dans laquelle chaque groupe $OAlEt_2$ est lié à une molécule de THF (Schéma 11). Contrairement au cas du composé **34**, sur lequel l'addition d'un équivalent de THF a fourni le composé **35** en libérant une molécule de $Al(i\text{-}Bu)_3$, le composé **44** est plutôt dissocié par le THF pour former le composé **45** (Schéma 11).

Schéma 11



Ces observations suggèrent que l'ouverture des cycles Al_2O_2 par le THF est faisable pour des associations intramoléculaires aussi bien que pour des associations intermoléculaires des groupes $OAlR_2$. Cependant, les cycles Al_2O_2 de structures planes, formés dans les dimères des aryloxydes de dialkylaluminium, ne sont pas rompus par le THF[52]. Nous proposons que les déformations des cycles Al_2O_2 dans les composés **44** et **34** sont à l'origine de la dissociation et de la disproportion obtenues en les co-cristallisant avec le THF (Schéma 11).

Nous demeurons convaincus que la double complexation d'un groupe carbonyle par un acide de Lewis bidentate fort est faisable et que les problèmes rencontrés dans la réalisation d'une telle complexation sont dus à la non-convenance des distances qui séparent les deux oxygènes hydroxyles dans les structures des diols utilisés. Le choix d'un diol de structure aussi rigide que le diol **19** et dans lequel la séparation des deux oxygènes hydroxyles serait plus courte, nous permettrait d'atteindre notre objectif.

CHAPITRE 7

CONCLUSION

Dans notre étude visant la double complexation d'un composé carbonylé par deux sites acides de Lewis, nous avons essayé dans un premier temps d'augmenter l'impact des résultats de Wuest et collaborateurs[25,40] qui confirment la faisabilité de la double coordination *intramoléculaire* de la fonction cétone par deux sites acides de Brønsted ou de Lewis. À cette fin, nous avons synthétisé diverses molécules possédant deux ligands basiques disposés symétriquement par rapport à une fonction cétone centrale, dans l'espoir d'utiliser la chélation pour fixer deux sites acides de Lewis dans une orientation favorisant une double complexation de la cétone par la présence unique de liens de coordination. Malheureusement, il nous a été impossible d'atteindre cet objectif en utilisant le $TiCl_4$ comme acide de Lewis à cause des répulsions stérique et electrostatique entre les atomes de chlore dans les doubles chélates hypothétiques **30**. L'utilisation d'autres acides de Lewis moins encombrés que le $TiCl_4$ ne nous a pas non plus aidés à démontrer que la double chélation et la double coordination sont possibles.

Par ailleurs, nous sommes parvenus à démontrer qu'une cétone simple est suffisamment basique pour être conjointement liée aux deux hydrogènes hydroxyles du diol **17** à l'état solide et nous avons essayé d'étendre ce résultat aux acides de Lewis.

Il ne nous a pas été possible de synthétiser un acide de Lewis bidentate possédant deux sites acides de Lewis indépendants à partir du diol **17** à cause de la proximité des deux oxygènes hydroxyles. Nous avons alors songé à espacer davantage les deux oxygènes hydroxyles en synthétisant le diol **18** et nous avons réussi à le convertir en les acides de Lewis bidentates réels **38** et **39**. Ces résultats sont importants puisque la conversion des groupes hydroxyles en alkoxydes de métal offre une stratégie efficace pour la construction de divers acides de Lewis bidentates forts et de propriétés différentes à partir d'un même précurseur organique.

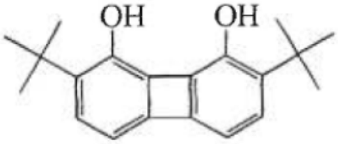
L'étude cristallographique du complexe 1:1 formé par l'acide de Lewis bidentate **38** et le diméthoxy-1,2 éthane a montré que le complexe est un oligomère. Une étude RMN ^1H à basse température du même complexe a avéré que c'est plutôt la forme monomérique **40** qui prédomine en solution. Cette observation reflète l'habilité de l'acide de Lewis bidentate **38** dans la reconnaissance et la coordination de deux sites basiques d'un même substrat bidentate.

Nous avons réussi à isoler un complexe 1:2 **41** formé par l'acide de Lewis bidentate **39** et l'acétate d'éthyle dans lequel chaque groupe $OTiCl_3$ complexe une seule molécule d'ester. Malheureusement, la rotation des groupes aryles autour de l'espaceur diyne a laissé la voie libre aux deux sites acides de Lewis d'agir indépendamment. La géométrie de pentacoordination inhabituelle du titane dans le complexe **41** est due à l'encombrement stérique créé par les substituants adjacents aux deux sites acides de Lewis.

Nous avons synthétisé le diol **19** de structure plus rigide dans lequel la distance séparant les deux oxygènes hydroxyles est égale à 5.9 Å et qui est en fait comprise entre les valeurs de 4.1 Å et 6.5 Å calculées pour les diols **17** et **18**, respectivement[54]. Nous avons réussi à convertir le diol **19** en l'acide de Lewis bidentate réel **42** et nous l'avons co-cristallisé avec deux équivalents de diméthyl-4,4' benzophénone. Dans le complexe **43** obtenu, chaque groupe $OTiCl_3$ est lié à une seule molécule de cétone. Nous proposons que l'encombrement stérique causé par les groupes t-Bu adjacents aux sites acides de Lewis est à l'origine de la pentacoordination du titane dans les deux structures **41** et **43**.

Par ailleurs, nous avons pu transformer le diol **19** en le traitant par deux équivalents de $AlEt_3$ et nous avons obtenu le dimère **44** formé par le bis(phénoxyde de diéthylaluminium) correspondant. Cette structure incorpore deux cycles Al_2O_2 moins déformés que celui du composé **34**. Malheureusement, l'association intermoléculaire des groupes $OAlEt_2$ n'a été guère favorable pour la complexation bidentate d'un substrat basique.

Malgré que nous n'ayons pas atteint notre objectif de construire un acide de Lewis bidentate fort et capable de participer dans une double complexation d'un groupe carbonyle, nous avons pu dégagé plusieurs nouvelles données instructives qui nous seront très utiles dans la suite de ce projet. Dans un avenir proche, nous voudrions synthétiser le biphénylènediol **46** où la distance séparant les deux oxygènes hydroxyles est égale à 3.8 Å. Bien que cette valeur soit inférieure à celle trouvée pour le diol **17** (4.1Å), la rigidité de la structure **46** empêcherait toute déformation pouvant rétrécir la distance séparant les deux oxygènes hydroxyles. Dans le cas du composé **34**, cette distance a été réduite à 2.54 Å par la déformation de l'espaceur acétylénique. Nous croyions que le bis(phénoxyde de trichlorotitane) correspondant aura de fortes chances de complexer doublement un composé carbonylé en adoptant une géométrie de pentacoordination.



46

Bien que nous n'ayons pas réussi à complexer doublement l'oxygène d'un groupe carbonyle par deux sites acides de Lewis, nous avons toutefois contribué à enrichir la chimie de coordination de l'aluminium et du titane par nos études synthétiques, structurales et thermodynamiques.

CHAPITRE 8

CONSIDÉRATIONS GÉNÉRALES SUR LA PARTIE EXPÉRIMENTALE

8.1 INSTRUMENTATION

Les points de fusion ont été mesurés avec un appareil à capillaire Thomas - Hoover et ne sont pas corrigés. Les spectres infrarouge ont été enregistrés avec un spectophotomètre Perkin-Elmer 1600 (FTIR). Les spectres des composés de titane et d'aluminium ont été enregistrés en utilisant une suspension de l'échantillon dans le Nujol entre deux plaques de NaCl. Les spectres des huiles et des solides à point de fusion bas ont été enregistrés en utilisant un film liquide entre deux plaques de NaCl. Les spectres des solides ont été enregistrés en utilisant une matrice solide de KBr.

Les spectres de résonance magnétique nucléaire du proton (RMN ^{1}H) à 25°C ont été enregistrés avec un appareil Bruker AMX 300 (300 MHz) alors que les spectres des études à température variable ont été enregistrés avec un appareil Bruker AMXR 400 (400 MHz). Les spectres de résonance magnétique nucléaire du carbone (RMN ^{13}C) à 25°C ont été enregistrés avec un appareil Bruker AMX 300 (75.4 MHz) alors que les spectres des études à température variable ont été enregistrés avec un appareil Bruker AMXR 400 (100.6 MHz). Les déplacements chimiques (δ) sont exprimés en partie par million (ppm) par rapport à une référence interne : le tétraméthylsilane (TMS) (δ ^{1}H = 0.00 ; ^{13}C = 0.00) ou le chloroforme ($CHCl_3$) (δ ^{1}H = 7.26 ; ^{13}C = 76.9) ou le dichlorométhane (CH_2Cl_2) (δ ^{1}H = 5.32 ; ^{13}C = 53.8) ou le toluène (δ ^{1}H = 2.09 ; ^{13}C = 20.4). Les constantes de couplage (J) sont exprimés en Hz. Les symboles descriptifs des spectres sont : s, singulet ; d, doublet ; dd, doublet de doublets ; bs, large singulet ; m, multiplet ; q, quadruplet.

Les spectres de masse (SM) à haute résolution (HR) ont été enregistrés avec un spectromètre Kratos MS-50 TATC par impact électronique (IE) ou par bombardement rapide d'atomes (FAB). Les analyses élémentaires ont été effectuées chez Galbraith Laboratories, Knoxville, Tennessee.

8.2 RÉACTIONS EFFECTUÉES DANS DES CONDITIONS ANHYDRES

À part les réactions faites en milieux aqueux, toutes les réactions ont été effectuées sous atmosphère d'argon passé à travers une colonne de tamis moléculaires. Toute la verrerie utilisée a été séchée pendant un minimum de douze heures à 140°C ou par séchage direct à la flamme et subséquemment refroidie soit par courant d'argon ou sous vide dans un dessicateur rempli de $CaSO_4$. La manipulation des produits sensibles à l'humidité a été réalisée à l'intérieur d'une boîte à gants Vacuum/Atmospheres M040-1 remplie d'argon.

8.3 PURIFICATION ET SÉCHAGE DES SOLVANTS ET RÉACTIFS

Les solvants et réactifs anhydres utilisés ont été séchés sous atmosphère d'argon comme suit :

- Le THF et le Et_2O ont été distillés sur le sodium en présence de benzophénone alors que le toluène a été distillé seulement sur le sodium.
- Le TMEDA, le DME, le pentane et l'acétonitrile ont été distillés sur CaH_2. Le DMF et la triéthylamine ont été séchés sur $MgSO_4$ puis distillés sur CaH_2.
- Le chloroforme et le dichlorométhane deutérés et non deutérés ont été distillés sur P_2O_5. L'anhydride acétique a été également distillé sur P_2O_5. L'acétate d'éthyle a été séché sur $MgSO_4$ puis distillé sur P_2O_5.
- La pyridine a été distillée sur NaOH.
- La diéthylamine a été séchée sur $MgSO_4$ puis distillée sur KOH.
- Le $TiCl_4$ a été distillé sur des tournures de cuivre.
- Tous les solvants utilisés dans les réactions des acides de Lewis ont été, après purification et séchage, passés sur une colonne remplie de tamis moléculaires 4 Å activé. Le tamis moléculaires a été activé pendant 18 heures sous 0.5 torr et à 180°C .

8.4 CHROMATOGRAPHIE

Toutes les chromatographies sur colonne à pression moyenne ont été effectuées selon la procédure de Still et collaborateurs[55] en utilisant un gel de silice Merck 60 (230-400 mesh) comme phase stationnaire. Tous les solvants d'élution ont été préalablement distillés. La purification de petites quantités de produits (< 75 mg) a été effectuée sur des plaques préparatives commerciales Whatman 20 x 20 cm enduite d'une couche de 1 mm de gel de silice F_{254}. Les chromatographies sur couche mince ont été effectuées avec des plaques commerciales Merck de 0.2 mm enduite de gel de silice 60 F_{254} sur aluminium. La visualisation des taches a été effectuée soit par la lumière ultraviolette ou par l'utilisation d'une solution acide de molybdate d'ammonium[56].

8.5 DIVERS

Les évaporations de solvant ont été faites avec évaporateur rotatif Büchi et toute trace de solvant résiduel a été enlevée sous vide (~ 1 torr). Pour l'évaporation des solvants utilisés dans les réactions des composés de titane et d'aluminium, nous avons utilisé soit un tube de Schlenk directement branché à une pompe mécanique ou par la technique de diffusion, en utilisant une trappe contenant du bibenzyle ou du fluorène, montée sur le contenant du solvant à évaporer.

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ANNEXE 1

Complexes of Ketodiesters and Related Compounds with $TiCl_4$. Attempts to Use Chelation to Promote the Simultaneous Coordination of Ketones by Two Lewis Acids

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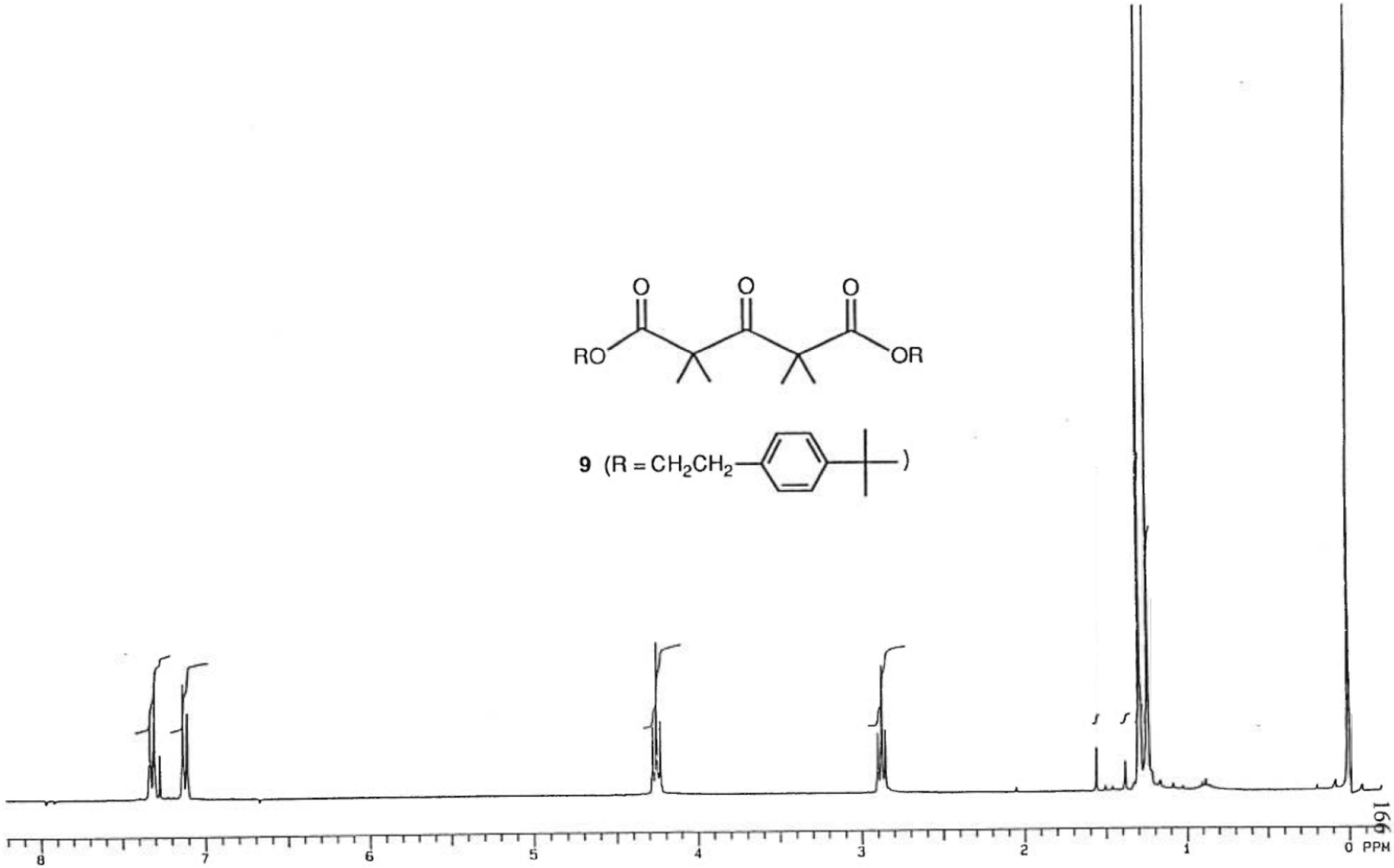
Supporting Information Available:

^{1}H and ^{13}C NMR spectra of compounds **9**, **10**, **11**, and **18** (8 pages)


O
O
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RO
OR
9 (R = CH$_2$CH$_2$–)
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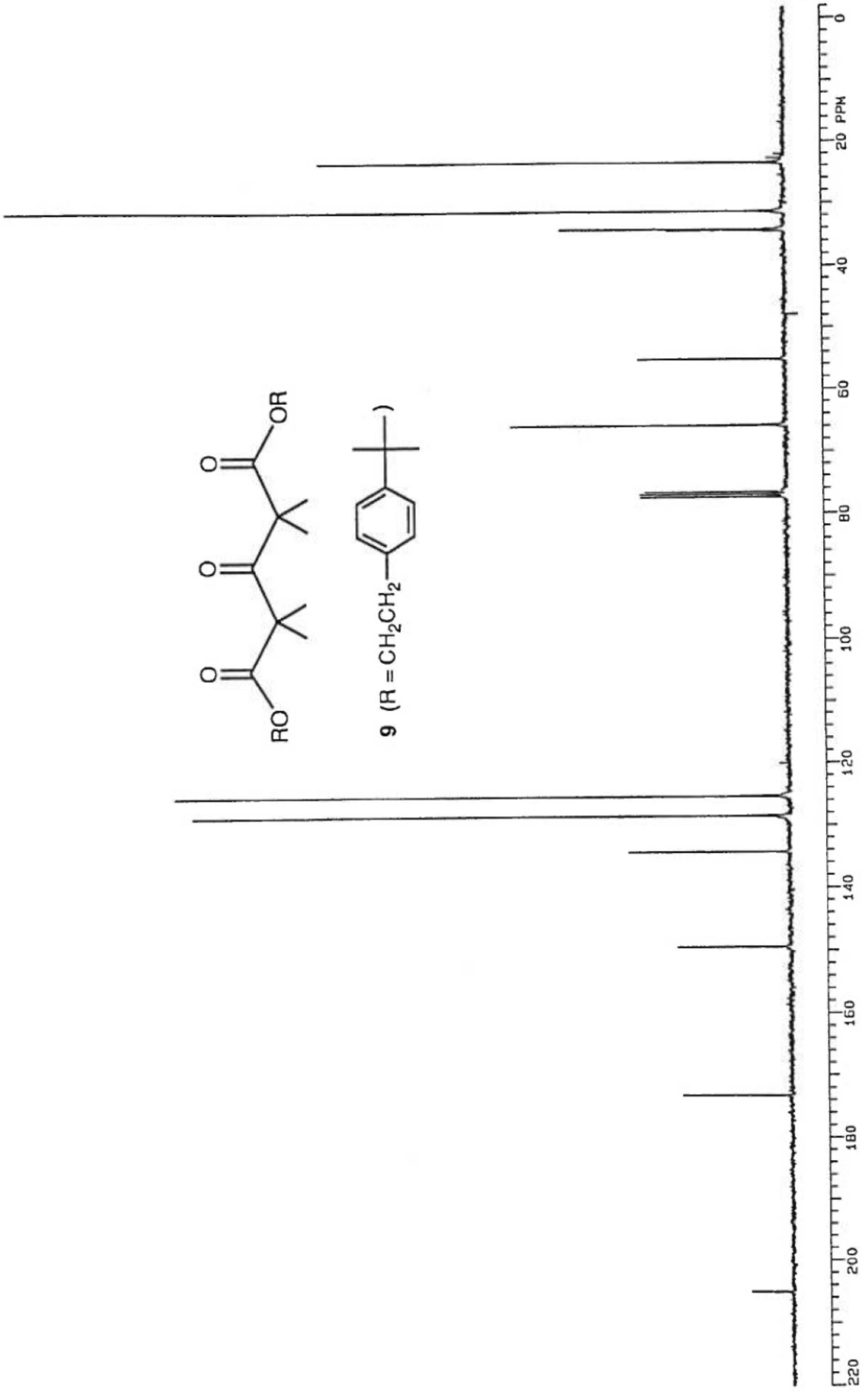

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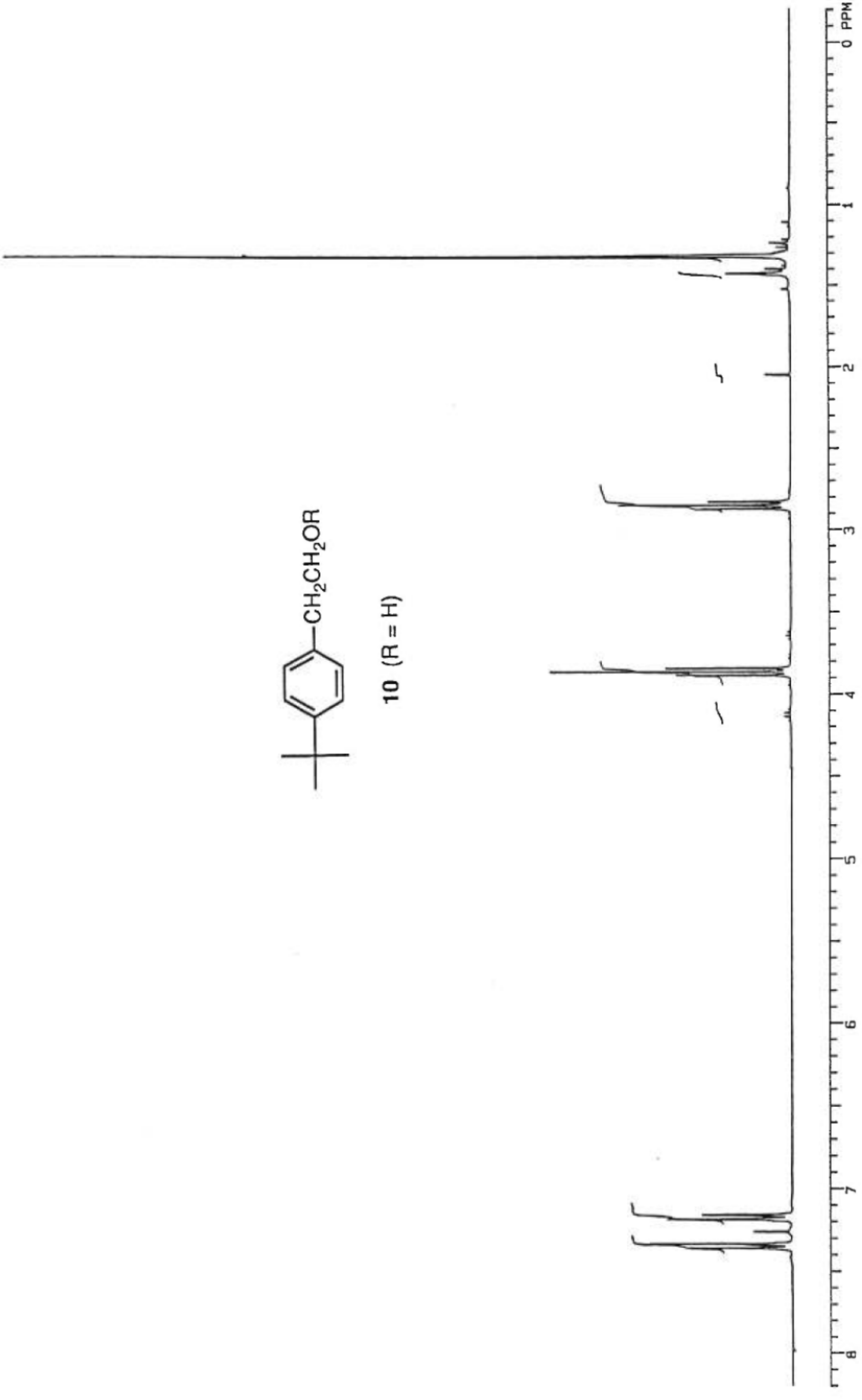

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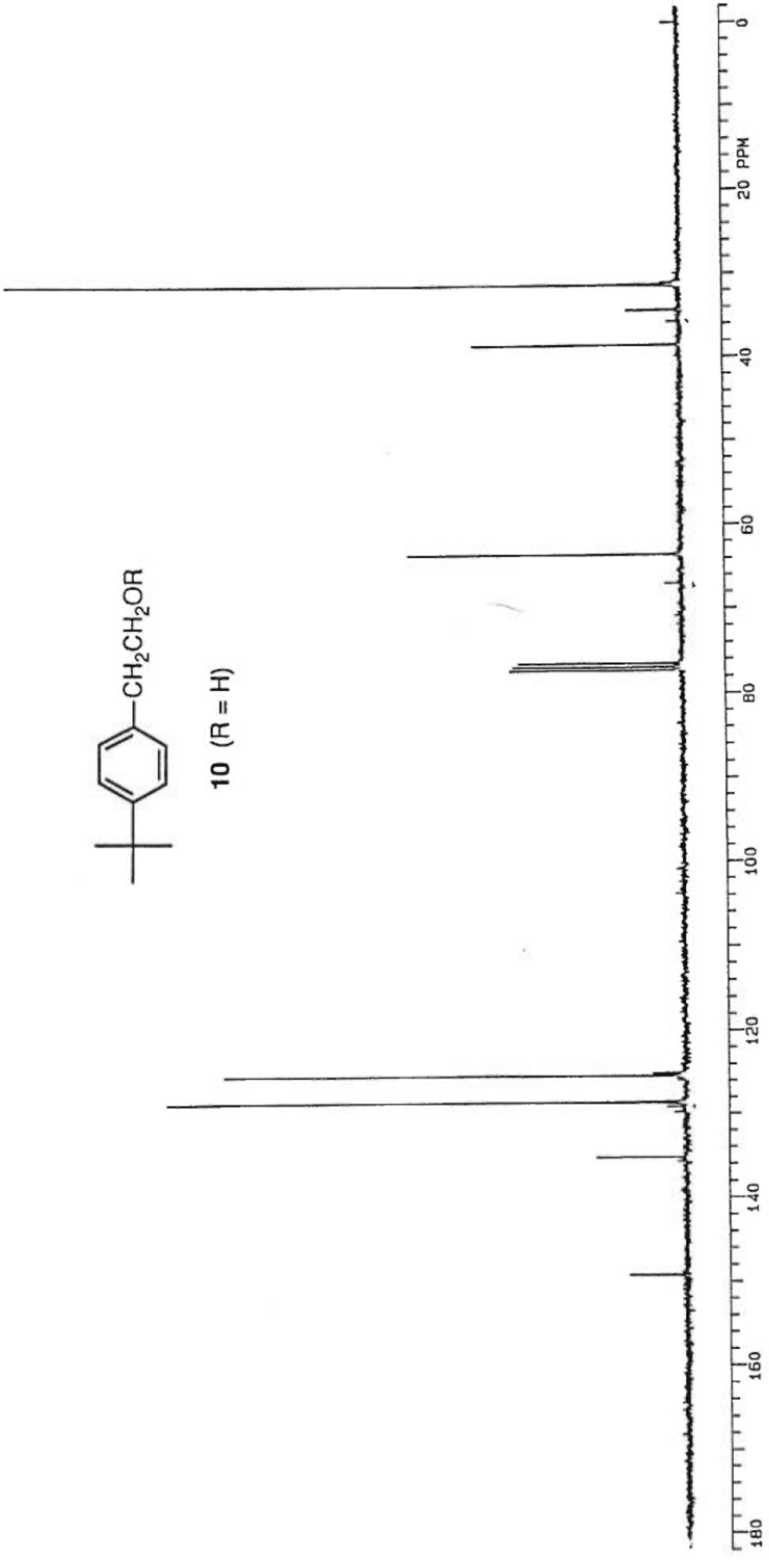

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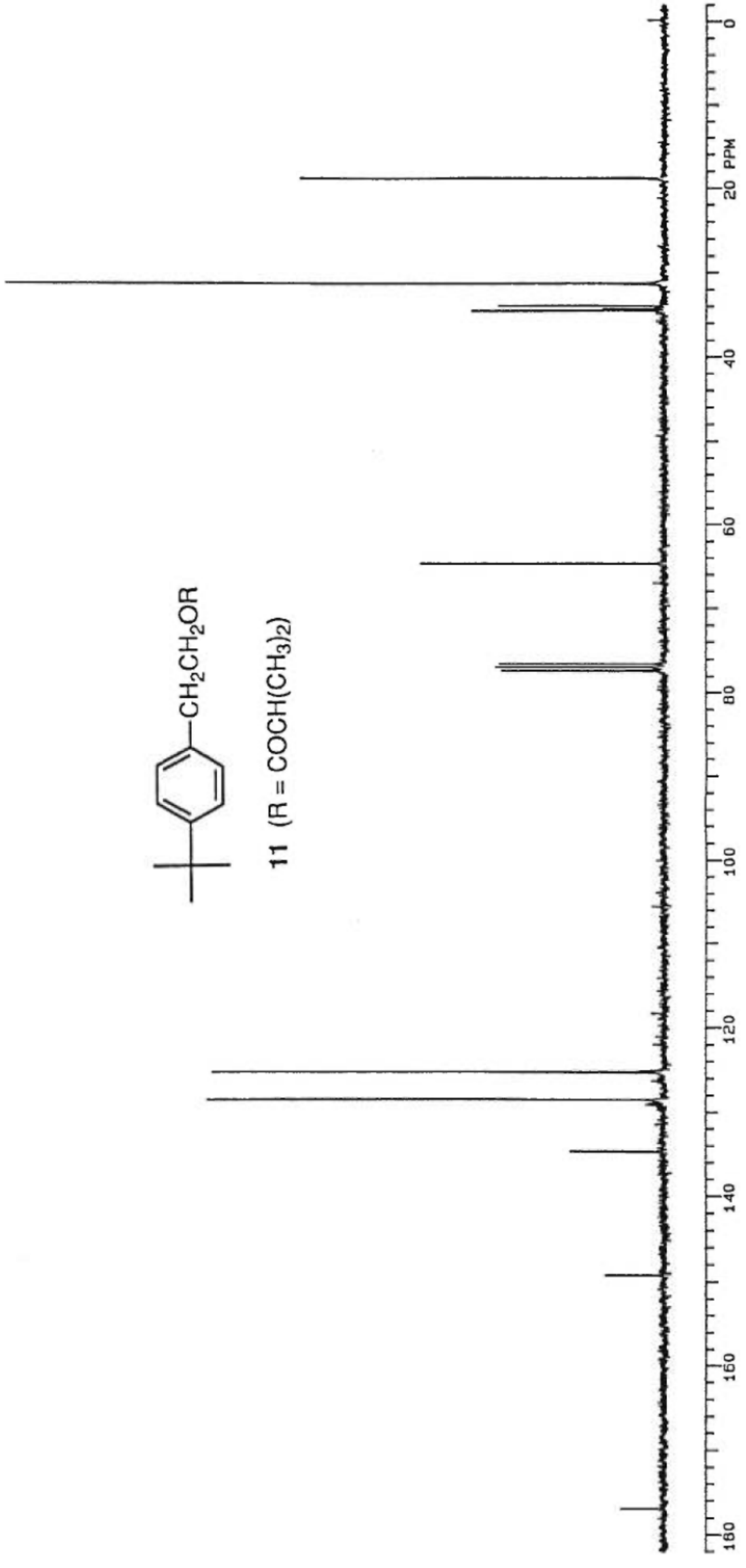
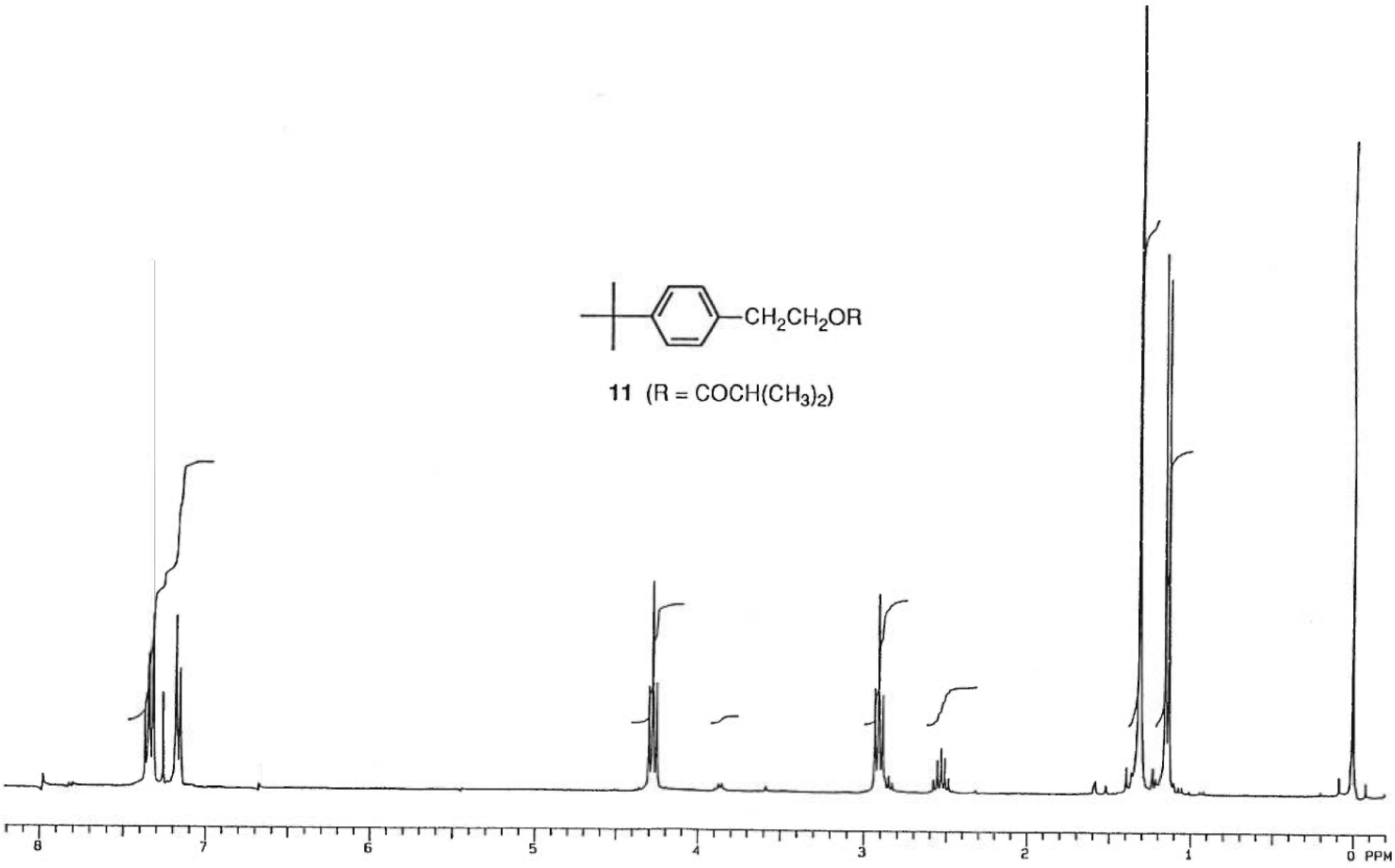


11 (R = COCH(CH$_3$)$_2$)



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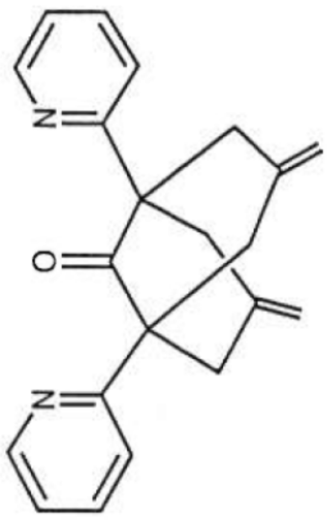

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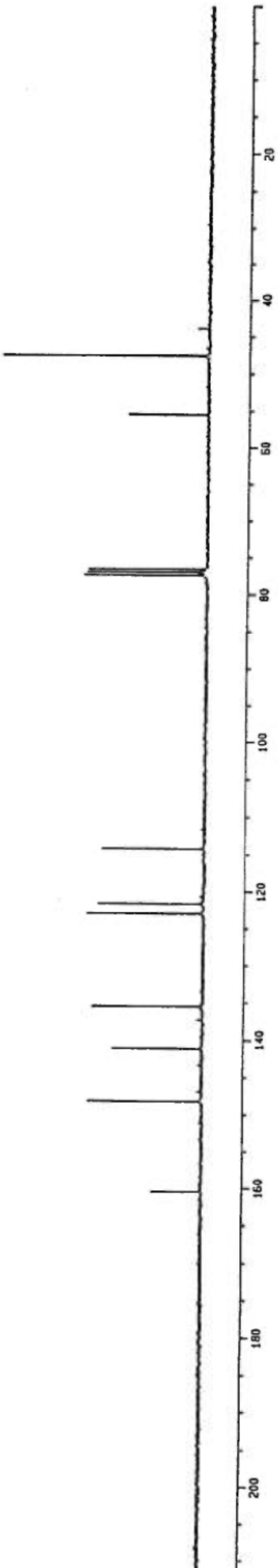

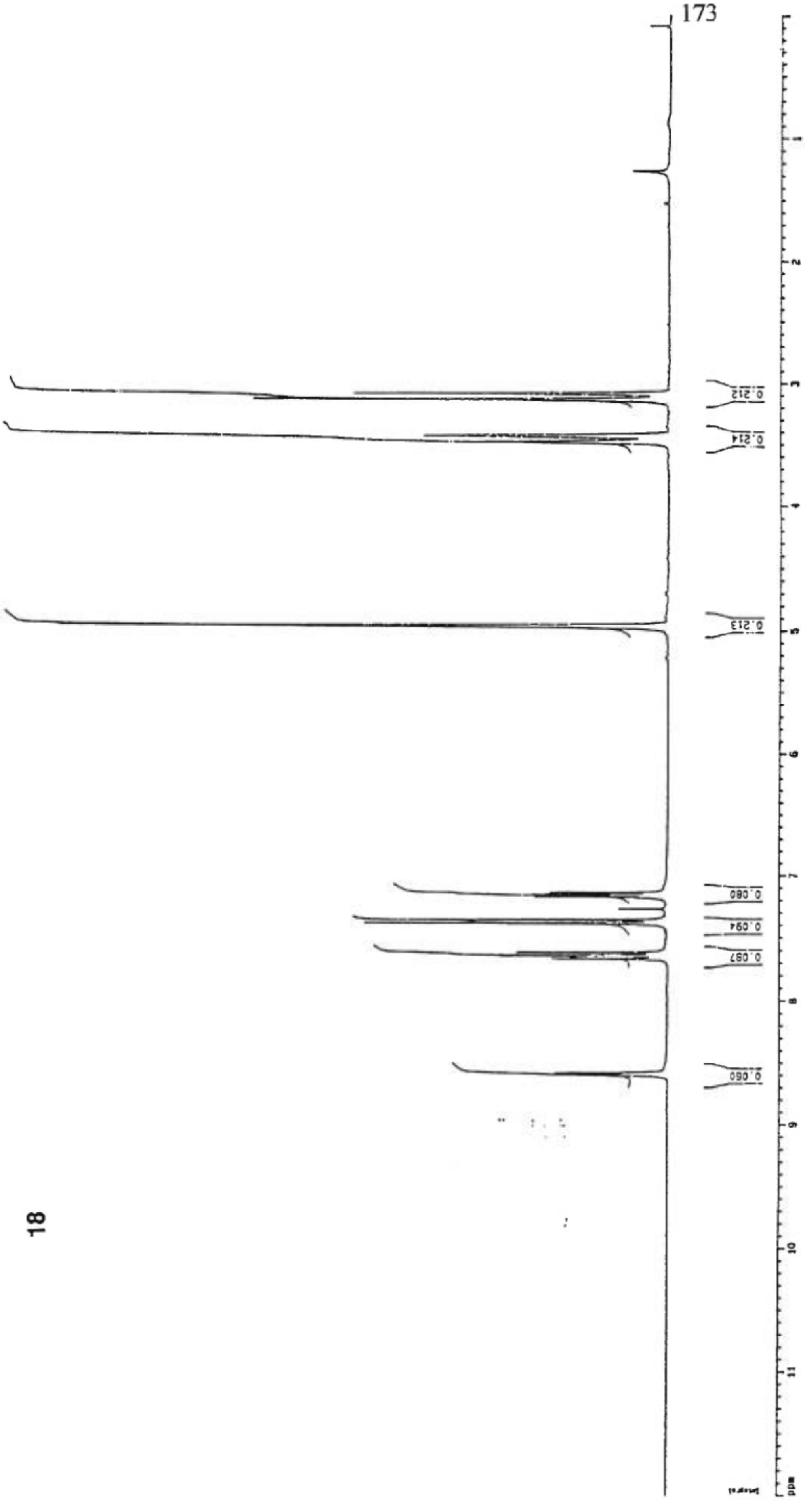

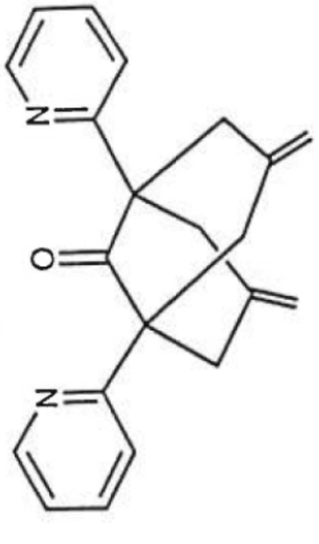

18

ANNEXE 2

SUPPORTING INFORMATION

Novel Complexes of Strong Bidentate Lewis Acids Derived from 2,2′-(1,3-Butadiyne-1,4-diyl)bis[phenol]

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I. Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes for the 1:1 complex of bidentate Lewis acid **8** with DME (16 pages).

II. Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes for the 1:2 complex of bidentate Lewis acid **11** with $CH_3COOC_2H_5$ (15 pages).

CRYSTAL AND MOLECULAR STRUCTURE OF

$C_{46}H_{74}A\ell_2O_4$ (JIW126)

Equipe Dr. WUEST
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C.P. 6128, Succ. A, Montréal, Québec, H3C 3J7 (Canada)

Structure résolue au laboratoire de diffraction des rayons X de l'Université de Montréal par Dr. Michel Simard, 24 avril 1997.

Table 1. Crystal data and structure refinement for $C_{46}H_{74}Al_2O_4$.

Crystal data

Crystal source	....	
Chemical formula, sum	C46 H74 Aℓ2 O4	
Chemical formula, moiety	C46 H74 Aℓ2 O4	
Chemical formula weight, M_r	745.01	
Cell setting	Triclinic	
Space group	P -1	
Unit cell dimensions (Å, °)	a = 8.967(3) b = 11.816(4) c = 12.551(4)	alpha = 67.11(3) beta = 73.45(2) gamma = 78.23(2)
Volume of unit cell, V ($Å^3$)	1167.8(7)	
Formula units per cell, Z	1	
Density calculated from formula and cell, D_x (Mg/m^3)	1.059	
Density from independent measurements, D_m (Mg/m^3)	....	
Measurement method, by flottation in	....	
F(000)	408	
Radiation type	CuKα	
Wavelength, λ (Å)	1.54056	
No. of reflections for cell measurement	25	

Table 1. (continued)

θ range (°)	20.00 to 22.50
Linear absorption coefficient, μ (mm^{-1})	0.843
Measurement temperature (K)	210(2)
Crystal shape	....
Colour	....
Size (mm)	0.38 x 0.19 x 0.17

Data collection

Diffractometer type	Nonius CAD-4
Data-collection method	\w/2\q scan
Absorption correction type	None
Maximum and minimum transmission values, T_{max} and T_{min}	1.00 and 1.00
No. of reflections measured	29061
No. of independent reflections	4418
No. of observed reflections	3425
Criterion for observed reflections	I>2\s(I)
R_{int}	0.079
Minimum and maximum values of θ (°)	3.92 to 69.80
Ranges of h,k,ℓ	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-15 \leq \ell \leq 15$

Table 1. (continued)

No. of standard reflections	5
Interval, time (min)	60
Intensity decay (%)	±7.9
Refinement	
Refinement method	Full-matrix on F^2
Final R indices, I>2sigma(I)	R1 = 0.0495, wR2 = 0.1364
R indices, all data	R1 = 0.0609, wR2 = 0.1420
Goodness-of-fit on F^2, S	0.982

$R1 = \Sigma(\|Fo| - |Fc\|)/\Sigma(|Fo|)$,
$wR2 = [\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]]^{1/2}$
$S = [\Sigma[w(Fo^2-Fc^2)^2]/(\text{No. of reflns - No. of params.})]^{1/2}$

No. of reflections used in refinement	4418
No. of parameters refined	237
No. of restraints	0
Method of refining and locating H atoms	see text
Weighting scheme	based on measured e.s.d's
Function minimized	$\Sigma w(Fo^2-Fc^2)^2$

$w = 1/[\sigma^2(Fo^2)+(0.0815P)^2]$ where $P=(Fo^2+2Fc^2)/3$

Maximum Δ/σ	0.004
$\Delta\rho_{max}$ (e/Å^3)	0.296

Table 1. (continued)

$\Delta\rho_{min}$ (e/Å^3)	-0.481
Extinction correction method	SHELXL96 (1996)
Secondary extinction value	0.0050(9)
Source of atomic scattering factors	International Tables for Crystallography (1992)

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2, x 10^2) for $C_{46}H_{74}A\ell_2O_4$.

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j a_i \cdot a_j$$

ATOM	X	Y	Z	U_{eq}
Aℓ	0.11451(6)	0.35811(5)	0.25510(5)	3.568(17)
O(1)	0.15951(15)	0.25052(11)	0.18520(11)	4.22(3)
C(1)	0.23125(19)	0.20326(15)	0.10040(15)	3.37(4)
C(2)	0.18512(19)	0.09439(15)	0.10215(15)	3.44(4)
C(3)	0.2557(2)	0.05637(16)	0.00623(17)	3.94(4)
C(4)	0.3698(2)	0.11693(18)	-0.09051(17)	4.15(4)
C(5)	0.4192(2)	0.21828(17)	-0.08738(16)	4.08(4)
C(6)	0.3524(2)	0.26150(16)	0.00682(16)	3.66(4)
C(7)	0.4101(2)	0.36577(18)	0.00680(17)	4.28(4)
C(8)	0.4667(2)	0.45155(18)	0.00198(17)	4.57(5)
C(9)	0.0601(2)	0.02289(16)	0.20540(17)	4.05(4)
C(10)	-0.0990(2)	0.09967(19)	0.2043(2)	5.22(5)
C(11)	0.1015(3)	-0.00950(19)	0.32523(18)	5.25(5)
C(12)	0.0451(3)	-0.09930(18)	0.1943(2)	5.59(6)
C(13)	0.4380(3)	0.0698(2)	-0.19187(19)	5.75(6)
C(21)	0.1163(3)	0.62645(18)	0.0892(2)	6.75(7)
O(22)	0.06927(17)	0.50461(11)	0.12323(12)	4.63(3)
C(23)	-0.0422(3)	0.5006(2)	0.06091(17)	5.20(5)
C(31)	-0.0906(2)	0.32882(18)	0.36688(17)	4.37(4)
C(32)	-0.1638(3)	0.4141(2)	0.4384(2)	5.67(6)
C(33)	-0.3003(3)	0.3643(2)	0.5390(2)	6.68(7)
C(34)	-0.2139(6)	0.5408(3)	0.3598(3)	15.5(2)
C(41)	0.2765(2)	0.4003(2)	0.30691(18)	5.01(5)
C(42)	0.3776(3)	0.2949(3)	0.3796(2)	6.60(7)
C(43)	0.2812(4)	0.2008(3)	0.4817(3)	8.91(9)
C(44)	0.4976(4)	0.2322(4)	0.3055(3)	10.34(12)

Table 3. Bond lengths (Å) and angles (°) for $C_{46}H_{74}A\ell_2O_4$.

Aℓ-O(1)	1.7336(13)	Aℓ-O(22)	1.9410(16)
Aℓ-C(41)	1.967(2)	Aℓ-C(31)	1.971(2)
O(1)-C(1)	1.336(2)	C(1)-C(6)	1.408(2)
C(1)-C(2)	1.420(2)	C(2)-C(3)	1.386(2)
C(2)-C(9)	1.535(2)	C(3)-C(4)	1.395(3)
C(4)-C(5)	1.377(2)	C(4)-C(13)	1.507(2)
C(5)-C(6)	1.400(2)	C(6)-C(7)	1.430(2)
C(7)-C(8)	1.197(3)	C(8)-C(8)[a]	1.374(3)
C(9)-C(10)	1.527(3)	C(9)-C(11)	1.536(3)
C(9)-C(12)	1.539(2)		
C(21)-O(22)	1.449(2)	O(22)-C(23)	1.452(2)
C(23)-C(23)[b]	1.505(4)		
C(31)-C(32)	1.533(3)	C(41)-C(42)	1.527(3)
C(32)-C(34)	1.499(4)	C(42)-C(44)	1.487(4)
C(32)-C(33)	1.508(3)	C(42)-C(43)	1.509(4)

O(1)-Aℓ-O(22)	98.98(7)	O(1)-Aℓ-C(41)	120.57(8)
O(22)-Aℓ-C(41)	104.78(8)	O(1)-Aℓ-C(31)	107.71(7)
O(22)-Aℓ-C(31)	103.97(8)	C(41)-Aℓ-C(31)	117.64(9)
C(1)-O(1)-Aℓ	156.55(12)	O(1)-C(1)-C(6)	120.57(15)
O(1)-C(1)-C(2)	120.56(15)	C(6)-C(1)-C(2)	118.86(15)
C(3)-C(2)-C(1)	117.39(16)	C(3)-C(2)-C(9)	121.41(15)
C(1)-C(2)-C(9)	121.19(15)	C(2)-C(3)-C(4)	124.43(16)
C(5)-C(4)-C(3)	117.28(17)	C(5)-C(4)-C(13)	122.06(18)
C(3)-C(4)-C(13)	120.64(17)	C(4)-C(5)-C(6)	121.03(17)
C(5)-C(6)-C(1)	120.81(15)	C(5)-C(6)-C(7)	118.77(16)
C(1)-C(6)-C(7)	120.42(16)	C(8)-C(7)-C(6)	175.9(2)
C(7)-C(8)-C(8)[a]	178.9(3)	C(10)-C(9)-C(2)	109.78(15)
C(10)-C(9)-C(11)	109.85(17)	C(2)-C(9)-C(11)	111.13(15)
C(10)-C(9)-C(12)	107.46(16)	C(2)-C(9)-C(12)	111.26(16)
C(11)-C(9)-C(12)	107.26(17)		
C(21)-O(22)-C(23)	114.01(16)	C(21)-O(22)-Aℓ	127.04(13)
C(23)-O(22)-Aℓ	118.27(12)	O(22)-C(23)-C(23)[b]	109.6(2)

Table 3. (continued)

C(32)-C(31)-Aℓ	119.39(14)	C(42)-C(41)-Aℓ	118.22(16)
C(34)-C(32)-C(33)	109.5(2)	C(44)-C(42)-C(43)	109.7(3)
C(34)-C(32)-C(31)	111.2(2)	C(44)-C(42)-C(41)	112.4(2)
C(33)-C(32)-C(31)	113.23(18)	C(43)-C(42)-C(41)	112.3(2)

Symmetry transformations used to generate equivalent atoms:

a: -x+1,-y+1,-z
b: -x,-y+1,-z

Table 4. Torsion angles (°) for $C_{46}H_{74}A\ell_2O_4$.

O(22)-Aℓ-O(1)-C(1)	51.0(3)	C(41)-Aℓ-O(1)-C(1)	-62.2(3)
C(31)-Aℓ-O(1)-C(1)	158.9(3)	Aℓ-O(1)-C(1)-C(6)	6.7(4)
Aℓ-O(1)-C(1)-C(2)	-172.4(2)	O(1)-C(1)-C(2)-C(3)	174.78(16)
C(6)-C(1)-C(2)-C(3)	-4.3(3)	O(1)-C(1)-C(2)-C(9)	-4.3(3)
C(6)-C(1)-C(2)-C(9)	176.58(16)	C(1)-C(2)-C(3)-C(4)	0.8(3)
C(9)-C(2)-C(3)-C(4)	179.91(17)	C(2)-C(3)-C(4)-C(5)	2.7(3)
C(2)-C(3)-C(4)-C(13)	-178.97(18)	C(3)-C(4)-C(5)-C(6)	-2.7(3)
C(13)-C(4)-C(5)-C(6)	179.01(18)	C(4)-C(5)-C(6)-C(1)	-0.8(3)
C(4)-C(5)-C(6)-C(7)	178.88(18)	O(1)-C(1)-C(6)-C(5)	-174.71(16)
C(2)-C(1)-C(6)-C(5)	4.4(3)	O(1)-C(1)-C(6)-C(7)	5.6(3)
C(2)-C(1)-C(6)-C(7)	-175.25(17)	C(5)-C(6)-C(7)-C(8)	-21.(3)
C(1)-C(6)-C(7)-C(8)	159.(3)	C(6)-C(7)-C(8)-C(8)^{a}	-80.(15)
C(3)-C(2)-C(9)-C(10)	-111.0(2)	C(1)-C(2)-C(9)-C(10)	68.1(2)
C(3)-C(2)-C(9)-C(11)	127.28(19)	C(1)-C(2)-C(9)-C(11)	-53.7(2)
C(3)-C(2)-C(9)-C(12)	7.8(3)	C(1)-C(2)-C(9)-C(12)	-173.11(17)
O(1)-Aℓ-O(22)-C(21)	-138.11(18)	C(41)-Aℓ-O(22)-C(21)	-13.1(2)
C(31)-Aℓ-O(22)-C(21)	110.99(19)	O(1)-Aℓ-O(22)-C(23)	52.01(14)
C(41)-Aℓ-O(22)-C(23)	177.05(13)	C(31)-Aℓ-O(22)-C(23)	-58.89(15)
C(21)-O(22)-C(23)-C(23)^{b}	79.5(3)	Aℓ-O(22)-C(23)-C(23)^{b}	-109.3(2)
O(1)-Aℓ-C(31)-C(32)	-177.68(15)	O(22)-Aℓ-C(31)-C(32)	-73.30(17)
C(41)-Aℓ-C(31)-C(32)	42.0(2)	Aℓ-C(31)-C(32)-C(34)	69.4(3)
Aℓ-C(31)-C(32)-C(33)	-166.84(17)	O(1)-Aℓ-C(41)-C(42)	-49.70(19)
O(22)-Aℓ-C(41)-C(42)	-159.78(15)	C(31)-Aℓ-C(41)-C(42)	85.38(18)
Aℓ-C(41)-C(42)-C(44)	75.4(3)	Aℓ-C(41)-C(42)-C(43)	-48.9(3)

Symmetry transformations used to generate equivalent atoms:

a: -x+1,-y+1,-z
b: -x,-y+1,-z

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$, x 10^2) for $C_{46}H_{74}A\ell_2O_4$.

ATOM	X	Y	Z	U_{iso}
H(3)	0.2247	-0.0150	0.0064	4.7
H(5)	0.4991	0.2591	-0.1495	4.9
H(10A)	-0.1774	0.0543	0.2700	7.8
H(10B)	-0.1269	0.1163	0.1300	7.8
H(10C)	-0.0938	0.1771	0.2123	7.8
H(11A)	0.0211	-0.0548	0.3888	7.9
H(11B)	0.1083	0.0659	0.3364	7.9
H(11C)	0.2014	-0.0600	0.3261	7.9
H(12A)	-0.0337	-0.1428	0.2610	8.4
H(12B)	0.1449	-0.1501	0.1942	8.4
H(12C)	0.0147	-0.0820	0.1209	8.4
H(13A)	0.5131	0.1239	-0.2518	8.6
H(13B)	0.3549	0.0681	-0.2264	8.6
H(13C)	0.4900	-0.0130	-0.1626	8.6
H(21A)	0.1918	0.6219	0.1332	10.1
H(21B)	0.0253	0.6822	0.1069	10.1
H(21C)	0.1632	0.6567	0.0047	10.1
H(23A)	-0.1203	0.5729	0.0541	6.2
H(23B)	-0.0967	0.4263	0.1057	6.2
H(31A)	-0.1651	0.3319	0.3216	5.2
H(31B)	-0.0812	0.2442	0.4238	5.2
H(32)	-0.0823	0.4220	0.4735	6.8
H(33A)	-0.3408	0.4214	0.5814	8.0
H(33B)	-0.2661	0.2847	0.5929	8.0
H(33C)	-0.3819	0.3546	0.5074	8.0
H(34A)	-0.1258	0.5732	0.2955	18.6
H(34B)	-0.2506	0.5948	0.4058	18.6
H(34C)	-0.2977	0.5365	0.3272	18.6
H(41A)	0.3465	0.4503	0.2358	6.0
H(41B)	0.2249	0.4530	0.3539	6.0
H(42)	0.4338	0.3313	0.4140	7.9
H(43A)	0.3498	0.1360	0.5255	10.7
H(43B)	0.2217	0.1653	0.4510	10.7
H(43C)	0.2099	0.2407	0.5340	10.7
H(44A)	0.5587	0.1662	0.3553	12.4
H(44B)	0.5660	0.2915	0.2448	12.4
H(44C)	0.4462	0.1982	0.2680	12.4

Table 6. Anisotropic parameters (Å^2, x 10^2) for $C_{46}H_{74}A\ell_2O_4$.

The anisotropic thermal parameters are the coefficients of the expression:
$T = \exp[-2\pi^2(U_{11}a^{*2}h^2+...+ 2U_{12}a^*b^*hk+...)]$.

ATOM	U11	U22	U33	U23	U13	U12
Aℓ	3.72(3)	3.48(3)	3.69(3)	-1.57(2)	-0.57(2)	-0.53(2)
O(1)	4.42(7)	3.82(7)	4.59(7)	-2.21(6)	0.32(6)	-1.23(5)
C(1)	3.21(8)	3.23(8)	3.73(9)	-1.39(7)	-0.40(7)	-0.69(7)
C(2)	3.06(8)	3.14(8)	4.19(9)	-1.39(7)	-0.54(7)	-0.68(6)
C(3)	3.56(9)	3.85(9)	4.94(10)	-2.14(8)	-0.69(8)	-0.75(7)
C(4)	3.54(9)	4.96(10)	4.47(10)	-2.40(8)	-0.63(8)	-0.49(8)
C(5)	3.36(9)	4.76(10)	4.07(10)	-1.59(8)	-0.14(7)	-1.28(8)
C(6)	3.30(9)	3.57(8)	4.21(9)	-1.42(7)	-0.51(7)	-1.02(7)
C(7)	4.09(10)	4.53(10)	4.30(10)	-1.68(8)	-0.04(8)	-1.64(8)
C(8)	4.64(11)	4.85(11)	4.31(10)	-1.76(8)	0.18(8)	-2.14(9)
C(9)	3.92(10)	3.30(8)	4.69(10)	-1.42(8)	-0.01(8)	-1.23(7)
C(10)	3.52(10)	4.79(11)	7.01(14)	-2.19(10)	0.11(9)	-1.38(8)
C(11)	5.71(12)	4.75(11)	4.58(11)	-1.03(9)	-0.06(9)	-1.88(9)
C(12)	6.14(13)	3.91(10)	6.61(14)	-2.07(10)	0.28(11)	-2.30(9)
C(13)	5.04(12)	7.61(15)	5.62(13)	-3.98(12)	0.00(10)	-1.29(11)
C(21)	9.6(2)	3.20(10)	7.29(16)	-0.78(10)	-2.47(14)	-1.80(11)
O(22)	5.86(9)	3.51(7)	4.73(7)	-1.10(6)	-1.71(6)	-0.91(6)
C(23)	5.14(12)	5.69(12)	4.74(11)	-1.35(10)	-1.86(10)	-0.44(9)
C(31)	4.16(10)	4.51(10)	4.47(10)	-1.97(8)	-0.43(8)	-0.56(8)
C(32)	5.13(12)	6.32(13)	6.04(13)	-3.60(11)	0.30(10)	-0.98(10)
C(33)	5.64(14)	8.21(17)	6.41(15)	-4.13(14)	0.55(11)	-0.81(12)
C(34)	21.6(5)	5.84(18)	10.3(3)	-2.50(18)	5.9(3)	2.8(2)
C(41)	4.56(11)	6.57(13)	4.53(11)	-2.51(10)	-0.59(9)	-1.44(10)
C(42)	4.90(13)	9.10(18)	5.96(14)	-2.11(13)	-1.72(11)	-1.52(12)
C(43)	7.42(19)	10.3(2)	6.81(17)	0.35(16)	-2.49(15)	-1.84(16)
C(44)	6.61(19)	13.3(3)	9.1(2)	-3.7(2)	-2.13(17)	3.08(19)

Table 7. Distances to the weighted least-squares planes for $C_{46}H_{74}A\ell_2O_4$.

Plane no. 1

*	-0.029	(0.001)	C(1)
*	0.016	(0.001)	C(2)
*	0.009	(0.001)	C(3)
*	-0.023	(0.001)	C(4)
*	0.010	(0.001)	C(5)
*	0.016	(0.001)	C(6)
	-0.335	(0.003)	Aℓ
	-0.129	(0.002)	O(1)
	0.075	(0.003)	C(7)
	0.155	(0.004)	C(8)
	0.050	(0.003)	C(9)
	-0.051	(0.003)	C(13)

Rms deviation of fitted atoms = 0.018

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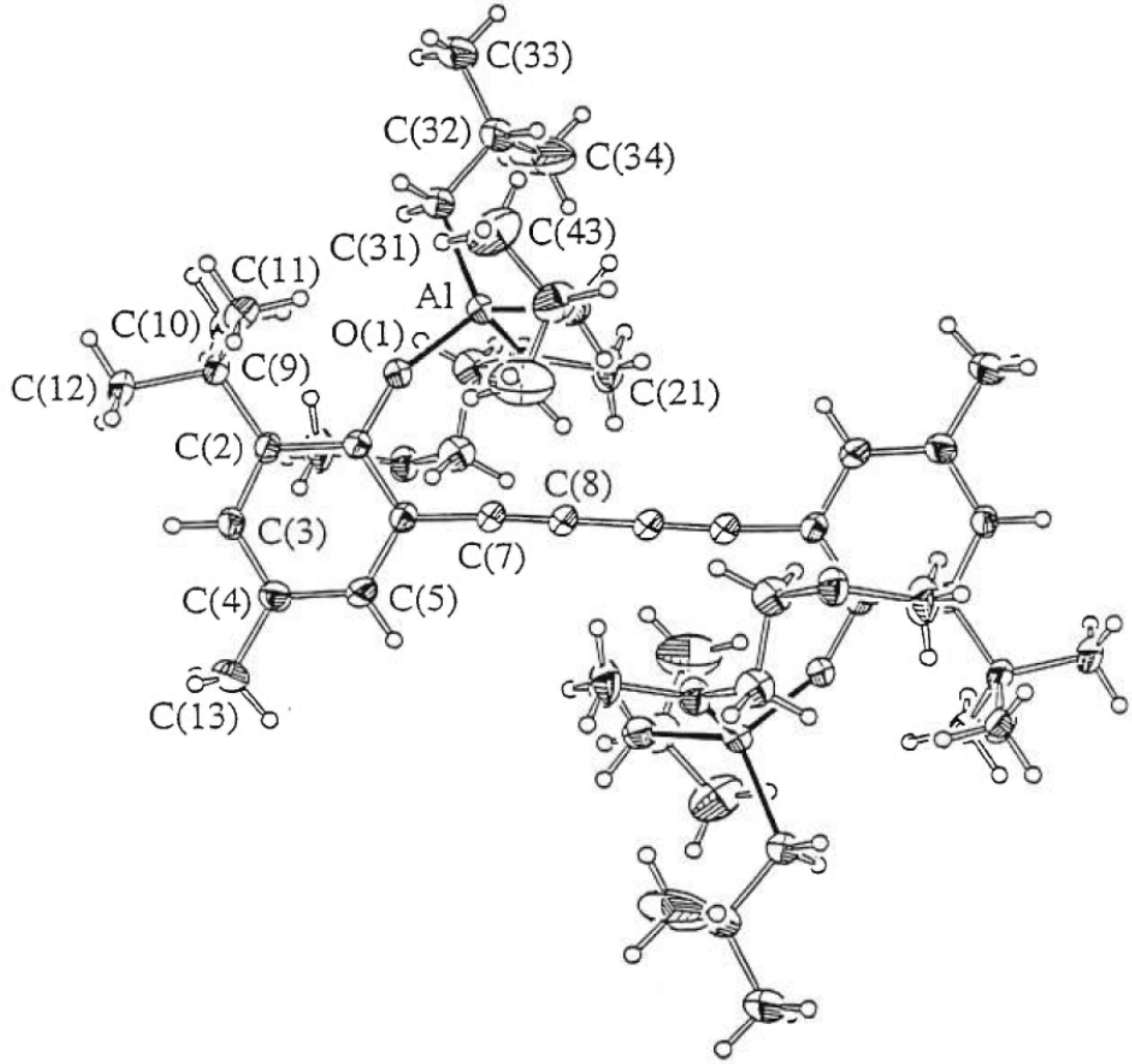
* indicates atoms used to define plane



ORTEP view of $C_{46}H_{74}A\ell_2O_4$

with the numbering scheme adopted. Ellipsoids drawn at

40% probality level. Hydrogens represented by sphere of arbitrary size.

Discussion of structure determination and refinement procedure

The structure was solved by direct method using SHELXS96 (Sheldrick, 1990) and difmap synthesis using SHELXL96 (Sheldrick, 1996). All non-hydrogen atoms anisotropic, hydrogen atoms isotropic. Hydrogen atoms were calculated at idealized positions using a riding model with different C-H distances for type of hydrogen. The isotropic displacement factors, U_{iso}, were adjusted to 50% higher value of the bonded carbon atom (methyl) and 20% higher (others).

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CRYSTAL AND MOLECULAR STRUCTURE OF

$C_{34}H_{44}C\ell_6O_6Ti_2$ (JIW130)

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Structure résolue au laboratoire de diffraction des rayons X de l'Université de Montréal par Dr. Michel Simard, 1 mai 1997.

Table 1. Crystal data and structure refinement for $C_{34}H_{44}C\ell_6O_6Ti_2$.

Crystal data

Crystal source	....	
Chemical formula, sum	C34 H44 Cℓ6 O6 Ti2	
Chemical formula, moiety	C34 H44 Cℓ6 O6 Ti2	
Chemical formula weight, M_r	857.19	
Cell setting	Triclinic	
Space group	P -1	
Unit cell dimensions (Å, °)	a = 8.691(2)	alpha = 90.29(3)
	b = 9.644(4)	beta = 98.83(2)
	c = 12.540(4)	gamma = 105.68(3)
Volume of unit cell, V (Å^3)	998.7(6)	
Formula units per cell, Z	1	
Density calculated from formula and cell, D_x (Mg/m^3)	1.425	
Density from independent measurements, D_m (Mg/m^3)	....	
Measurement method, by flottation in	....	
F(000)	442	
Radiation type	CuKα	
Wavelength, λ (Å)	1.54056	
No. of reflections for cell measurement	25	

Table 1. (continued)

θ range (°)	20.00 to 22.50
Linear absorption coefficient, μ (mm^{-1})	4.281
Measurement temperature (K)	210(2)
Crystal shape	....
Colour	....
Size (mm)	0.40 x 0.30 x 0.06
Data collection	
Diffractometer type	Nonius CAD-4
Data-collection method	\w/2\q scan
Absorption correction type	Integration
Maximum and minimum transmission values, T_{max} and T_{min}	0.37 and 0.12
No. of reflections measured	22669
No. of independent reflections	3710
No. of observed reflections	2979
Criterion for observed reflections	I>2\s(I)
R_{int}	0.106
Minimum and maximum values of θ (°)	3.57 to 69.79
Ranges of h,k,ℓ	$-10\leq h\leq 10$, $-11\leq k\leq 11$, $-15\leq \ell\leq 15$

Table 1. (continued)

No. of standard reflections	5
Interval, time (min)	60
Intensity decay (%)	±3.4

Refinement

Refinement method	Full-matrix on F^2
Final R indices, I>2sigma(I)	R1 = 0.0473, wR2 = 0.1204
R indices, all data	R1 = 0.0547, wR2 = 0.1232
Goodness-of-fit on F^2, S	0.986

$R1 = \Sigma(\|Fo| - |Fc\|)/\Sigma(|Fo|)$,
$wR2 = [\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]]^{1/2}$
$S = [\Sigma[w(Fo^2-Fc^2)^2]/(\text{No. of reflns - No. of params.})]^{1/2}$

No. of reflections used in refinement	3710
No. of parameters refined	218
No. of restraints	0
Method of refining and locating H atoms	see text
Weighting scheme	based on measured e.s.d's
Function minimized	$\Sigma w(Fo^2-Fc^2)^2$

$w = 1/[\sigma^2(Fo^2)+(0.0772P)^2]$ where $P=(Fo^2+2Fc^2)/3$

Maximum Δ/σ	0.000
$\Delta\rho_{max}$ (e/Å^3)	0.724

Table 1. (continued)

$\Delta\rho_{min}$ (e/Å^3)	-0.762
Extinction correction method	SHELXL96 (1996)
Secondary extinction value	0.0055(6)
Source of atomic scattering factors	International Tables for Crystallography (1992)

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2, x 10^2) for $C_{34}H_{44}C\ell_6O_6Ti_2$.

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a^*_ia^*_ja_i\cdot a_j$$

ATOM	X	Y	Z	U_{eq}
Ti	0.46684(6)	0.68402(5)	0.81773(4)	2.892(17)
Cℓ(1)	0.34140(10)	0.64066(9)	0.96522(6)	4.64(2)
Cℓ(2)	0.23959(10)	0.71617(12)	0.71853(7)	5.63(3)
Cℓ(3)	0.46925(12)	0.47100(8)	0.75477(7)	5.09(2)
O(1)	0.5908(2)	0.8055(2)	0.73866(15)	3.10(4)
C(1)	0.6619(3)	0.9390(3)	0.7093(2)	2.64(5)
C(2)	0.7255(3)	0.9598(3)	0.6113(2)	2.76(6)
C(3)	0.8051(4)	1.1021(3)	0.5936(2)	3.38(6)
C(4)	0.8215(4)	1.2196(3)	0.6641(3)	3.80(7)
C(5)	0.7513(4)	1.1950(3)	0.7567(2)	3.56(7)
C(6)	0.6705(3)	1.0551(3)	0.7796(2)	2.95(6)
C(7)	0.5954(4)	1.0274(3)	0.8736(2)	3.35(6)
C(8)	0.5335(4)	1.0083(3)	0.9532(2)	3.56(7)
C(9)	0.7063(4)	0.8353(3)	0.5304(2)	3.24(6)
C(10)	0.5280(4)	0.7505(4)	0.5014(3)	5.10(9)
C(11)	0.8061(5)	0.7353(4)	0.5778(3)	4.74(8)
C(12)	0.7638(5)	0.8901(4)	0.4242(3)	4.77(8)
C(13)	0.9079(5)	1.3698(4)	0.6373(4)	5.84(10)
O(21)	0.6743(3)	0.7160(2)	0.93267(17)	3.95(5)
O(22)	0.8951(3)	0.7447(3)	1.05428(19)	4.55(6)
C(21)	0.8928(4)	0.6316(4)	0.8879(3)	5.09(9)
C(22)	0.8098(4)	0.7007(3)	0.9591(2)	3.56(7)
C(23)	0.8244(4)	0.8132(4)	1.1317(3)	5.13(9)
C(24)	0.8916(5)	0.9734(4)	1.1343(3)	5.88(10)

Table 3. Bond lengths (Å) and angles (°) for $C_{34}H_{44}C\ell_6O_6Ti_2$.

Ti-O(1)	1.782(2)	Ti-O(21)	2.078(2)
Ti-Cℓ(3)	2.2037(13)	Ti-Cℓ(2)	2.2638(11)
Ti-Cℓ(1)	2.2726(11)	O(1)-C(1)	1.348(3)
C(1)-C(6)	1.401(4)	C(1)-C(2)	1.417(4)
C(2)-C(3)	1.395(4)	C(2)-C(9)	1.526(4)
C(3)-C(4)	1.396(4)	C(4)-C(5)	1.386(4)
C(4)-C(13)	1.506(4)	C(5)-C(6)	1.396(4)
C(6)-C(7)	1.425(4)	C(7)-C(8)	1.198(4)
C(8)-C(8)^a	1.379(6)	C(9)-C(11)	1.528(4)
C(9)-C(10)	1.530(4)	C(9)-C(12)	1.540(4)
O(21)-C(22)	1.222(4)	O(22)-C(22)	1.307(4)
O(22)-C(23)	1.467(4)	C(21)-C(22)	1.488(4)
C(23)-C(24)	1.494(5)		

O(1)-Ti-O(21)	86.24(10)	O(1)-Ti-Cℓ(3)	102.99(8)
O(21)-Ti-Cℓ(3)	96.34(8)	O(1)-Ti-Cℓ(2)	91.16(8)
O(21)-Ti-Cℓ(2)	161.54(7)	Cℓ(3)-Ti-Cℓ(2)	102.05(5)
O(1)-Ti-Cℓ(1)	150.27(7)	O(21)-Ti-Cℓ(1)	82.75(7)
Cℓ(3)-Ti-Cℓ(1)	105.61(5)	Cℓ(2)-Ti-Cℓ(1)	90.69(4)
C(1)-O(1)-Ti	152.56(18)	O(1)-C(1)-C(6)	117.3(2)
O(1)-C(1)-C(2)	121.0(2)	C(6)-C(1)-C(2)	121.7(3)
C(3)-C(2)-C(1)	115.4(3)	C(3)-C(2)-C(9)	122.5(2)
C(1)-C(2)-C(9)	122.1(2)	C(2)-C(3)-C(4)	124.3(3)
C(5)-C(4)-C(3)	118.3(3)	C(5)-C(4)-C(13)	121.1(3)
C(3)-C(4)-C(13)	120.5(3)	C(4)-C(5)-C(6)	120.3(3)
C(5)-C(6)-C(1)	119.9(3)	C(5)-C(6)-C(7)	121.3(3)
C(1)-C(6)-C(7)	118.8(3)	C(8)-C(7)-C(6)	178.1(3)
C(7)-C(8)-C(8)^a	177.6(4)	C(2)-C(9)-C(11)	110.0(3)
C(2)-C(9)-C(10)	110.4(2)	C(11)-C(9)-C(10)	109.8(3)
C(2)-C(9)-C(12)	111.4(2)	C(11)-C(9)-C(12)	108.3(3)
C(10)-C(9)-C(12)	106.9(3)	C(22)-O(21)-Ti	149.0(2)
C(22)-O(22)-C(23)	118.6(3)	O(21)-C(22)-O(22)	122.0(3)
O(21)-C(22)-C(21)	124.1(3)	O(22)-C(22)-C(21)	113.9(3)
O(22)-C(23)-C(24)	110.1(3)		

Symmetry transformations used to generate equivalent atoms:

a: -x+1,-y+2,-z+2

Table 4. Torsion angles (°) for $C_{34}H_{44}C\ell_6O_6Ti_2$.

O(21)-Ti-O(1)-C(1)	-85.7(4)	Cℓ(3)-Ti-O(1)-C(1)	178.6(4)
Cℓ(2)-Ti-O(1)-C(1)	76.0(4)	Cℓ(1)-Ti-O(1)-C(1)	-17.4(5)
Ti-O(1)-C(1)-C(6)	16.1(6)	Ti-O(1)-C(1)-C(2)	-164.0(3)
O(1)-C(1)-C(2)-C(3)	-176.1(2)	C(6)-C(1)-C(2)-C(3)	3.7(4)
O(1)-C(1)-C(2)-C(9)	4.6(4)	C(6)-C(1)-C(2)-C(9)	-175.6(3)
C(1)-C(2)-C(3)-C(4)	-1.1(5)	C(9)-C(2)-C(3)-C(4)	178.2(3)
C(2)-C(3)-C(4)-C(5)	-1.7(5)	C(2)-C(3)-C(4)-C(13)	-179.2(3)
C(3)-C(4)-C(5)-C(6)	1.8(5)	C(13)-C(4)-C(5)-C(6)	179.4(3)
C(4)-C(5)-C(6)-C(1)	0.7(5)	C(4)-C(5)-C(6)-C(7)	-179.1(3)
O(1)-C(1)-C(6)-C(5)	176.2(3)	C(2)-C(1)-C(6)-C(5)	-3.7(4)
O(1)-C(1)-C(6)-C(7)	-4.0(4)	C(2)-C(1)-C(6)-C(7)	176.2(3)
C(5)-C(6)-C(7)-C(8)	2.(10)	C(1)-C(6)-C(7)-C(8)	-177.(10)
C(6)-C(7)-C(8)-C(8)[a]	-24.(19)	C(3)-C(2)-C(9)-C(11)	112.4(3)
C(1)-C(2)-C(9)-C(11)	-68.4(4)	C(3)-C(2)-C(9)-C(10)	-126.3(3)
C(1)-C(2)-C(9)-C(10)	53.0(4)	C(3)-C(2)-C(9)-C(12)	-7.7(4)
C(1)-C(2)-C(9)-C(12)	171.6(3)	O(1)-Ti-O(21)-C(22)	-67.1(4)
Cℓ(3)-Ti-O(21)-C(22)	35.6(4)	Cℓ(2)-Ti-O(21)-C(22)	-149.4(3)
Cℓ(1)-Ti-O(21)-C(22)	140.6(4)	Ti-O(21)-C(22)-O(22)	-178.1(3)
Ti-O(21)-C(22)-C(21)	1.9(6)	C(23)-O(22)-C(22)-O(21)	0.7(5)
C(23)-O(22)-C(22)-C(21)	-179.4(3)	C(22)-O(22)-C(23)-C(24)	-101.1(4)

Symmetry transformations used to generate equivalent atoms:

a: -x+1,-y+2,-z+2

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$, x 10^2) for $C_{34}H_{44}C\ell_6O_6Ti_2$.

ATOM	X	Y	Z	U_{iso}
H(3)	0.8506	1.1200	0.5300	4.1
H(5)	0.7580	1.2728	0.8043	4.3
H(10A)	0.5176	0.6717	0.4500	7.6
H(10B)	0.4657	0.8139	0.4697	7.6
H(10C)	0.4876	0.7121	0.5663	7.6
H(11A)	0.7932	0.6565	0.5258	7.1
H(11B)	0.7691	0.6971	0.6436	7.1
H(11C)	0.9194	0.7890	0.5939	7.1
H(12A)	0.7501	0.8087	0.3745	7.2
H(12B)	0.8772	0.9438	0.4391	7.2
H(12C)	0.7003	0.9524	0.3922	7.2
H(13A)	0.9485	1.3659	0.5698	8.8
H(13B)	0.9976	1.4111	0.6946	8.8
H(13C)	0.8331	1.4290	0.6301	8.8
H(21A)	0.9988	0.6315	0.9259	7.6
H(21B)	0.9049	0.6850	0.8230	7.6
H(21C)	0.8290	0.5331	0.8684	7.6
H(23A)	0.8488	0.7783	1.2039	6.2
H(23B)	0.7064	0.7875	1.1108	6.2
H(24A)	0.8440	1.0177	1.1856	8.8
H(24B)	0.8662	1.0078	1.0630	8.8
H(24C)	1.0081	0.9986	1.1560	8.8

Table 6. Anisotropic parameters (Å^2, x 10^2) for $C_{34}H_{44}C\ell_6O_6Ti_2$.

The anisotropic thermal parameters are the coefficients of the expression:
$T = \exp[-2\pi^2(U_{11}a^{*2}h^2+...+ 2U_{12}a^*b^*hk+...)]$.

ATOM	U11	U22	U33	U23	U13	U12
Ti	2.79(3)	2.75(3)	3.01(3)	-0.124(19)	0.80(2)	0.375(19)
Cℓ(1)	4.90(5)	4.97(5)	4.19(4)	0.33(3)	2.17(3)	0.79(4)
Cℓ(2)	3.43(4)	8.04(7)	5.26(5)	0.82(4)	0.19(4)	1.59(4)
Cℓ(3)	6.85(6)	2.97(4)	5.22(5)	-0.84(3)	1.60(4)	0.64(4)
O(1)	3.01(10)	3.06(10)	3.04(10)	-0.16(8)	1.00(8)	0.21(8)
C(1)	2.46(13)	2.80(13)	2.72(13)	0.08(10)	0.56(10)	0.74(10)
C(2)	2.64(14)	3.16(14)	2.71(12)	0.11(11)	0.71(11)	1.01(11)
C(3)	3.55(16)	3.46(15)	3.55(14)	0.53(12)	1.54(12)	1.11(12)
C(4)	4.12(17)	2.98(15)	4.41(17)	0.24(13)	1.49(14)	0.72(13)
C(5)	3.95(17)	3.06(15)	3.76(15)	-0.55(12)	1.02(13)	0.91(13)
C(6)	2.72(14)	3.39(15)	2.76(13)	-0.22(11)	0.57(11)	0.82(11)
C(7)	3.32(15)	3.61(15)	3.30(14)	-0.40(12)	0.70(12)	1.19(12)
C(8)	3.59(16)	4.20(17)	3.19(14)	-0.39(13)	0.86(12)	1.38(13)
C(9)	3.64(16)	3.30(15)	3.01(13)	-0.21(12)	1.04(12)	1.07(12)
C(10)	4.06(19)	6.5(2)	4.04(17)	-2.29(17)	0.63(15)	0.28(17)
C(11)	6.1(2)	4.86(19)	4.58(18)	0.31(15)	1.85(16)	3.16(17)
C(12)	6.5(2)	4.9(2)	3.10(15)	-0.32(14)	1.82(15)	1.32(17)
C(13)	7.4(3)	3.06(17)	7.2(3)	0.60(17)	3.4(2)	0.48(17)
O(21)	3.70(12)	4.07(12)	3.96(11)	-0.06(9)	0.02(9)	1.17(10)
O(22)	3.25(12)	5.91(15)	4.18(12)	-0.34(11)	0.18(10)	0.94(11)
C(21)	4.19(19)	6.1(2)	5.4(2)	-0.20(18)	1.45(16)	1.65(17)
C(22)	3.11(15)	3.43(15)	3.85(15)	0.40(12)	0.68(12)	0.36(12)
C(23)	4.3(2)	6.9(2)	3.83(17)	-0.64(17)	0.86(15)	0.75(17)
C(24)	4.4(2)	6.3(2)	6.5(2)	-1.1(2)	0.52(18)	1.01(18)

Table 7. Distances to the weighted least-squares planes for $C_{34}H_{44}C\ell_6O_6Ti_2$.

Plane no. 1

*	0.023	(0.002)	C(1)
*	-0.014	(0.002)	C(2)
*	-0.005	(0.002)	C(3)
*	0.016	(0.002)	C(4)
*	-0.008	(0.002)	C(5)
*	-0.012	(0.002)	C(6)
	-0.044	(0.005)	Ti
	0.097	(0.004)	O(1)
	-0.054	(0.005)	C(7)
	-0.092	(0.006)	C(8)
	-0.077	(0.005)	C(9)
	0.007	(0.006)	C(13)

Rms deviation of fitted atoms = 0.014

Plane no. 2

*	0.069	(0.001)	Cℓ(1)
*	-0.070	(0.001)	Cℓ(2)
*	0.085	(0.001)	O(1)
*	-0.085	(0.001)	O(21)
	-0.422	(0.001)	Ti

Rms deviation of fitted atoms = 0.078

Angle to previous plane (with approximate esd) = 80.37 (0.08)

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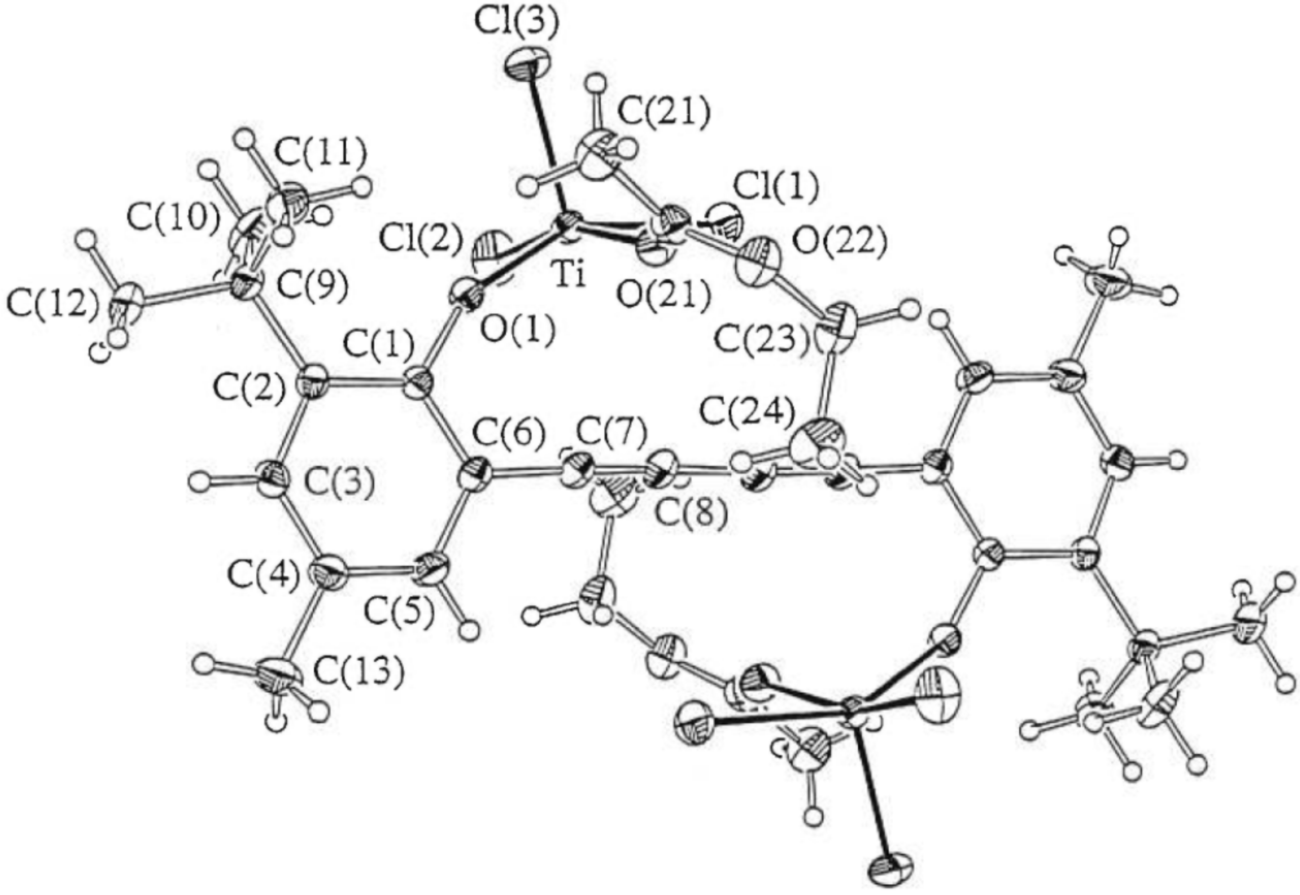
* indicates atoms used to define plane



ORTEP view of $C_{34}H_{44}C\ell_6O_6Ti_2$

with the numbering scheme adopted. Ellipsoids drawn at

40% probality level. Hydrogens represented by sphere of arbitrary size.

Discussion of structure determination and refinement procedure

The structure was solved by direct method using SHELXS96 (Sheldrick, 1990) and difmap synthesis using SHELXL96 (Sheldrick, 1996). All non-hydrogen atoms anisotropic, hydrogen atoms isotropic. Hydrogen atoms were calculated at idealized positions using a riding model with different C-H distances for type of hydrogen. The isotropic displacement factors, U_{iso}, were adjusted to 50% higher value of the bonded carbon atom (methyl) and 20% higher (others).

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ANNEXE 3

SUPPORTING INFORMATION

Novel Complexes of Strong Bidentate Lewis Acids Derived from 2,7-Bis(1,1-dimethylethyl)fluorene-1,8-diol

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I. Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes for bis(trichlorotitanium phenoxide) **7** (17 pages).

II. Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes for the CH_2Cl_2 solvate of the 1:2 complex of bis(trichlorotitanium phenoxide) 7 with 4,4´-dimethylbenzophenone (23 pages).

III. Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes for the dimer **9** of bis(diethylaluminum phenoxide) **8** (30 pages).

CRYSTAL AND MOLECULAR STRUCTURE OF

$C_{21}H_{24}C\ell_6O_2Ti_2$ (JIW104)

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Structure résolue au laboratoire de diffraction des rayons X de l'Université de Montréal par Dr. Michel Simard, 26 février 1996.

Table 1. Crystal data and structure refinement for $C_{21}H_{24}C\ell_6O_2Ti_2$.

Crystal data

Crystal source	....	
Chemical formula, sum	C21 H24 Cℓ6 O2 Ti2	
Chemical formula, moiety	Ti2 Cℓ6 O2 C21 H24	
Chemical formula weight, M_r	616.90	
Cell setting	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions (Å, °)	a = 15.551(6) b = 9.988(5) c = 19.842(10)	$\alpha = 90$ $\beta = 113.96(4)$ $\gamma = 90$
Volume of unit cell, V (Å^3)	2816(2)	
Formula units per cell, Z	4	
Density calculated from formula and cell, D_x (Mg/m^3)	1.455	
Density from independent measurements, D_m (Mg/m^3)	....	
Measurement method, by flottation in	....	
F(000)	1248	
Radiation type	Copper Kα	
Wavelength, λ (Å)	1.54056	
No. of reflections for cell measurement	25	

Table 1. (continued)

θ range (°)	20.00 to 25.00
Linear absorption coefficient, μ (mm^{-1})	10.39
Measurement temperature (K)	225(2)
Crystal shape	....
Colour	....
Size (mm)	0.64 x 0.28 x 0.18
Data collection	
Diffractometer type	Nonius CAD-4
Data-collection method	$\omega/2\theta$
Absorption correction type	Integration
Maximum and minimum transmission values, T_{max} and T_{min}	0.43 and 0.07
No. of reflections measured	19488
No. of independent reflections	5338
No. of observed reflections	3585
Criterion for observed reflections	I>2sigma(I)
R_{int}	0.082
Minimum and maximum values of θ (°)	3.11 to 69.91
Ranges of h,k,ℓ	$-18 \le h \le 17$, $0 \le k \le 12$, $0 \le \ell \le 24$

Table 1. (continued)

No. of standard reflections	5
Interval, time (min)	60
Intensity decay (%)	±8.5

Refinement

Refinement method	Full-matrix on F^2
Final R indices, I>2sigma(I)	R1 = 0.0608, wR2 = 0.1512
R indices, all data	R1 = 0.0843, wR2 = 0.1617
Goodness-of-fit on F^2, S	0.920

$R1 = \Sigma(\|Fo| - |Fc\|)/\Sigma(|Fo|)$,
$wR2 = [\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]]^{1/2}$
$S = [\Sigma[w(Fo^2-Fc^2)^2]/(\text{No. of reflns - No. of params.})]^{1/2}$

No. of reflections used in refinement	5338
No. of parameters refined	281
No. of restraints	0
Method of refining and locating H atoms	see text
Weighting scheme	based on measured e.s.d's
Function minimized	$\Sigma w(Fo^2-Fc^2)^2$

$w = 1/[\sigma^2(Fo^2)+(0.0950P)^2]$ where $P=(Fo^2+2Fc^2)/3$

Maximum Δ/σ	0.000
$\Delta\rho_{max}$ (e/Å^3)	0.974

Table 1. (continued)

$\Delta\rho_{min}$ (e/Å^3)	-0.743
Extinction correction method	SHELXL-93 (1995)
Secondary extinction value	0.00057(11)
Source of atomic scattering factors	International Tables for Crystallography (1992)

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2, x 10^2) for $C_{21}H_{24}C\ell_6O_2Ti_2$.

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j a_i \cdot a_j$$

ATOM	X	Y	Z	U_{eq}
Ti(1)	0.67393(5)	0.10855(8)	0.40740(4)	3.63(2)
Ti(1')	0.27561(5)	0.01455(9)	0.30215(5)	4.47(2)
Cℓ(1)	0.58339(14)	0.1440(2)	0.29315(8)	9.77(6)
Cℓ(2)	0.60279(9)	0.17142(12)	0.47676(7)	5.40(3)
Cℓ(3)	0.80517(10)	0.22012(14)	0.43729(10)	7.37(4)
Cℓ(1')	0.34084(14)	0.12859(14)	0.40489(9)	8.17(5)
Cℓ(2')	0.33895(14)	0.0755(2)	0.22826(10)	10.37(7)
Cℓ(3')	0.12571(10)	0.0556(2)	0.25173(14)	11.71(8)
O(1)	0.6971(2)	-0.0602(3)	0.4214(2)	3.84(7)
O(1')	0.2967(2)	-0.1540(3)	0.3225(2)	4.07(7)
C(1)	0.6880(3)	-0.1963(4)	0.4306(2)	3.19(8)
C(2)	0.7674(3)	-0.2795(4)	0.4591(2)	3.70(9)
C(3)	0.7491(3)	-0.4131(5)	0.4686(3)	4.38(10)
C(4)	0.6604(3)	-0.4640(5)	0.4524(3)	4.27(10)
C(5)	0.5841(3)	-0.3782(4)	0.4239(2)	3.40(9)
C(6)	0.5981(3)	-0.2431(4)	0.4133(2)	3.05(8)
C(7)	0.5049(3)	-0.1704(4)	0.3820(2)	3.36(8)
C(8)	0.8680(3)	-0.2283(5)	0.4782(3)	5.31(12)
C(9)	0.8957(4)	-0.1269(6)	0.5416(3)	6.9(2)
C(10)	0.8741(4)	-0.1644(6)	0.4095(3)	6.4(2)
C(11)	0.9394(3)	-0.3449(6)	0.5024(4)	8.5(2)
C(1')	0.3383(3)	-0.2767(4)	0.3457(2)	3.18(8)
C(2')	0.2838(3)	-0.3918(5)	0.3408(2)	3.91(10)
C(3')	0.3350(3)	-0.5093(5)	0.3670(3)	5.02(12)
C(4')	0.4318(3)	-0.5166(5)	0.3959(3)	4.69(11)
C(5')	0.4826(3)	-0.4019(4)	0.3988(2)	3.51(9)
C(6')	0.4362(3)	-0.2814(4)	0.3741(2)	3.14(8)
C(8')	0.1759(3)	-0.3905(5)	0.3105(3)	4.66(11)
C(9')	0.1347(4)	-0.3415(6)	0.2294(3)	6.5(2)
C(10')	0.1433(3)	-0.3012(6)	0.3581(3)	5.74(14)
C(11')	0.1366(3)	-0.5319(6)	0.3104(4)	7.0(2)

Table 3. Bond lengths (Å) and angles (°) for $C_{21}H_{24}C\ell_6O_2Ti_2$.

Ti(1)-O(1)	1.723(3)	Ti(1')-O(1')	1.731(3)
Ti(1)-Cℓ(1)	2.157(2)	Ti(1')-Cℓ(2')	2.159(2)
Ti(1)-Cℓ(2)	2.179(2)	Ti(1')-Cℓ(3')	2.170(2)
Ti(1)-Cℓ(3)	2.185(2)	Ti(1')-Cℓ(1')	2.192(2)
O(1)-C(1)	1.386(5)	O(1')-C(1')	1.375(5)
C(1)-C(6)	1.379(5)	C(1)-C(2)	1.402(5)
C(2)-C(3)	1.393(6)	C(2)-C(8)	1.541(6)
C(3)-C(4)	1.380(6)	C(4)-C(5)	1.385(6)
C(5)-C(6)	1.395(6)	C(5)-C(5')	1.469(5)
C(6)-C(7)	1.511(5)	C(7)-C(6')	1.503(5)
C(8)-C(9)	1.534(7)	C(8)-C(10)	1.543(8)
C(8)-C(11)	1.545(7)	C(1')-C(6')	1.394(5)
C(1')-C(2')	1.408(6)	C(2')-C(3')	1.395(7)
C(2')-C(8')	1.535(5)	C(3')-C(4')	1.379(6)
C(4')-C(5')	1.379(6)	C(5')-C(6')	1.387(6)
C(8')-C(10')	1.527(7)	C(8')-C(11')	1.538(7)
C(8')-C(9')	1.550(7)		
O(1)-Ti(1)-Cℓ(1)	109.55(12)	O(1')-Ti(1')-Cℓ(2')	109.67(12)
O(1)-Ti(1)-Cℓ(2)	107.87(11)	O(1')-Ti(1')-Cℓ(3')	110.96(11)
Cℓ(1)-Ti(1)-Cℓ(2)	109.53(8)	Cℓ(2')-Ti(1')-Cℓ(3')	109.55(10)
O(1)-Ti(1)-Cℓ(3)	110.12(11)	O(1')-Ti(1')-Cℓ(1')	108.43(11)
Cℓ(1)-Ti(1)-Cℓ(3)	109.91(8)	Cℓ(2')-Ti(1')-Cℓ(1')	108.59(9)
Cℓ(2)-Ti(1)-Cℓ(3)	109.84(7)	Cℓ(3')-Ti(1')-Cℓ(1')	109.60(10)
C(1)-O(1)-Ti(1)	162.7(3)	C(1')-O(1')-Ti(1')	164.6(3)
C(6)-C(1)-O(1)	116.6(3)	C(6)-C(1)-C(2)	122.5(4)
O(1)-C(1)-C(2)	120.9(3)	C(3)-C(2)-C(1)	115.4(4)
C(3)-C(2)-C(8)	121.8(4)	C(1)-C(2)-C(8)	122.8(4)
C(4)-C(3)-C(2)	124.0(4)	C(3)-C(4)-C(5)	118.5(4)
C(4)-C(5)-C(6)	120.0(4)	C(4)-C(5)-C(5')	131.5(4)
C(6)-C(5)-C(5')	108.5(4)	C(1)-C(6)-C(5)	119.7(4)
C(1)-C(6)-C(7)	130.2(4)	C(5)-C(6)-C(7)	110.2(3)
C(6')-C(7)-C(6)	102.1(3)	C(9)-C(8)-C(2)	109.9(4)
C(9)-C(8)-C(10)	110.7(4)	C(2)-C(8)-C(10)	109.9(4)
C(9)-C(8)-C(11)	108.4(5)	C(2)-C(8)-C(11)	110.9(4)
C(10)-C(8)-C(11)	107.0(4)	O(1')-C(1')-C(6')	116.9(4)

Table 3. (continued)

O(1')-C(1')-C(2')	121.1(3)	C(6')-C(1')-C(2')	121.9(4)
C(3')-C(2')-C(1')	115.2(4)	C(3')-C(2')-C(8')	121.4(4)
C(1')-C(2')-C(8')	123.5(4)	C(4')-C(3')-C(2')	124.1(4)
C(3')-C(4')-C(5')	119.0(4)	C(4')-C(5')-C(6')	120.0(4)
C(4')-C(5')-C(5)	131.8(4)	C(6')-C(5')-C(5)	108.2(4)
C(5')-C(6')-C(1')	119.9(4)	C(5')-C(6')-C(7)	111.0(3)
C(1')-C(6')-C(7)	129.1(4)	C(10')-C(8')-C(2')	110.3(4)
C(10')-C(8')-C(11')	107.8(4)	C(2')-C(8')-C(11')	111.3(4)
C(10')-C(8')-C(9')	110.8(4)	C(2')-C(8')-C(9')	109.6(4)
C(11')-C(8')-C(9')	106.9(4)		

Table 4. Torsion angles (°) for $C_{21}H_{24}C\ell_6O_2Ti_2$.

Cℓ(1)-Ti(1)-O(1)-C(1)	-73.8(9)	Cℓ(2)-Ti(1)-O(1)-C(1)	45.4(9)
Cℓ(3)-Ti(1)-O(1)-C(1)	165.2(9)	Cℓ(2')-Ti(1')-O(1')-C(1')	59.3(10)
Cℓ(3')-Ti(1')-O(1')-C(1')	-180.0(10)	Cℓ(1')-Ti(1')-O(1')-C(1')	-59.1(10)
Ti(1)-O(1)-C(1)-C(6)	12.1(11)	Ti(1)-O(1)-C(1)-C(2)	-165.2(7)
C(6)-C(1)-C(2)-C(3)	0.2(6)	O(1)-C(1)-C(2)-C(3)	177.3(4)
C(6)-C(1)-C(2)-C(8)	179.7(4)	O(1)-C(1)-C(2)-C(8)	-3.2(6)
C(1)-C(2)-C(3)-C(4)	-0.4(7)	C(8)-C(2)-C(3)-C(4)	-180.0(5)
C(2)-C(3)-C(4)-C(5)	0.9(7)	C(3)-C(4)-C(5)-C(6)	-1.0(6)
C(3)-C(4)-C(5)-C(5')	177.4(4)	O(1)-C(1)-C(6)-C(5)	-177.6(3)
C(2)-C(1)-C(6)-C(5)	-0.3(6)	O(1)-C(1)-C(6)-C(7)	3.2(6)
C(2)-C(1)-C(6)-C(7)	-179.5(4)	C(4)-C(5)-C(6)-C(1)	0.7(6)
C(5')-C(5)-C(6)-C(1)	-178.0(3)	C(4)-C(5)-C(6)-C(7)	-179.9(4)
C(5')-C(5)-C(6)-C(7)	1.3(4)	C(1)-C(6)-C(7)-C(6')	177.7(4)
C(5)-C(6)-C(7)-C(6')	-1.5(4)	C(3)-C(2)-C(8)-C(9)	-115.7(5)
C(1)-C(2)-C(8)-C(9)	64.8(6)	C(3)-C(2)-C(8)-C(10)	122.2(5)
C(1)-C(2)-C(8)-C(10)	-57.3(6)	C(3)-C(2)-C(8)-C(11)	4.1(7)
C(1)-C(2)-C(8)-C(11)	-175.4(5)	Ti(1')-O(1')-C(1')-C(6')	-3.0(12)
Ti(1')-O(1')-C(1')-C(2')	176.9(8)	O(1')-C(1')-C(2')-C(3')	-179.4(4)
C(6')-C(1')-C(2')-C(3')	0.5(6)	O(1')-C(1')-C(2')-C(8')	-0.4(6)
C(6')-C(1')-C(2')-C(8')	179.5(4)	C(1')-C(2')-C(3')-C(4')	0.0(7)
C(8')-C(2')-C(3')-C(4')	-179.0(5)	C(2')-C(3')-C(4')-C(5')	-0.8(8)
C(3')-C(4')-C(5')-C(6')	1.0(7)	C(3')-C(4')-C(5')-C(5)	-178.0(5)
C(4)-C(5)-C(5')-C(4')	0.0(8)	C(6)-C(5)-C(5')-C(4')	178.5(5)
C(4)-C(5)-C(5')-C(6')	-179.1(4)	C(6)-C(5)-C(5')-C(6')	-0.6(5)
C(4')-C(5')-C(6')-C(1')	-0.5(6)	C(5)-C(5')-C(6')-C(1')	178.7(3)
C(4')-C(5')-C(6')-C(7)	-179.6(4)	C(5)-C(5')-C(6')-C(7)	-0.4(5)
O(1')-C(1')-C(6')-C(5')	179.6(3)	C(2')-C(1')-C(6')-C(5')	-0.2(6)
O(1')-C(1')-C(6')-C(7)	-1.4(6)	C(2')-C(1')-C(6')-C(7)	178.7(4)
C(6)-C(7)-C(6')-C(5')	1.2(4)	C(6)-C(7)-C(6')-C(1')	-177.8(4)
C(3')-C(2')-C(8')-C(10')	117.0(5)	C(1')-C(2')-C(8')-C(10')	-61.9(6)
C(3')-C(2')-C(8')-C(11')	-2.6(7)	C(1')-C(2')-C(8')-C(11')	178.5(4)
C(3')-C(2')-C(8')-C(9')	-120.7(5)	C(1')-C(2')-C(8')-C(9')	60.4(6)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$, x 10^2) for $C_{21}H_{24}Cl_6O_2Ti_2$.

ATOM	X	Y	Z	U_{iso}
H(3)	0.8005(3)	-0.4723(5)	0.4873(3)	5.3
H(4)	0.6519(3)	-0.5548(5)	0.4604(3)	5.1
H(7A)	0.5019(3)	-0.1009(4)	0.4158(2)	4.0
H(7B)	0.4935(3)	-0.1297(4)	0.3341(2)	4.0
H(9A)	0.9591(4)	-0.0950(6)	0.5533(3)	10.4
H(9B)	0.8932(4)	-0.1696(6)	0.5847(3)	10.4
H(9C)	0.8524(4)	-0.0518(6)	0.5269(3)	10.4
H(10A)	0.8564(4)	-0.2300(6)	0.3701(3)	9.6
H(10B)	0.9381(4)	-0.1347(6)	0.4215(3)	9.6
H(10C)	0.8318(4)	-0.0884(6)	0.3936(3)	9.6
H(11A)	0.9229(3)	-0.4100(6)	0.4629(4)	12.7
H(11B)	0.9382(3)	-0.3872(6)	0.5460(4)	12.7
H(11C)	1.0021(3)	-0.3105(6)	0.5136(4)	12.7
H(3')	0.3013(3)	-0.5886(5)	0.3648(3)	6.0
H(4')	0.4627(3)	-0.5984(5)	0.4133(3)	5.6
H(9A')	0.1562(4)	-0.3995(6)	0.2002(3)	9.8
H(9B')	0.1555(4)	-0.2506(6)	0.2274(3)	9.8
H(9C')	0.0665(4)	-0.3437(6)	0.2098(3)	9.8
H(10A')	0.0751(3)	-0.3012(6)	0.3383(3)	8.6
H(10B')	0.1656(3)	-0.2105(6)	0.3578(3)	8.6
H(10C')	0.1684(3)	-0.3350(6)	0.4082(3)	8.6
H(11A')	0.1564(3)	-0.5907(6)	0.2805(4)	10.4
H(11B')	0.0684(3)	-0.5283(6)	0.2901(4)	10.4
H(11C')	0.1602(3)	-0.5657(6)	0.3605(4)	10.4

Table 6. Anisotropic parameters ($Å^2$, x 10^2) for $C_{21}H_{24}C\ell_6O_2Ti_2$.

The anisotropic thermal parameters are the coefficients of the expression:

$$T = \exp[-2\pi^2(U_{11}a^{*2}h^2+...+ 2U_{12}a^{*}b^{*}hk+...)].$$

ATOM	U11	U22	U33	U23	U13	U12
Ti(1)	3.96(4)	3.21(4)	4.23(4)	0.03(3)	2.20(3)	-0.33(3)
Ti(1')	3.54(4)	4.56(5)	5.18(5)	1.27(4)	1.65(3)	0.92(4)
Cℓ(1)	11.77(14)	11.6(2)	4.35(7)	2.60(9)	1.67(8)	-1.54(12)
Cℓ(2)	7.03(7)	4.15(6)	6.77(7)	-0.15(6)	4.62(6)	0.23(6)
Cℓ(3)	6.16(8)	5.21(8)	12.27(12)	-2.09(8)	5.30(8)	-2.28(6)
Cℓ(1')	12.27(14)	4.49(8)	6.78(9)	-0.30(7)	2.88(9)	0.64(8)
Cℓ(2')	10.26(13)	14.0(2)	8.94(12)	5.70(12)	6.09(11)	2.78(12)
Cℓ(3')	3.94(7)	9.72(14)	19.0(2)	5.09(14)	2.08(10)	2.11(8)
O(1)	3.51(14)	2.8(2)	5.3(2)	-0.57(13)	1.94(13)	-0.43(12)
O(1')	3.13(13)	3.9(2)	4.8(2)	0.18(14)	1.20(12)	0.53(12)
C(1)	3.4(2)	2.9(2)	3.6(2)	-0.5(2)	1.7(2)	-0.1(2)
C(2)	3.0(2)	3.9(2)	4.4(2)	-0.5(2)	1.7(2)	0.0(2)
C(3)	3.4(2)	3.8(2)	5.7(3)	0.5(2)	1.6(2)	0.7(2)
C(4)	3.6(2)	3.3(2)	5.9(3)	0.4(2)	1.9(2)	0.2(2)
C(5)	3.6(2)	3.3(2)	3.7(2)	-0.1(2)	1.8(2)	-0.2(2)
C(6)	3.3(2)	2.9(2)	3.1(2)	-0.4(2)	1.5(2)	0.1(2)
C(7)	2.9(2)	3.2(2)	4.0(2)	-0.2(2)	1.5(2)	0.0(2)
C(8)	3.0(2)	4.6(3)	8.2(3)	0.1(3)	2.1(2)	-0.1(2)
C(9)	4.5(3)	7.1(4)	7.5(4)	-0.6(3)	0.6(3)	-1.4(3)
C(10)	4.6(3)	6.4(4)	9.8(4)	-0.6(3)	4.5(3)	-0.5(3)
C(11)	3.1(2)	6.5(4)	15.2(6)	1.6(4)	3.0(3)	0.5(2)
C(1')	3.0(2)	3.4(2)	3.2(2)	-0.2(2)	1.3(2)	0.0(2)
C(2')	3.1(2)	4.5(3)	4.2(2)	-0.5(2)	1.6(2)	-0.6(2)
C(3')	4.0(2)	4.3(3)	7.0(3)	-0.1(2)	2.5(2)	-1.2(2)
C(4')	3.9(2)	3.5(2)	6.8(3)	1.1(2)	2.2(2)	-0.1(2)
C(5')	3.0(2)	3.6(2)	3.9(2)	-0.3(2)	1.4(2)	0.0(2)
C(6')	3.3(2)	3.1(2)	3.2(2)	-0.2(2)	1.6(2)	0.0(2)
C(8')	2.7(2)	5.5(3)	5.6(3)	-0.5(2)	1.5(2)	-1.0(2)
C(9')	4.3(3)	8.5(4)	5.1(3)	-0.5(3)	0.2(2)	-0.8(3)
C(10')	3.7(2)	7.5(4)	6.5(3)	-1.0(3)	2.5(2)	-0.9(2)
C(11')	3.7(2)	6.3(4)	10.4(5)	-0.3(3)	2.4(3)	-1.9(2)

Table 7. Distances to the weighted least-squares planes for $C_{21}H_{24}C\ell_6O_2Ti_2$.

Plane no. 1

*	0.000 (0.003)	C(1)
*	0.000 (0.003)	C(2)
*	-0.002 (0.003)	C(3)
*	0.004 (0.003)	C(4)
*	-0.004 (0.003)	C(5)
*	0.002 (0.003)	C(6)
	0.058 (0.006)	O(1)
	-0.007 (0.006)	C(7)
	-0.009 (0.008)	C(8)

Rms deviation of fitted atoms = 0.003

Plane no. 2

*	0.004 (0.003)	C(1')
*	-0.003 (0.003)	C(2')
*	-0.002 (0.004)	C(3')
*	0.005 (0.004)	C(4')
*	-0.005 (0.003)	C(5')
*	0.000 (0.003)	C(6')
	0.016 (0.006)	O(1')
	-0.021 (0.006)	C(7)
	0.013 (0.007)	C(8')

Rms deviation of fitted atoms = 0.003

Angle to previous plane (with approximate esd) = 3.18 (0.15)

Plane no. 3

*	0.006 (0.003)	C(5)
*	-0.009 (0.002)	C(6)
*	0.008 (0.002)	C(7)
*	0.000 (0.003)	C(5')
*	-0.005 (0.003)	C(6')

Rms deviation of fitted atoms = 0.006

Table 7. (continued)

Plane no. 4

*	-0.026 (0.003)	C(1)
*	-0.044 (0.004)	C(2)
*	-0.021 (0.004)	C(3)
*	0.026 (0.004)	C(4)
*	0.034 (0.004)	C(5)
*	0.016 (0.003)	C(6)
*	0.031 (0.003)	C(7)
*	-0.012 (0.003)	C(1')
*	-0.044 (0.004)	C(2')
*	-0.028 (0.004)	C(3')
*	0.016 (0.004)	C(4')
*	0.030 (0.004)	C(5')
*	0.022 (0.003)	C(6')
	0.010 (0.004)	O(1)
	-0.011 (0.004)	O(1')
	-0.097 (0.006)	C(8)
	-0.070 (0.006)	C(8')

Rms deviation of fitted atoms = 0.028

Angle to previous plane (with approximate esd) = 0.17 (0.13)

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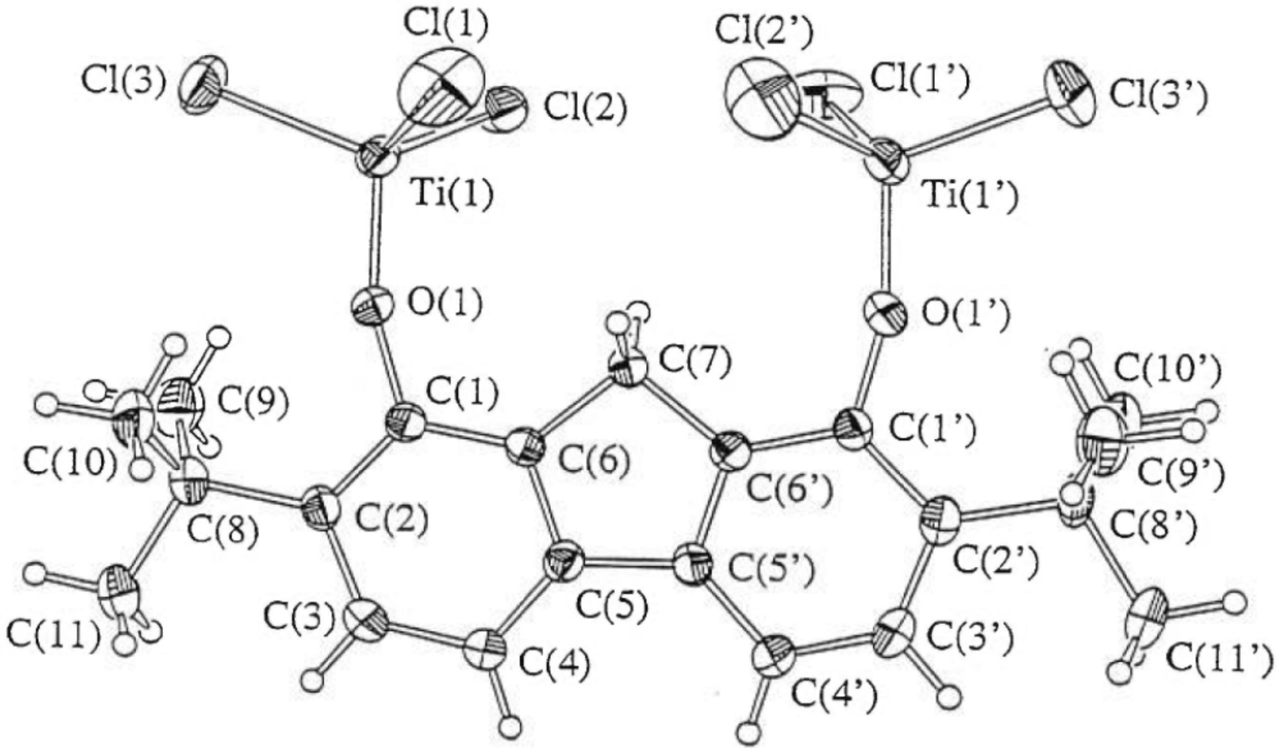
* indicates atoms used to define plane



ORTEP view of $C_{21}H_{24}C\ell_6O_2Ti_2$

with the numbering scheme adopted. Ellipsoids drawn at

40% probality level. Hydrogens represented by sphere of arbitrary size.

Discussion of structure determination and refinement procedure

The structure was solved by direct method using SHELXS-86 (Sheldrick, 1985) and difmap synthesis using SHELXL-93 (Sheldrick, 1995). All non-hydrogen atoms anisotropic, hydrogen atoms isotropic. Hydrogen atoms were calculated at idealized positions using a riding model with different C-H distances for type of hydrogen. The isotropic displacement factors, U_{iso}, were adjusted to 50% higher value of the bonded carbon atom (methyl) and 20% higher (others).

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CRYSTAL AND MOLECULAR STRUCTURE OF

$C_{51}H_{52}C\ell_6O_4Ti_2 \cdot CH_2C\ell_2$ (JIW133)

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Structure résolue au laboratoire de diffraction des rayons X de l'Université de Montréal par Michel Simard.

Table 1. Crystal data and structure refinement for $C_{51}H_{52}C\ell_6O_4Ti_2\cdot CH_2C\ell_2$.

Crystal data

Crystal source	....	
Chemical formula, sum	C52 H54 Cℓ8 O4 Ti2	
Chemical formula, moiety	$C_{51}H_{52}C\ell_6O_4Ti_2\cdot CH_2C\ell_2$	
Chemical formula weight, M_r	1122.35	
Cell setting	Monoclinic	
Space group	P 21/c	
Unit cell dimensions (Å, °)	a = 12.756(3)	alpha = 90
	b = 21.458(13)	beta = 101.28(2)
	c = 20.047(7)	gamma = 90
Volume of unit cell, V (Å^3)	5381(4)	
Formula units per cell, Z	4	
Density calculated from formula and cell, D_x (Mg/m^3)	1.385	
Density from independent measurements, D_m (Mg/m^3)	not measured	
Measurement method, by flottation in	none	
F(000)	2312	
Radiation type	CuKα	
Wavelength, λ (Å)	1.54056	
No. of reflections for cell measurement	25	

Table 1. (continued)

θ range (°)	20.00 to 22.50
Linear absorption coefficient, μ (mm^{-1})	4.181
Measurement temperature (K)	210(2)
Crystal shape	plate
Colour	black
Size (mm)	0.70 x 0.43 x 0.11
Data collection	
Diffractometer type	Nonius CAD-4
Data-collection method	$\omega/2\theta$ scan
Absorption correction type	Integration
Maximum and minimum transmission values, T_{max} and T_{min}	0.47 and 0.06
No. of reflections measured	38277
No. of independent reflections	10208
No. of observed reflections	7119
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.065
Minimum and maximum values of θ (°)	3.05 to 69.87
Ranges of h,k,ℓ	$-15 \leq h \leq 15$, $-26 \leq k \leq 26$, $-24 \leq \ell \leq 24$

Table 1. (continued)

No. of standard reflections	5
Interval, time (min)	60
Intensity decay (%)	7.7
Refinement	
Refinement method	Full-matrix on F^2
Final R indices, $I>2\sigma(I)$	$R1 = 0.0598$, $wR2 = 0.1715$
R indices, all data	$R1 = 0.0795$, $wR2 = 0.1813$
Goodness-of-fit on F^2, S	0.981

$R1 = \Sigma(\|Fo| - |Fc\|)/\Sigma(|Fo|)$,
$wR2 = [\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]]^{1/2}$ and
$GoF = [\Sigma[w(Fo^2-Fc^2)^2]/(\text{No. of reflns - No. of params.})]^{1/2}$

No. of reflections used in refinement	10208
No. of parameters refined	600
No. of restraints	0
Method of refining and locating H atoms	see text
Weighting scheme	based on measured e.s.d's
Function minimized	$\Sigma w(Fo^2-Fc^2)$

$w=1/[\sigma^2(Fo^2)+(0.1060P)^2]$ where $P=(Fo^2+2Fc^2)/3$

Maximum Δ/σ	0.011
$\Delta\rho_{max}$ (e/Å^3)	0.639

Table 1. (continued)

$\Delta\rho_{min}$ (e/Å^3)	-1.164
Extinction correction method	SHELXL96 (Sheldrick, 1996)
Secondary extinction value	0.00039(8)
Source of atomic scattering factors	International Tables for Crystallography (1992)

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^2$) for $C_{51}H_{52}C\ell_6O_4Ti_2 \cdot CH_2C\ell_2$.

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j a_i \cdot a_j$$

ATOM	X	Y	Z	U_{eq}
Ti(1)	0.28130(5)	0.34753(3)	0.64456(4)	3.659(19)
Ti(1')	-0.11346(5)	0.20535(3)	0.54380(3)	3.508(18)
Cℓ(1)	0.28348(9)	0.24977(5)	0.60329(6)	4.94(3)
Cℓ(2)	0.15133(11)	0.41981(6)	0.64270(7)	6.68(4)
Cℓ(3)	0.44294(9)	0.39054(6)	0.66754(6)	5.97(3)
Cℓ(1')	-0.02319(10)	0.29116(5)	0.52630(5)	4.95(3)
Cℓ(2')	-0.03125(9)	0.12443(5)	0.60602(5)	4.70(3)
Cℓ(3')	-0.27652(9)	0.20216(9)	0.47813(6)	7.78(5)
O(1)	0.2701(2)	0.32282(14)	0.72681(13)	3.99(6)
C(1)	0.2300(3)	0.30240(18)	0.78156(18)	3.32(8)
C(2)	0.2897(3)	0.30808(19)	0.84858(19)	3.78(9)
C(3)	0.2415(3)	0.2846(2)	0.90015(19)	4.22(9)
C(4)	0.1393(3)	0.2597(2)	0.8894(2)	3.99(9)
C(5)	0.0814(3)	0.25756(18)	0.82341(19)	3.42(8)
C(6)	0.1267(3)	0.27741(17)	0.76933(18)	3.30(8)
C(7)	0.0498(3)	0.26792(19)	0.70301(19)	3.52(8)
C(8)	0.3990(3)	0.3397(2)	0.8645(2)	4.99(11)
C(9)	0.3854(4)	0.4080(3)	0.8415(3)	6.13(13)
C(10)	0.4791(4)	0.3052(3)	0.8303(2)	6.45(15)
C(11)	0.4459(4)	0.3392(3)	0.9416(2)	6.52(15)
O(1')	-0.15810(19)	0.23046(13)	0.61790(13)	3.71(6)
C(1')	-0.1469(3)	0.22692(17)	0.68735(18)	3.28(8)
C(2')	-0.2315(3)	0.20760(18)	0.7186(2)	3.73(8)
C(3')	-0.2095(3)	0.2054(2)	0.7895(2)	4.14(9)
C(4')	-0.1098(3)	0.2195(2)	0.8291(2)	4.10(9)
C(5')	-0.0286(3)	0.23853(17)	0.79629(19)	3.39(8)
C(6')	-0.0472(3)	0.24339(17)	0.72605(19)	3.26(8)
C(8')	-0.3417(3)	0.1881(2)	0.6780(2)	4.61(10)
C(9')	-0.3306(4)	0.1285(2)	0.6375(3)	5.56(12)
C(10')	-0.3907(4)	0.2406(2)	0.6303(3)	5.83(13)
C(11')	-0.4206(4)	0.1742(3)	0.7244(3)	7.10(16)

Table 2. (continued)

O(20)	0.2636(3)	0.37094(16)	0.54300(15)	5.23(8)
C(20)	0.2775(4)	0.3898(2)	0.4865(2)	4.61(10)
C(21)	0.1833(4)	0.4052(2)	0.4343(2)	4.79(10)
C(22)	0.0892(4)	0.4244(2)	0.4524(3)	5.55(12)
C(23)	-0.0004(4)	0.4370(2)	0.4024(3)	5.72(12)
C(24)	0.0021(4)	0.4291(2)	0.3345(2)	5.21(11)
C(25)	0.0942(4)	0.4084(3)	0.3169(3)	6.18(13)
C(26)	0.1860(4)	0.3965(2)	0.3658(2)	5.57(12)
C(27)	-0.0950(4)	0.4411(3)	0.2795(3)	6.47(14)
C(28)	0.3868(4)	0.3959(2)	0.4734(2)	4.58(10)
C(29)	0.4139(4)	0.4449(3)	0.4340(3)	6.35(13)
C(30)	0.5157(4)	0.4514(3)	0.4240(3)	6.88(15)
C(31)	0.5952(4)	0.4094(3)	0.4515(3)	6.49(14)
C(32)	0.5685(4)	0.3608(3)	0.4899(3)	6.23(13)
C(33)	0.4656(4)	0.3548(2)	0.5021(2)	5.32(11)
C(34)	0.7080(5)	0.4167(4)	0.4396(3)	9.3(2)
O(20')	-0.0601(2)	0.16533(13)	0.46332(13)	4.06(6)
C(20')	-0.0198(3)	0.12445(18)	0.4301(2)	3.65(8)
C(21')	0.0772(3)	0.09133(19)	0.4625(2)	3.91(9)
C(22')	0.1536(3)	0.1211(2)	0.5119(2)	4.18(9)
C(23')	0.2458(3)	0.0910(2)	0.5394(2)	5.23(11)
C(24')	0.2654(4)	0.0298(2)	0.5223(3)	6.02(13)
C(25')	0.1884(4)	-0.0007(2)	0.4750(3)	6.29(14)
C(26')	0.0952(3)	0.0295(2)	0.4455(2)	5.08(11)
C(27')	0.3670(5)	-0.0029(3)	0.5520(4)	9.4(2)
C(28')	-0.0717(3)	0.11334(18)	0.3600(2)	3.77(8)
C(29')	-0.0132(3)	0.09276(19)	0.3116(2)	4.33(9)
C(30')	-0.0637(4)	0.0874(2)	0.2437(2)	4.97(11)
C(31')	-0.1707(4)	0.1007(2)	0.2227(2)	5.08(11)
C(32')	-0.2281(4)	0.1215(2)	0.2702(2)	5.24(11)
C(33')	-0.1796(3)	0.1284(2)	0.3379(2)	4.65(10)
C(34')	-0.2222(5)	0.0954(3)	0.1487(2)	6.97(15)
Cℓ(4)	0.4044(2)	0.01033(13)	0.74018(13)	14.29(9)
Cℓ(5)	0.28620(18)	0.12540(10)	0.71610(11)	11.02(7)
C(40)	0.2796(6)	0.0439(3)	0.7171(4)	10.1(2)

Table 3. Bond lengths (Å) and angles (°) for $C_{51}H_{52}C\ell_6O_4Ti_2\cdot CH_2C\ell_2$.

Ti(1)-O(1)	1.764(3)	Ti(1)-O(20)	2.066(3)
Ti(1)-Cℓ(3)	2.2234(14)	Ti(1)-Cℓ(1)	2.2573(17)
Ti(1)-Cℓ(2)	2.2652(15)	Ti(1')-O(1')	1.776(3)
Ti(1')-O(20')	2.058(3)	Ti(1')-Cℓ(3')	2.2345(13)
Ti(1')-Cℓ(1')	2.2356(16)	Ti(1')-Cℓ(2')	2.2714(15)
O(1)-C(1)	1.370(4)	C(1)-C(6)	1.399(5)
C(1)-C(2)	1.414(5)	C(2)-C(3)	1.396(6)
C(2)-C(8)	1.527(6)	C(3)-C(4)	1.386(6)
C(4)-C(5)	1.385(5)	C(5)-C(6)	1.392(5)
C(5)-C(5')	1.460(5)	C(6)-C(7)	1.504(5)
C(7)-C(6')	1.498(5)	C(8)-C(10)	1.529(6)
C(8)-C(9)	1.535(7)	C(8)-C(11)	1.543(6)
O(1')-C(1')	1.374(4)	C(1')-C(6')	1.400(5)
C(1')-C(2')	1.411(5)	C(2')-C(3')	1.395(5)
C(2')-C(8')	1.538(5)	C(3')-C(4')	1.394(6)
C(4')-C(5')	1.393(5)	C(5')-C(6')	1.385(5)
C(8')-C(11')	1.528(6)	C(8')-C(10')	1.530(6)
C(8')-C(9')	1.536(6)	O(20)-C(20)	1.248(5)
C(20)-C(21)	1.468(6)	C(20)-C(28)	1.473(6)
C(21)-C(22)	1.384(6)	C(21)-C(26)	1.392(6)
C(22)-C(23)	1.392(6)	C(23)-C(24)	1.378(7)
C(24)-C(25)	1.367(7)	C(24)-C(27)	1.511(6)
C(25)-C(26)	1.396(7)	C(28)-C(33)	1.377(6)
C(28)-C(29)	1.399(6)	C(29)-C(30)	1.359(7)
C(30)-C(31)	1.387(8)	C(31)-C(32)	1.378(7)
C(31)-C(34)	1.512(7)	C(32)-C(33)	1.388(7)
O(20')-C(20')	1.269(4)	C(20')-C(28')	1.451(5)
C(20')-C(21')	1.464(5)	C(21')-C(26')	1.400(6)
C(21')-C(22')	1.400(5)	C(22')-C(23')	1.360(6)
C(23')-C(24')	1.392(7)	C(24')-C(25')	1.388(7)
C(24')-C(27')	1.491(7)	C(25')-C(26')	1.380(6)
C(28')-C(33')	1.400(6)	C(28')-C(29')	1.406(5)
C(29')-C(30')	1.391(6)	C(30')-C(31')	1.377(7)
C(31')-C(32')	1.384(6)	C(31')-C(34')	1.505(6)
C(32')-C(33')	1.384(6)	Cℓ(4)-C(40)	1.726(8)
Cℓ(5)-C(40)	1.750(7)		

O(1)-Ti(1)-O(20)	168.79(13)	O(1)-Ti(1)-Cℓ(3)	99.92(10)

Table 3. (continued)

O(20)-Ti(1)-Cℓ(3)	91.22(10)	O(1)-Ti(1)-Cℓ(1)	94.14(11)
O(20)-Ti(1)-Cℓ(1)	82.62(10)	Cℓ(3)-Ti(1)-Cℓ(1)	112.60(6)
O(1)-Ti(1)-Cℓ(2)	91.64(10)	O(20)-Ti(1)-Cℓ(2)	83.05(10)
Cℓ(3)-Ti(1)-Cℓ(2)	111.43(7)	Cℓ(1)-Ti(1)-Cℓ(2)	133.77(6)
O(1')-Ti(1')-O(20')	172.84(13)	O(1')-Ti(1')-Cℓ(3')	95.07(9)
O(20')-Ti(1')-Cℓ(3')	86.44(9)	O(1')-Ti(1')-Cℓ(1')	98.08(10)
O(20')-Ti(1')-Cℓ(1')	87.77(9)	Cℓ(3')-Ti(1')-Cℓ(1')	112.43(7)
O(1')-Ti(1')-Cℓ(2')	87.80(10)	O(20')-Ti(1')-Cℓ(2')	85.62(9)
Cℓ(3')-Ti(1')-Cℓ(2')	125.22(7)	Cℓ(1')-Ti(1')-Cℓ(2')	121.28(6)
C(1)-O(1)-Ti(1)	162.9(2)	O(1)-C(1)-C(6)	117.9(3)
O(1)-C(1)-C(2)	121.2(3)	C(6)-C(1)-C(2)	120.9(3)
C(3)-C(2)-C(1)	116.1(4)	C(3)-C(2)-C(8)	121.4(4)
C(1)-C(2)-C(8)	122.5(4)	C(4)-C(3)-C(2)	124.2(4)
C(5)-C(4)-C(3)	118.1(4)	C(4)-C(5)-C(6)	120.6(4)
C(4)-C(5)-C(5')	131.3(4)	C(6)-C(5)-C(5')	108.1(3)
C(5)-C(6)-C(1)	120.1(3)	C(5)-C(6)-C(7)	110.4(3)
C(1)-C(6)-C(7)	129.5(3)	C(6')-C(7)-C(6)	102.1(3)
C(2)-C(8)-C(10)	110.7(4)	C(2)-C(8)-C(9)	108.4(4)
C(10)-C(8)-C(9)	111.9(4)	C(2)-C(8)-C(11)	111.5(4)
C(10)-C(8)-C(11)	106.5(4)	C(9)-C(8)-C(11)	107.8(4)
C(1')-O(1')-Ti(1')	147.6(2)	O(1')-C(1')-C(6')	116.8(3)
O(1')-C(1')-C(2')	121.9(3)	C(6')-C(1')-C(2')	121.3(3)
C(3')-C(2')-C(1')	116.3(3)	C(3')-C(2')-C(8')	120.7(4)
C(1')-C(2')-C(8')	123.0(3)	C(4')-C(3')-C(2')	123.6(4)
C(5')-C(4')-C(3')	118.3(4)	C(6')-C(5')-C(4')	120.5(3)
C(6')-C(5')-C(5)	108.6(3)	C(4')-C(5')-C(5)	130.9(3)
C(5')-C(6')-C(1')	120.1(3)	C(5')-C(6')-C(7)	110.6(3)
C(1')-C(6')-C(7)	129.3(3)	C(11')-C(8')-C(10')	106.7(4)
C(11')-C(8')-C(9')	107.4(4)	C(10')-C(8')-C(9')	110.6(4)
C(11')-C(8')-C(2')	111.9(4)	C(10')-C(8')-C(2')	110.4(4)
C(9')-C(8')-C(2')	109.7(3)	C(20)-O(20)-Ti(1)	165.0(3)
O(20)-C(20)-C(21)	118.5(4)	O(20)-C(20)-C(28)	119.8(4)
C(21)-C(20)-C(28)	121.7(4)	C(22)-C(21)-C(26)	119.2(4)
C(22)-C(21)-C(20)	120.8(4)	C(26)-C(21)-C(20)	119.9(4)
C(21)-C(22)-C(23)	120.1(5)	C(24)-C(23)-C(22)	120.9(5)
C(25)-C(24)-C(23)	118.9(4)	C(25)-C(24)-C(27)	119.3(5)
C(23)-C(24)-C(27)	121.8(5)	C(24)-C(25)-C(26)	121.5(5)
C(21)-C(26)-C(25)	119.3(5)	C(33)-C(28)-C(29)	118.5(5)
C(33)-C(28)-C(20)	120.5(4)	C(29)-C(28)-C(20)	120.9(4)
C(30)-C(29)-C(28)	120.6(5)	C(29)-C(30)-C(31)	121.3(5)

Table 3. (continued)

C(32)-C(31)-C(30)	118.2(5)	C(32)-C(31)-C(34)	120.8(6)
C(30)-C(31)-C(34)	121.0(5)	C(31)-C(32)-C(33)	121.0(5)
C(28)-C(33)-C(32)	120.3(5)	C(20')-O(20')-Ti(1')	158.4(3)
O(20')-C(20')-C(28')	117.8(3)	O(20')-C(20')-C(21')	119.8(3)
C(28')-C(20')-C(21')	122.4(3)	C(26')-C(21')-C(22')	118.6(4)
C(26')-C(21')-C(20')	121.2(4)	C(22')-C(21')-C(20')	120.2(4)
C(23')-C(22')-C(21')	119.8(4)	C(22')-C(23')-C(24')	122.1(4)
C(25')-C(24')-C(23')	118.3(4)	C(25')-C(24')-C(27')	119.7(5)
C(23')-C(24')-C(27')	122.0(5)	C(26')-C(25')-C(24')	120.4(5)
C(25')-C(26')-C(21')	120.6(4)	C(33')-C(28')-C(29')	118.4(4)
C(33')-C(28')-C(20')	120.2(4)	C(29')-C(28')-C(20')	121.1(4)
C(30')-C(29')-C(28')	119.6(4)	C(31')-C(30')-C(29')	121.6(4)
C(30')-C(31')-C(32')	118.9(4)	C(30')-C(31')-C(34')	120.1(5)
C(32')-C(31')-C(34')	121.0(5)	C(31')-C(32')-C(33')	120.9(4)
C(32')-C(33')-C(28')	120.6(4)	Cℓ(4)-C(40)-Cℓ(5)	112.1(5)

Table 4. Torsion angles (°) for $C_{51}H_{52}C\ell_6O_4Ti_2 \cdot CH_2C\ell_2$.

O(20)-Ti(1)-O(1)-C(1)	-9.6(14)	Cℓ(3)-Ti(1)-O(1)-C(1)	163.9(9)
Cℓ(1)-Ti(1)-O(1)-C(1)	-82.3(9)	Cℓ(2)-Ti(1)-O(1)-C(1)	51.8(9)
Ti(1)-O(1)-C(1)-C(6)	15.2(11)	Ti(1)-O(1)-C(1)-C(2)	-162.9(7)
O(1)-C(1)-C(2)-C(3)	-178.9(4)	C(6)-C(1)-C(2)-C(3)	3.1(6)
O(1)-C(1)-C(2)-C(8)	2.9(6)	C(6)-C(1)-C(2)-C(8)	-175.1(4)
C(1)-C(2)-C(3)-C(4)	-3.2(6)	C(8)-C(2)-C(3)-C(4)	175.0(4)
C(2)-C(3)-C(4)-C(5)	0.3(7)	C(3)-C(4)-C(5)-C(6)	2.9(6)
C(3)-C(4)-C(5)-C(5')	-175.2(4)	C(4)-C(5)-C(6)-C(1)	-2.9(6)
C(5')-C(5)-C(6)-C(1)	175.6(3)	C(4)-C(5)-C(6)-C(7)	177.5(4)
C(5')-C(5)-C(6)-C(7)	-4.0(4)	O(1)-C(1)-C(6)-C(5)	-178.3(3)
C(2)-C(1)-C(6)-C(5)	-0.2(6)	O(1)-C(1)-C(6)-C(7)	1.1(6)
C(2)-C(1)-C(6)-C(7)	179.3(4)	C(5)-C(6)-C(7)-C(6')	2.9(4)
C(1)-C(6)-C(7)-C(6')	-176.6(4)	C(3)-C(2)-C(8)-C(10)	120.3(5)
C(1)-C(2)-C(8)-C(10)	-61.6(6)	C(3)-C(2)-C(8)-C(9)	-116.5(4)
C(1)-C(2)-C(8)-C(9)	61.6(5)	C(3)-C(2)-C(8)-C(11)	2.0(6)
C(1)-C(2)-C(8)-C(11)	-179.9(4)	O(20')-Ti(1')-O(1')-C(1')	40.2(12)
Cℓ(3')-Ti(1')-O(1')-C(1')	142.1(5)	Cℓ(1')-Ti(1')-O(1')-C(1')	-104.3(5)
Cℓ(2')-Ti(1')-O(1')-C(1')	16.9(5)	Ti(1')-O(1')-C(1')-C(6')	59.1(6)
Ti(1')-O(1')-C(1')-C(2')	-120.9(4)	O(1')-C(1')-C(2')-C(3')	179.3(3)
C(6')-C(1')-C(2')-C(3')	-0.6(6)	O(1')-C(1')-C(2')-C(8')	1.0(6)
C(6')-C(1')-C(2')-C(8')	-179.0(4)	C(1')-C(2')-C(3')-C(4')	-1.6(6)
C(8')-C(2')-C(3')-C(4')	176.8(4)	C(2')-C(3')-C(4')-C(5')	1.7(7)
C(3')-C(4')-C(5')-C(6')	0.3(6)	C(3')-C(4')-C(5')-C(5)	178.4(4)
C(4)-C(5)-C(5')-C(6')	-178.3(4)	C(6)-C(5)-C(5')-C(6')	3.5(4)
C(4)-C(5)-C(5')-C(4')	3.5(7)	C(6)-C(5)-C(5')-C(4')	-174.8(4)
C(4')-C(5')-C(6')-C(1')	-2.4(6)	C(5)-C(5')-C(6')-C(1')	179.1(3)
C(4')-C(5')-C(6')-C(7)	176.8(4)	C(5)-C(5')-C(6')-C(7)	-1.6(4)
O(1')-C(1')-C(6')-C(5')	-177.3(3)	C(2')-C(1')-C(6')-C(5')	2.6(6)
O(1')-C(1')-C(6')-C(7)	3.5(6)	C(2')-C(1')-C(6')-C(7)	-176.5(4)
C(6)-C(7)-C(6')-C(5')	-0.7(4)	C(6)-C(7)-C(6')-C(1')	178.5(4)
C(3')-C(2')-C(8')-C(11')	6.1(6)	C(1')-C(2')-C(8')-C(11')	-175.6(4)
C(3')-C(2')-C(8')-C(10')	124.8(4)	C(1')-C(2')-C(8')-C(10')	-56.9(5)
C(3')-C(2')-C(8')-C(9')	-113.0(4)	C(1')-C(2')-C(8')-C(9')	65.3(5)
O(1)-Ti(1)-O(20)-C(20)	178.3(10)	Cℓ(3)-Ti(1)-O(20)-C(20)	4.7(12)
Cℓ(1)-Ti(1)-O(20)-C(20)	-107.9(12)	Cℓ(2)-Ti(1)-O(20)-C(20)	116.2(12)
Ti(1)-O(20)-C(20)-C(21)	-158.5(10)	Ti(1)-O(20)-C(20)-C(28)	21.8(15)
O(20)-C(20)-C(21)-C(22)	27.4(7)	C(28)-C(20)-C(21)-C(22)	-152.9(4)
O(20)-C(20)-C(21)-C(26)	-148.4(5)	C(28)-C(20)-C(21)-C(26)	31.3(7)

Table 4. (continued)

C(26)-C(21)-C(22)-C(23)	-2.2(7)	C(20)-C(21)-C(22)-C(23)	-178.1(5)
C(21)-C(22)-C(23)-C(24)	1.6(8)	C(22)-C(23)-C(24)-C(25)	0.3(8)
C(22)-C(23)-C(24)-C(27)	178.6(5)	C(23)-C(24)-C(25)-C(26)	-1.5(8)
C(27)-C(24)-C(25)-C(26)	-179.9(5)	C(22)-C(21)-C(26)-C(25)	1.0(7)
C(20)-C(21)-C(26)-C(25)	176.9(5)	C(24)-C(25)-C(26)-C(21)	0.9(8)
O(20)-C(20)-C(28)-C(33)	34.2(7)	C(21)-C(20)-C(28)-C(33)	-145.5(5)
O(20)-C(20)-C(28)-C(29)	-143.2(5)	C(21)-C(20)-C(28)-C(29)	37.1(7)
C(33)-C(28)-C(29)-C(30)	0.4(8)	C(20)-C(28)-C(29)-C(30)	177.9(5)
C(28)-C(29)-C(30)-C(31)	1.0(9)	C(29)-C(30)-C(31)-C(32)	-0.4(9)
C(29)-C(30)-C(31)-C(34)	179.5(6)	C(30)-C(31)-C(32)-C(33)	-1.5(8)
C(34)-C(31)-C(32)-C(33)	178.5(5)	C(29)-C(28)-C(33)-C(32)	-2.3(7)
C(20)-C(28)-C(33)-C(32)	-179.8(4)	C(31)-C(32)-C(33)-C(28)	2.9(8)
O(1')-Ti(1')-O(20')-C(20')	-12.2(14)	Cℓ(3')-Ti(1')-O(20')-C(20')	-114.6(7)
Cℓ(1')-Ti(1')-O(20')-C(20')	132.7(7)	Cℓ(2')-Ti(1')-O(20')-C(20')	11.1(7)
Ti(1')-O(20')-C(20')-C(28')	136.4(6)	Ti(1')-O(20')-C(20')-C(21')	-44.9(9)
O(20')-C(20')-C(21')-C(26')	147.7(4)	C(28')-C(20')-C(21')-C(26')	-33.6(6)
O(20')-C(20')-C(21')-C(22')	-31.5(6)	C(28')-C(20')-C(21')-C(22')	147.1(4)
C(26')-C(21')-C(22')-C(23')	3.8(7)	C(20')-C(21')-C(22')-C(23')	-176.9(4)
C(21')-C(22')-C(23')-C(24')	-3.0(7)	C(22')-C(23')-C(24')-C(25')	0.8(8)
C(22')-C(23')-C(24')-C(27')	179.4(5)	C(23')-C(24')-C(25')-C(26')	0.5(9)
C(27')-C(24')-C(25')-C(26')	-178.2(6)	C(24')-C(25')-C(26')-C(21')	0.5(8)
C(22')-C(21')-C(26')-C(25')	-2.6(7)	C(20')-C(21')-C(26')-C(25')	178.1(4)
O(20')-C(20')-C(28')-C(33')	-23.2(6)	C(21')-C(20')-C(28')-C(33')	158.1(4)
O(20')-C(20')-C(28')-C(29')	151.0(4)	C(21')-C(20')-C(28')-C(29')	-27.7(6)
C(33')-C(28')-C(29')-C(30')	-0.5(6)	C(20')-C(28')-C(29')-C(30')	-174.8(4)
C(28')-C(29')-C(30')-C(31')	-1.3(7)	C(29')-C(30')-C(31')-C(32')	1.8(7)
C(29')-C(30')-C(31')-C(34')	179.1(4)	C(30')-C(31')-C(32')-C(33')	-0.6(7)
C(34')-C(31')-C(32')-C(33')	-177.8(5)	C(31')-C(32')-C(33')-C(28')	-1.2(7)
C(29')-C(28')-C(33')-C(32')	1.7(7)	C(20')-C(28')-C(33')-C(32')	176.0(4)

Table 5. Hydrogen coordinates and isotropic displacement parameters (Å^2 x 10^2) for $C_{51}H_{52}C\ell_6O_4Ti_2 \cdot CH_2C\ell_2$.

ATOM	X	Y	Z	U_{iso}
H(3)	0.2808	0.2858	0.9450	5.1
H(4)	0.1102	0.2446	0.9259	4.8
H(7A)	0.0344	0.3072	0.6782	4.2
H(7B)	0.0774	0.2377	0.6741	4.2
H(9A)	0.4541	0.4288	0.8517	9.2
H(9B)	0.3359	0.4286	0.8654	9.2
H(9C)	0.3575	0.4096	0.7929	9.2
H(10A)	0.5479	0.3258	0.8412	9.7
H(10B)	0.4538	0.3053	0.7814	9.7
H(10C)	0.4862	0.2625	0.8466	9.7
H(11A)	0.5149	0.3598	0.9500	9.8
H(11B)	0.4543	0.2965	0.9576	9.8
H(11C)	0.3978	0.3611	0.9655	9.8
H(3')	-0.2648	0.1937	0.8117	5.0
H(4')	-0.0978	0.2164	0.8768	4.9
H(9'1)	-0.2814	0.1359	0.6071	8.3
H(9'2)	-0.3999	0.1168	0.6112	8.3
H(9'3)	-0.3034	0.0950	0.6687	8.3
H(10D)	-0.3430	0.2509	0.5997	8.7
H(10E)	-0.4010	0.2771	0.6569	8.7
H(10F)	-0.4590	0.2272	0.6040	8.7
H(11D)	-0.3926	0.1409	0.7557	10.7
H(11E)	-0.4886	0.1615	0.6971	10.7
H(11F)	-0.4307	0.2113	0.7501	10.7
H(22)	0.0857	0.4290	0.4986	6.7
H(23)	-0.0635	0.4511	0.4151	6.9
H(25)	0.0959	0.4020	0.2707	7.4
H(26)	0.2489	0.3828	0.3527	6.7
H(27A)	-0.1586	0.4412	0.2992	9.7
H(27B)	-0.1009	0.4087	0.2453	9.7
H(27C)	-0.0877	0.4813	0.2586	9.7
H(29)	0.3613	0.4736	0.4142	7.6
H(30)	0.5326	0.4850	0.3979	8.3

Table 5. (continued)

H(32)	0.6208	0.3313	0.5080	7.5
H(33)	0.4497	0.3224	0.5301	6.4
H(34A)	0.7069	0.4404	0.3983	13.9
H(34B)	0.7386	0.3759	0.4352	13.9
H(34C)	0.7509	0.4385	0.4778	13.9
H(22')	0.1412	0.1617	0.5260	5.0
H(23')	0.2979	0.1122	0.5709	6.3
H(25')	0.1997	-0.0421	0.4629	7.5
H(26')	0.0434	0.0083	0.4138	6.1
H(27D)	0.3854	-0.0317	0.5188	14.0
H(27E)	0.3578	-0.0257	0.5922	14.0
H(27F)	0.4238	0.0275	0.5643	14.0
H(29')	0.0596	0.0826	0.3250	5.2
H(30')	-0.0238	0.0745	0.2115	6.0
H(32')	-0.3010	0.1311	0.2563	6.3
H(33')	-0.2196	0.1433	0.3693	5.6
H(34D)	-0.2984	0.0884	0.1446	10.4
H(34E)	-0.1909	0.0607	0.1285	10.4
H(34F)	-0.2107	0.1336	0.1253	10.4
H(40A)	0.2350	0.0309	0.7492	12.1
H(40B)	0.2457	0.0290	0.6718	12.1

Table 6. Anisotropic parameters (Å^2 x 10^2) for $C_{51}H_{52}C\ell_6O_4Ti_2\cdot CH_2C\ell_2$.

The anisotropic thermal parameters are the coefficients of the expression:

$$T = \exp[-2\pi^2(U_{11}a^{*2}h^2+...+ 2U_{12}a^*b^*hk+...)].$$

ATOM	U11	U22	U33	U23	U13	U12
Ti(1)	3.32(4)	4.39(4)	3.07(4)	0.13(3)	0.15(3)	-0.32(3)
Ti(1')	2.72(3)	4.74(4)	2.68(3)	-0.48(3)	-0.45(3)	0.26(3)
Cℓ(1)	5.51(6)	4.51(5)	4.52(6)	-0.52(4)	0.32(5)	-0.24(5)
Cℓ(2)	7.56(8)	6.38(7)	6.59(8)	1.30(6)	2.61(7)	2.66(6)
Cℓ(3)	4.80(6)	7.80(8)	5.18(7)	-0.28(6)	0.61(5)	-2.49(6)
Cℓ(1')	6.47(7)	5.06(5)	3.25(5)	-0.23(4)	0.75(5)	-0.90(5)
Cℓ(2')	5.27(6)	4.52(5)	4.02(5)	0.21(4)	0.20(4)	0.64(4)
Cℓ(3')	2.90(5)	15.22(14)	4.42(6)	-3.30(8)	-1.25(5)	1.24(7)
O(1)	3.02(13)	5.58(16)	3.04(14)	0.05(12)	-0.23(11)	-0.71(12)
C(1)	3.06(18)	4.39(19)	2.29(17)	-0.10(15)	-0.03(14)	-0.14(15)
C(2)	3.12(19)	4.9(2)	2.9(2)	-0.36(17)	-0.34(15)	0.22(16)
C(3)	3.9(2)	5.9(2)	2.35(19)	-0.28(18)	-0.64(16)	0.16(19)
C(4)	4.1(2)	5.2(2)	2.38(19)	-0.09(17)	-0.02(16)	-0.11(18)
C(5)	3.40(19)	4.05(19)	2.65(19)	-0.06(15)	0.17(15)	-0.02(16)
C(6)	3.18(18)	4.04(19)	2.31(18)	-0.24(15)	-0.36(15)	-0.28(15)
C(7)	2.85(18)	4.6(2)	2.80(19)	0.05(16)	-0.26(15)	-0.56(15)
C(8)	3.4(2)	7.7(3)	3.4(2)	-1.2(2)	-0.39(17)	-0.8(2)
C(9)	5.4(3)	7.8(3)	4.7(3)	-1.6(3)	-0.4(2)	-2.3(3)
C(10)	3.4(2)	11.5(5)	4.0(3)	-0.7(3)	-0.2(2)	0.9(3)
C(11)	3.8(2)	11.2(4)	3.9(3)	-1.5(3)	-0.8(2)	-1.0(3)
O(1')	2.68(12)	5.19(15)	2.88(14)	-0.24(12)	-0.39(10)	0.18(11)
C(1')	3.14(18)	3.98(18)	2.51(18)	-0.17(15)	0.01(15)	0.16(15)
C(2')	3.11(19)	4.4(2)	3.5(2)	-0.51(17)	0.19(16)	-0.10(16)
C(3')	3.5(2)	5.2(2)	3.8(2)	-0.22(18)	0.89(17)	-0.66(18)
C(4')	4.2(2)	5.2(2)	2.8(2)	-0.10(17)	0.65(17)	-0.62(18)
C(5')	3.52(19)	3.72(18)	2.67(19)	-0.27(15)	-0.03(15)	-0.14(15)
C(6')	2.98(18)	3.95(19)	2.74(19)	-0.13(15)	0.28(15)	-0.23(15)
C(8')	2.72(19)	6.3(3)	4.6(2)	-0.3(2)	0.35(18)	-0.44(19)
C(9')	3.9(2)	6.5(3)	5.7(3)	-1.2(2)	-0.2(2)	-1.2(2)
C(10')	3.4(2)	7.4(3)	6.3(3)	0.2(3)	-0.1(2)	1.1(2)

Table 6. (continued)

C(11')	3.7(2)	10.8(5)	6.9(4)	-1.3(3)	1.3(2)	-1.3(3)
O(20)	5.52(18)	6.41(19)	3.64(16)	1.09(15)	0.57(14)	0.67(15)
C(20)	5.8(3)	4.7(2)	3.2(2)	0.66(18)	0.39(19)	0.5(2)
C(21)	4.9(2)	4.7(2)	4.4(3)	0.65(19)	0.0(2)	-0.23(19)
C(22)	5.5(3)	6.0(3)	5.0(3)	0.9(2)	0.4(2)	0.5(2)
C(23)	4.5(2)	6.5(3)	5.6(3)	0.6(2)	-0.4(2)	0.4(2)
C(24)	5.1(3)	4.5(2)	5.2(3)	0.2(2)	-1.0(2)	-0.4(2)
C(25)	6.9(3)	7.2(3)	3.8(3)	0.4(2)	-0.5(2)	-0.2(3)
C(26)	5.7(3)	6.9(3)	3.9(2)	-0.1(2)	0.2(2)	0.5(2)
C(27)	5.9(3)	6.2(3)	6.0(3)	-0.1(3)	-2.0(2)	-0.5(2)
C(28)	5.1(2)	5.3(2)	3.0(2)	0.37(18)	0.02(18)	-0.1(2)
C(29)	6.0(3)	7.3(3)	5.2(3)	2.0(3)	-0.2(2)	-0.2(3)
C(30)	6.3(3)	8.7(4)	5.4(3)	2.2(3)	0.6(3)	-1.3(3)
C(31)	6.0(3)	9.2(4)	4.4(3)	0.4(3)	1.0(2)	-0.9(3)
C(32)	6.1(3)	8.0(3)	4.7(3)	0.6(3)	1.2(2)	1.1(3)
C(33)	5.7(3)	6.2(3)	4.0(2)	0.9(2)	0.8(2)	0.7(2)
C(34)	6.2(4)	14.0(6)	7.7(4)	0.9(4)	1.4(3)	-0.4(4)
O(20')	3.82(14)	4.93(15)	3.11(14)	-0.71(12)	-0.13(11)	0.63(12)
C(20')	3.5(2)	3.85(19)	3.3(2)	-0.30(16)	0.14(16)	-0.25(16)
C(21')	3.5(2)	4.2(2)	3.8(2)	-0.39(17)	0.22(17)	0.02(17)
C(22')	3.5(2)	4.6(2)	4.1(2)	-0.13(18)	-0.09(17)	-0.03(17)
C(23')	3.7(2)	5.8(3)	5.4(3)	0.0(2)	-1.0(2)	-0.2(2)
C(24')	4.2(2)	6.0(3)	7.0(3)	0.6(3)	-1.1(2)	0.8(2)
C(25')	5.2(3)	4.5(2)	8.3(4)	-0.4(2)	-0.7(3)	0.8(2)
C(26')	4.3(2)	4.1(2)	6.2(3)	-0.1(2)	-0.4(2)	0.41(18)
C(27')	6.0(3)	8.9(4)	11.6(6)	0.1(4)	-2.3(3)	2.4(3)
C(28')	3.9(2)	4.1(2)	3.1(2)	-0.54(16)	0.22(16)	-0.14(16)
C(29')	4.2(2)	4.6(2)	4.0(2)	-0.64(18)	0.50(18)	-0.02(18)
C(30')	6.1(3)	5.1(2)	3.8(2)	-0.99(19)	1.3(2)	-0.4(2)
C(31')	6.6(3)	4.6(2)	3.4(2)	-0.44(19)	-0.6(2)	-0.3(2)
C(32')	4.6(2)	6.3(3)	4.3(2)	-0.8(2)	-0.4(2)	0.2(2)
C(33')	3.5(2)	6.1(3)	4.0(2)	-0.7(2)	0.01(18)	0.50(19)
C(34')	8.7(4)	7.3(3)	3.9(3)	-0.5(2)	-1.2(3)	-0.3(3)
Cℓ(4)	14.1(2)	14.0(2)	13.4(2)	0.31(16)	-0.83(16)	3.66(17)
Cℓ(5)	12.59(16)	10.30(13)	11.02(15)	2.81(12)	4.36(13)	0.37(12)
C(40)	11.1(6)	8.4(5)	11.3(6)	0.5(4)	3.9(5)	1.1(4)

Table 7. Distances to the weighted least-squares planes for $C_{51}H_{52}C\ell_6O_4Ti_2 \cdot CH_2C\ell_2$.

Plane no. 1

*	-0.012 (0.003)	C(1)
*	0.022 (0.003)	C(2)
*	-0.012 (0.003)	C(3)
*	-0.010 (0.003)	C(4)
*	0.021 (0.003)	C(5)
*	-0.010 (0.003)	C(6)
	0.137 (0.007)	Ti(1)
	-0.006 (0.006)	O(1)
	0.131 (0.007)	C(8)

Rms deviation of fitted atoms = 0.015

Plane no. 2

*	-0.022 (0.002)	C(5)
*	0.020 (0.002)	C(6)
*	-0.011 (0.002)	C(7)
*	0.014 (0.002)	C(5')
*	-0.002 (0.002)	C(6')

Rms deviation of fitted atoms = 0.016

Angle to previous plane (with approximate esd) = 3.46 (0.18)

Plane no. 3

*	-0.010 (0.003)	C(1')
*	-0.005 (0.003)	C(2')
*	0.013 (0.003)	C(3')
*	-0.006 (0.003)	C(4')
*	-0.008 (0.003)	C(5')
*	0.016 (0.003)	C(6')
	-0.884 (0.007)	Ti(1')
	-0.040 (0.005)	O(1')
	-0.056 (0.007)	C(8')

Rms deviation of fitted atoms = 0.010

Angle to previous plane (with approximate esd) = 3.08 (0.16)

Table 7. (continued)

Plane no. 4

*	0.010 (0.003)	C(21)
*	-0.012 (0.003)	C(22)
*	0.003 (0.004)	C(23)
*	0.008 (0.003)	C(24)
*	-0.009 (0.004)	C(25)
*	0.001 (0.004)	C(26)
	-0.616 (0.008)	O(20)
	-0.048 (0.007)	C(20)
	-0.007 (0.008)	C(27)

Rms deviation of fitted atoms = 0.008

Plane no. 5

*	-0.006 (0.003)	C(28)
*	-0.005 (0.004)	C(29)
*	0.008 (0.004)	C(30)
*	0.001 (0.004)	C(31)
*	-0.012 (0.004)	C(32)
*	0.015 (0.003)	C(33)
	0.676 (0.008)	O(20)
	0.027 (0.008)	C(20)
	0.005 (0.010)	C(34)

Rms deviation of fitted atoms = 0.009

Angle to previous plane (with approximate esd) = 58.70 (0.17)

Plane no. 6

*	-0.017 (0.003)	C(21')
*	0.018 (0.003)	C(22')
*	-0.007 (0.004)	C(23')
*	-0.005 (0.004)	C(24')
*	0.006 (0.004)	C(25')
*	0.005 (0.004)	C(26')
	0.511 (0.008)	O(20')
	-0.058 (0.007)	C(20')
	-0.046 (0.010)	C(27)'

Rms deviation of fitted atoms = 0.011

Table 7. (continued)

Plane no. 7

*	-0.008	(0.003)	C(28')
*	-0.002	(0.003)	C(29')
*	0.011	(0.003)	C(30')
*	-0.008	(0.003)	C(31')
*	-0.002	(0.003)	C(32')
*	0.010	(0.003)	C(33')
	0.629	(0.007)	O(20')
	0.091	(0.006)	C(20')
	0.027	(0.008)	C(34')

Rms deviation of fitted atoms = 0.008

Angle to previous plane (with approximate esd) = 52.78 (0.18)

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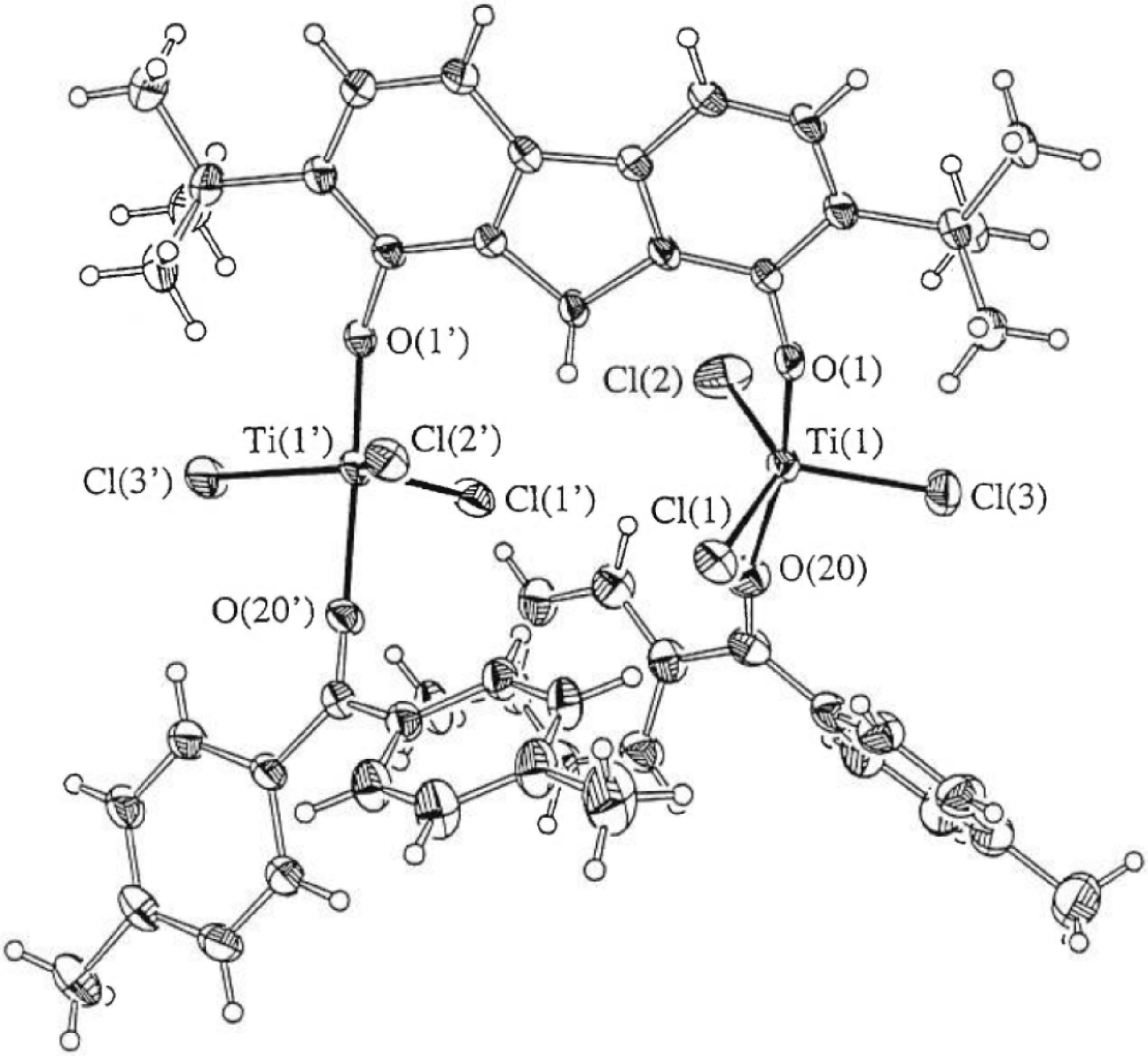
* indicates atoms used to define plane



ORTEP view of $C_{51}H_{52}C\ell_6O_4Ti_2 \cdot CH_2C\ell_2$

with the numbering scheme adopted. Ellipsoids drawn at

40% probality level. Hydrogens represented by sphere of arbitrary size.

Discussion of structure determination and refinement procedure

A crystal of the compound was attached to a glass fiber and transferred rapidly under a cold stream of nitrogen to a Nonius CAD-4 system equipped with a low temperature gas-stream cryostat for data collection at 210(2)K.

The structure was solved by direct methods using SHELXS96 (Sheldrick, 1990) and difmap synthesis using NRCVAX (Gabe et al, 1989) and SHELXL96 (Sheldrick, 1996).

All non-hydrogen atoms are treated as anisotropic, hydrogen atoms isotropic. Hydrogen atoms were placed in ideal positions and refined as riding atoms with different C-H distances for different types of carbon hydrogen. The isotropic displacement factors, U_{iso}, were adjusted to 50% (methyl) and 20% (others) higher value of the bonded carbon atom. The hydrogen atoms of the methyl groups directly attached to the phenyl rings were located from a difference circular Fourier map, and were allowed to refine by their torsion angles.

A small hole remained in this structure accounting for 12.8 electrons and 58.6Å^3 of the volume of the cell.

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Molecular graphic

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CRYSTAL AND MOLECULAR STRUCTURE OF

$(C_{58}H_{88}A\ell_4O_4)_{0.88}(C_{58}H_{87}A\ell_4O_4Br)_{0.12}$ (JIW145)

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Structure résolue au laboratoire de diffraction des rayons X de l'Université de Montréal par Michel Simard.

Table 1. Crystal data and structure refinement for $(C_{58}H_{88}A\ell_4O_4)_{0.88}(C_{58}H_{87}A\ell_4\text{-}O_4Br)_{0.12}$.

Crystal data

Crystal source	....	
Chemical formula, sum	C58 H87.88 Aℓ4 Br0.12 O4	
Chemical formula, moiety	$(C_{58}H_{88}A\ell_4O_4)_{0.88}(C_{58}H_{87}A\ell_4O_4Br)_{0.12}$	
Chemical formula weight, M_r	966.672	
Cell setting	Triclinic	
Space group	P -1	
Unit cell dimensions (Å, °)	a = 12.330(5)	alpha = 73.95(3)
	b = 14.588(3)	beta = 84.88(4)
	c = 16.638(9)	gamma = 79.97(2)
Volume of unit cell, V (Å^3)	2829(2)	
Formula units per cell, Z	2	
Density calculated from formula and cell, D_x (Mg/m^3)	1.1347	
Density from independent measurements, D_m (Mg/m^3)	not measured	
Measurement method, by flottation in	none	
F(000)	1048.2	
Radiation type	CuKα	
Wavelength, λ (Å)	1.54056	
No. of reflections for cell measurement	25	

Table 1. (continued)

θ range (°)	20.00 to 21.00
Linear absorption coefficient, μ (mm^{-1})	1.186
Measurement temperature (K)	225(2)
Crystal shape	block
Colour	colourless
Size (mm)	0.58 x 0.46 x 0.38
Data collection	
Diffractometer type	Nonius CAD-4
Data-collection method	$\omega/2\theta$ scan
Absorption correction type	Integration
Maximum and minimum transmission values, T_{max} and T_{min}	0.80 and 0.52
No. of reflections measured	45681
No. of independent reflections	10709
No. of observed reflections	8609
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.072
Minimum and maximum values of θ (°)	2.76 to 69.81
Ranges of h,k,ℓ	$-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-20 \leq \ell \leq 20$

Table 1. (continued)

No. of standard reflections	5
Interval, time (min)	60
Intensity decay (%)	4.0

Refinement

Refinement method	Full-matrix on F^2
Final R indices, $I>2\sigma(I)$	$R1 = 0.0581$, $wR2 = 0.1662$
R indices, all data	$R1 = 0.0680$, $wR2 = 0.1733$
Goodness-of-fit on F^2, S	1.031

$R1 = \Sigma(||Fo| - |Fc||)/\Sigma(|Fo|)$,
$wR2 = [\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]]^{1/2}$ and
$GoF = [\Sigma[w(Fo^2-Fc^2)^2]/(\text{No. of reflns - No. of params.})]^{1/2}$

No. of reflections used in refinement	10709
No. of parameters refined	693
No. of restraints	12
Method of refining and locating H atoms	see text
Weighting scheme	based on measured e.s.d's
Function minimized	$\Sigma w(Fo^2-Fc^2)$

$w=1/[\sigma^2(Fo^2)+(0.1266P)^2]$ where $P=(Fo^2+2Fc^2)/3$

Maximum Δ/σ	0.013
$\Delta\rho_{max}$ (e/Å^3)	0.686

Table 1. (continued)

$\Delta\rho_{min}$ (e/Å^3)	-0.407
Extinction correction method	none
Source of atomic scattering factors	International Tables for Crystallography (1992)

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($\AA^2 \times 10^2$) for $(C_{58}H_{88}A\ell_4O_4)_{0.88}(C_{58}H_{87}A\ell_4O_4Br)_{0.12}$.

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a^*_ia^*_ja_i \cdot a_j$$

ATOM	X	Y	Z	U_{eq}
Br(1)[a]	0.5775(11)	-0.1609(9)	0.4922(8)	8.0(3)
Br(2)[b]	0.6806(10)	-0.1282(7)	0.5871(6)	6.3(2)
Br(3)[c]	0.883(3)	0.635(3)	-0.092(2)	7.4(9)
Br(4)[d]	0.8750(6)	0.7124(4)	-0.0016(4)	6.58(16)
Aℓ(1)	0.76430(5)	0.12765(4)	0.10168(4)	3.353(15)
Aℓ(2)	0.93635(5)	0.32094(5)	0.35599(4)	3.811(16)
Aℓ(3)	0.56816(5)	0.26540(5)	0.10116(4)	3.728(16)
Aℓ(4)	0.71544(6)	0.36731(5)	0.41973(4)	4.123(17)
O(11)	0.62909(11)	0.14163(10)	0.16400(8)	3.43(3)
C(11)	0.60423(17)	0.07969(15)	0.24292(13)	3.51(4)
C(12)	0.53292(19)	0.00995(17)	0.25239(14)	4.32(5)
C(13)	0.5290(2)	-0.05667(19)	0.33100(16)	5.47(6)
C(14)	0.5845(2)	-0.05543(19)	0.39846(15)	5.28(6)
C(15)	0.64524(18)	0.01816(15)	0.38971(13)	3.89(5)
C(16)	0.65410(16)	0.08666(14)	0.31245(12)	3.39(4)
C(17)	0.71923(17)	0.16167(15)	0.32228(12)	3.39(4)
C(18)[e]	0.4453(4)	0.0139(4)	0.1922(3)	4.85(10)
C(19)[e]	0.4914(5)	0.0227(4)	0.1020(3)	5.95(13)
C(110)[e]	0.3571(3)	0.1012(3)	0.1943(2)	6.70(12)
C(111)[e]	0.3881(5)	-0.0747(4)	0.2174(3)	7.99(16)
C(112)	0.7587(2)	0.03864(16)	0.03314(15)	4.64(5)
C(113)	0.7799(3)	-0.0668(2)	0.0852(2)	7.85(9)
C(114)	0.90159(19)	0.1041(2)	0.15830(15)	5.06(6)
C(115)	1.0061(2)	0.0673(3)	0.1124(2)	7.58(9)
C(116)[f]	0.4647(15)	-0.0060(14)	0.1782(12)	4.85(10)
C(117)[f]	0.5076(13)	-0.1031(9)	0.1576(11)	8.5(5)
C(118)[f]	0.3476(12)	-0.0071(18)	0.2177(11)	9.5(7)
C(119)[f]	0.4535(18)	0.0700(15)	0.0961(12)	9.0(8)
O(21)	0.82810(12)	0.26007(10)	0.42597(9)	3.73(3)
C(21)	0.80779(17)	0.16466(15)	0.46082(12)	3.57(4)
C(22)	0.84046(19)	0.11074(16)	0.54148(13)	4.04(5)

Table 2. (continued)

C(23)	0.7951(2)	0.02524(17)	0.57575(13)	4.53(5)
C(24)	0.7265(2)	-0.00871(17)	0.53352(14)	4.67(5)
C(25)	0.70655(18)	0.04043(16)	0.45128(13)	3.84(5)
C(26)	0.74802(17)	0.12635(15)	0.41404(12)	3.46(4)
C(28)[g]	0.9335(10)	0.1269(7)	0.5920(7)	4.31(9)
C(29)[g]	0.9982(5)	0.2079(4)	0.5457(3)	7.31(19)
C(210)[g]	0.8837(5)	0.1446(6)	0.6749(4)	8.0(2)
C(211)[g]	1.0200(4)	0.0363(4)	0.6127(3)	6.48(14)
C(212)	1.0462(2)	0.3845(2)	0.3896(2)	6.65(8)
C(213)	1.1667(3)	0.3358(3)	0.3917(3)	9.79(13)
C(214)	1.00856(19)	0.23518(18)	0.28882(14)	4.49(5)
C(215)	1.0702(2)	0.2787(3)	0.20703(18)	6.70(8)
C(216)[h]	0.9207(15)	0.1349(10)	0.5926(10)	4.31(9)
C(217)[h]	0.9013(7)	0.2386(5)	0.6006(4)	6.4(2)
C(218)[h]	0.9290(9)	0.0677(8)	0.6808(5)	8.8(3)
C(219)[h]	1.0301(6)	0.1181(7)	0.5446(6)	7.8(3)
O(31)	0.71638(11)	0.25918(9)	0.05708(8)	3.22(3)
C(31)	0.77078(16)	0.33974(14)	0.02044(12)	3.18(4)
C(32)	0.80006(19)	0.36769(16)	-0.06612(13)	3.89(5)
C(33)	0.8406(2)	0.45554(18)	-0.09565(14)	5.04(6)
C(34)	0.8529(2)	0.51385(18)	-0.04545(15)	5.07(6)
C(35)	0.82875(18)	0.48261(15)	0.03859(13)	3.82(4)
C(36)	0.79159(16)	0.39368(14)	0.07312(12)	3.24(4)
C(37)	0.78289(17)	0.37363(14)	0.16777(12)	3.32(4)
C(38)	0.8049(2)	0.30569(17)	-0.12807(14)	4.57(5)
C(39)	0.9017(2)	0.22336(19)	-0.10360(19)	6.04(7)
C(310)	0.6988(2)	0.2645(2)	-0.12797(17)	5.99(7)
C(311)	0.8295(3)	0.3624(2)	-0.21861(16)	7.52(10)
C(312)	0.4718(2)	0.2808(2)	0.00924(17)	5.90(7)
C(313)	0.4582(3)	0.3879(3)	-0.0438(2)	8.26(10)
C(314)	0.5091(2)	0.3479(2)	0.17432(17)	5.36(6)
C(315)	0.3864(3)	0.3600(4)	0.1911(3)	12.7(2)
O(41)	0.81050(12)	0.41843(10)	0.33096(8)	3.59(3)
C(41)	0.81164(17)	0.49219(14)	0.25556(12)	3.45(4)
C(42)	0.81649(18)	0.58961(15)	0.25231(14)	3.93(5)
C(43)	0.8383(2)	0.65031(16)	0.17331(15)	4.66(5)
C(44)	0.8512(2)	0.62145(17)	0.10034(15)	4.71(5)
C(45)	0.83444(18)	0.52850(15)	0.10522(13)	3.78(4)
C(46)	0.81157(16)	0.46506(14)	0.18184(13)	3.34(4)
C(48)	0.7877(2)	0.63397(17)	0.32714(16)	4.87(6)

Table 2. (continued)

C(49)	0.8614(3)	0.5860(2)	0.39986(17)	6.10(7)
C(410)	0.6660(3)	0.6270(2)	0.3523(2)	6.75(8)
C(411)	0.7963(3)	0.74251(19)	0.30290(19)	6.72(8)
C(412)	0.7120(3)	0.4054(3)	0.52474(18)	7.76(10)
C(413)	0.6329(4)	0.3572(4)	0.5899(2)	12.59(19)
C(414)	0.5682(2)	0.3679(2)	0.38578(18)	5.82(6)
C(415)	0.5015(3)	0.2885(3)	0.4287(3)	8.75(11)

a: Occ. = 0.03
b: Occ. = 0.03
c: Occ. = 0.01
d: Occ. = 0.05
e: Occ. = 0.768(6)
f: Occ. = 0.232(6)
g: Occ. = 0.591(5)
h: Occ. = 0.409(5)

Table 3. Bond lengths (Å) and angles (°) for $(C_{58}H_{88}A\ell_4O_4)_{0.88}(C_{58}H_{87}A\ell_4O_4Br)_{0.12}$.

Br(1)-C(14)	1.872(12)	Br(2)-C(24)	1.883(9)
Br(3)-C(34)	1.81(3)	Br(4)-C(44)	1.878(6)
Aℓ(1)-Aℓ(3)	2.8615(13)	Aℓ(2)-Aℓ(4)	2.8708(16)
Aℓ(1)-O(31)	1.8648(16)	Aℓ(2)-O(21)	1.8680(18)
Aℓ(1)-O(11)	1.8937(17)	Aℓ(2)-O(41)	1.9034(17)
Aℓ(1)-C(114)	1.943(3)	Aℓ(2)-C(214)	1.953(2)
Aℓ(1)-C(112)	1.963(2)	Aℓ(2)-C(212)	1.966(3)
Aℓ(3)-O(11)	1.8819(17)	Aℓ(4)-O(41)	1.8702(18)
Aℓ(3)-O(31)	1.9042(17)	Aℓ(4)-O(21)	1.8886(18)
Aℓ(3)-C(314)	1.951(3)	Aℓ(4)-C(414)	1.947(3)
Aℓ(3)-C(312)	1.960(3)	Aℓ(4)-C(412)	1.969(3)
O(11)-C(11)	1.415(2)	O(21)-C(21)	1.409(2)
C(11)-C(16)	1.393(3)	C(21)-C(26)	1.396(3)
C(11)-C(12)	1.425(3)	C(21)-C(22)	1.409(3)
C(12)-C(13)	1.400(3)	C(22)-C(23)	1.409(3)
C(12)-C(18)	1.521(6)	C(22)-C(28)	1.567(15)
C(12)-C(116)	1.642(19)	C(22)-C(216)	1.50(2)
C(13)-C(14)	1.371(4)	C(23)-C(24)	1.378(3)
C(14)-C(15)	1.382(3)	C(24)-C(25)	1.380(3)
C(15)-C(16)	1.402(3)	C(25)-C(26)	1.398(3)
C(15)-C(25)	1.461(3)		
C(16)-C(17)	1.516(3)	C(17)-C(26)	1.523(3)
C(18)-C(111)	1.519(6)	C(28)-C(211)	1.525(10)
C(18)-C(110)	1.530(6)	C(28)-C(210)	1.528(10)
C(18)-C(19)	1.536(6)	C(28)-C(29)	1.530(10)
C(112)-C(113)	1.533(4)	C(212)-C(213)	1.529(5)
C(114)-C(115)	1.531(3)	C(214)-C(215)	1.529(3)
C(116)-C(119)	1.502(19)	C(216)-C(219)	1.522(14)
C(116)-C(118)	1.532(17)	C(216)-C(218)	1.524(14)
C(116)-C(117)	1.543(16)	C(216)-C(217)	1.530(14)
O(31)-C(31)	1.417(2)	O(41)-C(41)	1.410(2)
C(31)-C(36)	1.395(3)	C(41)-C(46)	1.389(3)
C(31)-C(32)	1.416(3)	C(41)-C(42)	1.419(3)

Table 3. (continued)

C(32)-C(33)	1.402(3)	C(42)-C(43)	1.400(3)
C(32)-C(38)	1.539(3)	C(42)-C(48)	1.543(3)
C(33)-C(34)	1.380(3)	C(43)-C(44)	1.379(3)
C(34)-C(35)	1.368(3)	C(44)-C(45)	1.386(3)
C(35)-C(36)	1.404(3)	C(45)-C(46)	1.391(3)
C(35)-C(45)	1.457(3)		
C(36)-C(37)	1.517(3)	C(37)-C(46)	1.520(3)
C(38)-C(310)	1.531(3)	C(48)-C(49)	1.512(4)
C(38)-C(39)	1.533(4)	C(48)-C(410)	1.535(4)
C(38)-C(311)	1.537(3)	C(48)-C(411)	1.543(3)
C(312)-C(313)	1.556(4)	C(412)-C(413)	1.500(5)
C(314)-C(315)	1.502(4)	C(414)-C(415)	1.516(4)
O(31)-Aℓ(1)-O(11)	80.34(7)	O(21)-Aℓ(2)-O(41)	78.95(7)
O(31)-Aℓ(1)-C(114)	111.84(10)	O(21)-Aℓ(2)-C(214)	108.02(9)
O(11)-Aℓ(1)-C(114)	119.01(9)	O(41)-Aℓ(2)-C(214)	128.43(9)
O(31)-Aℓ(1)-C(112)	118.87(9)	O(21)-Aℓ(2)-C(212)	126.21(12)
O(11)-Aℓ(1)-C(112)	109.33(9)	O(41)-Aℓ(2)-C(212)	104.64(11)
C(114)-Aℓ(1)-C(112)	113.69(11)	C(214)-Aℓ(2)-C(212)	109.79(12)
O(31)-Aℓ(1)-Aℓ(3)	41.12(5)	O(21)-Aℓ(2)-Aℓ(4)	40.43(5)
O(11)-Aℓ(1)-Aℓ(3)	40.57(5)	O(41)-Aℓ(2)-Aℓ(4)	40.04(5)
C(114)-Aℓ(1)-Aℓ(3)	132.20(8)	C(214)-Aℓ(2)-Aℓ(4)	135.20(8)
C(112)-Aℓ(1)-Aℓ(3)	114.10(9)	C(212)-Aℓ(2)-Aℓ(4)	114.95(10)
O(11)-Aℓ(3)-O(31)	79.64(7)	O(41)-Aℓ(4)-O(21)	79.27(7)
O(11)-Aℓ(3)-C(314)	110.85(10)	O(41)-Aℓ(4)-C(414)	113.66(11)
O(31)-Aℓ(3)-C(314)	121.94(10)	O(21)-Aℓ(4)-C(414)	121.84(10)
O(11)-Aℓ(3)-C(312)	120.62(11)	O(41)-Aℓ(4)-C(412)	119.02(11)
O(31)-Aℓ(3)-C(312)	108.07(11)	O(21)-Aℓ(4)-C(412)	107.60(14)
C(314)-Aℓ(3)-C(312)	112.57(12)	C(414)-Aℓ(4)-C(412)	112.12(15)
O(11)-Aℓ(3)-Aℓ(1)	40.88(5)	O(41)-Aℓ(4)-Aℓ(2)	40.90(5)
O(31)-Aℓ(3)-Aℓ(1)	40.09(5)	O(21)-Aℓ(4)-Aℓ(2)	39.90(5)
C(314)-Aℓ(3)-Aℓ(1)	133.14(8)	C(414)-Aℓ(4)-Aℓ(2)	135.65(9)
C(312)-Aℓ(3)-Aℓ(1)	114.29(10)	C(412)-Aℓ(4)-Aℓ(2)	112.22(12)
C(11)-O(11)-Aℓ(3)	135.36(13)	C(21)-O(21)-Aℓ(2)	136.91(13)
C(11)-O(11)-Aℓ(1)	124.84(13)	C(21)-O(21)-Aℓ(4)	121.74(13)
Aℓ(3)-O(11)-Aℓ(1)	98.56(7)	Aℓ(2)-O(21)-Aℓ(4)	99.67(8)
C(16)-C(11)-O(11)	117.97(17)	C(26)-C(21)-C(22)	120.39(19)
C(16)-C(11)-C(12)	119.89(19)	C(26)-C(21)-O(21)	117.34(18)

Table 3. (continued)

O(11)-C(11)-C(12)	122.12(18)	C(22)-C(21)-O(21)	122.18(18)
C(13)-C(12)-C(11)	116.2(2)	C(21)-C(22)-C(23)	116.2(2)
C(13)-C(12)-C(18)	116.9(3)	C(21)-C(22)-C(216)	126.0(5)
C(11)-C(12)-C(18)	125.6(3)	C(23)-C(22)-C(216)	117.8(5)
C(13)-C(12)-C(116)	117.1(7)	C(21)-C(22)-C(28)	127.3(4)
C(11)-C(12)-C(116)	126.4(7)	C(23)-C(22)-C(28)	115.9(4)
C(14)-C(13)-C(12)	124.3(2)	C(24)-C(23)-C(22)	123.7(2)
C(13)-C(14)-C(15)	118.3(2)	C(23)-C(24)-C(25)	118.2(2)
C(13)-C(14)-Br(1)	115.3(4)	C(23)-C(24)-Br(2)	117.7(3)
C(15)-C(14)-Br(1)	126.3(4)	C(25)-C(24)-Br(2)	123.7(3)
C(14)-C(15)-C(16)	120.5(2)	C(24)-C(25)-C(26)	120.7(2)
C(14)-C(15)-C(25)	130.1(2)	C(24)-C(25)-C(15)	130.5(2)
C(16)-C(15)-C(25)	109.42(18)	C(26)-C(25)-C(15)	108.78(18)
C(11)-C(16)-C(15)	120.28(19)	C(21)-C(26)-C(25)	119.97(19)
C(11)-C(16)-C(17)	130.53(18)	C(21)-C(26)-C(17)	130.50(18)
C(15)-C(16)-C(17)	109.16(18)	C(25)-C(26)-C(17)	109.51(18)
C(16)-C(17)-C(26)	103.01(16)		
C(111)-C(18)-C(12)	112.6(4)	C(211)-C(28)-C(210)	107.4(8)
C(111)-C(18)-C(110)	107.1(4)	C(211)-C(28)-C(29)	104.8(8)
C(12)-C(18)-C(110)	107.6(3)	C(210)-C(28)-C(29)	110.0(8)
C(111)-C(18)-C(19)	106.8(4)	C(211)-C(28)-C(22)	109.9(7)
C(12)-C(18)-C(19)	113.0(4)	C(210)-C(28)-C(22)	109.2(7)
C(110)-C(18)-C(19)	109.5(4)	C(29)-C(28)-C(22)	115.2(7)
C(119)-C(116)-C(118)	105.6(16)	C(22)-C(216)-C(219)	102.8(10)
C(119)-C(116)-C(117)	106.8(15)	C(22)-C(216)-C(218)	112.8(11)
C(118)-C(116)-C(117)	109.5(15)	C(219)-C(216)-C(218)	108.7(12)
C(119)-C(116)-C(12)	119.5(15)	C(22)-C(216)-C(217)	116.2(11)
C(118)-C(116)-C(12)	102.5(11)	C(219)-C(216)-C(217)	108.6(11)
C(117)-C(116)-C(12)	112.4(13)	C(218)-C(216)-C(217)	107.4(11)
C(113)-C(112)-Aℓ(1)	111.3(2)	C(213)-C(212)-Aℓ(2)	118.2(2)
C(115)-C(114)-Aℓ(1)	116.69(19)	C(215)-C(214)-Aℓ(2)	118.56(19)
C(31)-O(31)-Aℓ(1)	134.06(12)	C(41)-O(41)-Aℓ(4)	141.45(13)
C(31)-O(31)-Aℓ(3)	125.41(12)	C(41)-O(41)-Aℓ(2)	118.97(13)
Aℓ(1)-O(31)-Aℓ(3)	98.79(7)	Aℓ(4)-O(41)-Aℓ(2)	99.06(8)
C(36)-C(31)-C(32)	120.45(18)	C(46)-C(41)-O(41)	116.79(17)
C(36)-C(31)-O(31)	117.01(17)	C(46)-C(41)-C(42)	119.92(19)
C(32)-C(31)-O(31)	122.51(17)	O(41)-C(41)-C(42)	123.26(18)
C(33)-C(32)-C(31)	116.35(19)	C(43)-C(42)-C(41)	116.40(19)
C(33)-C(32)-C(38)	116.99(19)	C(43)-C(42)-C(48)	118.8(2)

Table 3. (continued)

C(31)-C(32)-C(38)	126.22(19)	C(41)-C(42)-C(48)	124.4(2)
C(34)-C(33)-C(32)	123.8(2)	C(44)-C(43)-C(42)	124.0(2)
C(35)-C(34)-C(33)	118.4(2)	C(43)-C(44)-C(45)	117.6(2)
C(35)-C(34)-Br(3)	120.9(11)	C(43)-C(44)-Br(4)	119.1(2)
C(33)-C(34)-Br(3)	120.2(11)	C(45)-C(44)-Br(4)	123.0(2)
C(34)-C(35)-C(36)	121.0(2)	C(44)-C(45)-C(46)	121.0(2)
C(34)-C(35)-C(45)	130.0(2)	C(44)-C(45)-C(35)	129.8(2)
C(36)-C(35)-C(45)	108.99(18)	C(46)-C(45)-C(35)	109.07(18)
C(31)-C(36)-C(35)	119.61(18)	C(41)-C(46)-C(45)	120.21(18)
C(31)-C(36)-C(37)	131.21(18)	C(41)-C(46)-C(37)	129.97(18)
C(35)-C(36)-C(37)	109.18(17)	C(45)-C(46)-C(37)	109.72(17)
C(36)-C(37)-C(46)	102.69(16)		
C(310)-C(38)-C(39)	110.0(2)	C(49)-C(48)-C(410)	111.8(2)
C(310)-C(38)-C(311)	107.0(2)	C(49)-C(48)-C(411)	106.8(2)
C(39)-C(38)-C(311)	107.1(2)	C(410)-C(48)-C(411)	106.0(2)
C(310)-C(38)-C(32)	113.9(2)	C(49)-C(48)-C(42)	113.1(2)
C(39)-C(38)-C(32)	106.5(2)	C(410)-C(48)-C(42)	106.8(2)
C(311)-C(38)-C(32)	112.1(2)	C(411)-C(48)-C(42)	112.1(2)
C(313)-C(312)-Aℓ(3)	108.6(2)	C(413)-C(412)-Aℓ(4)	112.4(3)
C(315)-C(314)-Aℓ(3)	115.9(2)	C(415)-C(414)-Aℓ(4)	121.8(2)

Table 4. Torsion angles (°) for $(C_{58}H_{88}A\ell_4O_4)_{0.88}(C_{58}H_{87}A\ell_4O_4Br)_{0.12}$.

O(31)-Aℓ(1)-Aℓ(3)-O(11)	-161.01(10)	C(114)-Aℓ(1)-Aℓ(3)-O(11)	-86.99(14)
C(112)-Aℓ(1)-Aℓ(3)-O(11)	92.02(11)	O(11)-Aℓ(1)-Aℓ(3)-O(31)	161.01(10)
C(114)-Aℓ(1)-Aℓ(3)-O(31)	74.03(13)	C(112)-Aℓ(1)-Aℓ(3)-O(31)	-106.97(11)
O(31)-Aℓ(1)-Aℓ(3)-C(314)	-90.72(14)	O(11)-Aℓ(1)-Aℓ(3)-C(314)	70.29(14)
C(114)-Aℓ(1)-Aℓ(3)-C(314)	-16.70(17)	C(112)-Aℓ(1)-Aℓ(3)-C(314)	162.31(14)
O(31)-Aℓ(1)-Aℓ(3)-C(312)	89.57(12)	O(11)-Aℓ(1)-Aℓ(3)-C(312)	-109.42(12)
C(114)-Aℓ(1)-Aℓ(3)-C(312)	163.59(15)	C(112)-Aℓ(1)-Aℓ(3)-C(312)	-17.40(13)
O(21)-Aℓ(2)-Aℓ(4)-O(41)	-159.62(10)	C(214)-Aℓ(2)-Aℓ(4)-O(41)	-99.95(13)
C(212)-Aℓ(2)-Aℓ(4)-O(41)	83.08(14)	O(41)-Aℓ(2)-Aℓ(4)-O(21)	159.62(10)
C(214)-Aℓ(2)-Aℓ(4)-O(21)	59.67(13)	C(212)-Aℓ(2)-Aℓ(4)-O(21)	-117.30(14)
O(21)-Aℓ(2)-Aℓ(4)-C(414)	-87.31(15)	O(41)-Aℓ(2)-Aℓ(4)-C(414)	72.31(15)
C(214)-Aℓ(2)-Aℓ(4)-C(414)	-27.64(17)	C(212)-Aℓ(2)-Aℓ(4)-C(414)	155.39(17)
O(21)-Aℓ(2)-Aℓ(4)-C(412)	91.19(14)	O(41)-Aℓ(2)-Aℓ(4)-C(412)	-109.20(14)
C(214)-Aℓ(2)-Aℓ(4)-C(412)	150.85(15)	C(212)-Aℓ(2)-Aℓ(4)-C(412)	-26.11(17)
O(31)-Aℓ(3)-O(11)-C(11)	154.72(18)	C(314)-Aℓ(3)-O(11)-C(11)	34.3(2)
C(312)-Aℓ(3)-O(11)-C(11)	-100.3(2)	Aℓ(1)-Aℓ(3)-O(11)-C(11)	167.0(2)
O(31)-Aℓ(3)-O(11)-Aℓ(1)	-12.30(6)	C(314)-Aℓ(3)-O(11)-Aℓ(1)	-132.68(10)
C(312)-Aℓ(3)-O(11)-Aℓ(1)	92.67(12)	O(31)-Aℓ(1)-O(11)-C(11)	-156.37(15)
C(114)-Aℓ(1)-O(11)-C(11)	-46.68(18)	C(112)-Aℓ(1)-O(11)-C(11)	86.29(16)
Aℓ(3)-Aℓ(1)-O(11)-C(11)	-168.91(17)	O(31)-Aℓ(1)-O(11)-Aℓ(3)	12.53(6)
C(114)-Aℓ(1)-O(11)-Aℓ(3)	122.23(11)	C(112)-Aℓ(1)-O(11)-Aℓ(3)	-104.80(10)
Aℓ(3)-O(11)-C(11)-C(16)	-90.7(2)	Aℓ(1)-O(11)-C(11)-C(16)	73.6(2)
Aℓ(3)-O(11)-C(11)-C(12)	90.9(2)	Aℓ(1)-O(11)-C(11)-C(12)	-104.8(2)
C(16)-C(11)-C(12)-C(13)	-8.1(3)	O(11)-C(11)-C(12)-C(13)	170.2(2)
C(16)-C(11)-C(12)-C(18)	158.7(3)	O(11)-C(11)-C(12)-C(18)	-22.9(4)
C(16)-C(11)-C(12)-C(116)	178.0(7)	O(11)-C(11)-C(12)-C(116)	-3.6(7)
C(11)-C(12)-C(13)-C(14)	3.2(4)	C(18)-C(12)-C(13)-C(14)	-164.9(3)
C(116)-C(12)-C(13)-C(14)	177.6(6)	C(12)-C(13)-C(14)-C(15)	2.4(4)
C(12)-C(13)-C(14)-Br(1)	-173.3(5)	C(13)-C(14)-C(15)-C(16)	-3.2(4)
Br(1)-C(14)-C(15)-C(16)	172.1(6)	C(13)-C(14)-C(15)-C(25)	176.2(3)
Br(1)-C(14)-C(15)-C(25)	-8.5(7)	O(11)-C(11)-C(16)-C(15)	-170.75(18)
C(12)-C(11)-C(16)-C(15)	7.7(3)	O(11)-C(11)-C(16)-C(17)	11.2(3)
C(12)-C(11)-C(16)-C(17)	-170.4(2)	C(14)-C(15)-C(16)-C(11)	-1.8(3)
C(25)-C(15)-C(16)-C(11)	178.68(19)	C(14)-C(15)-C(16)-C(17)	176.6(2)
C(25)-C(15)-C(16)-C(17)	-2.9(2)	C(11)-C(16)-C(17)-C(26)	179.3(2)
C(15)-C(16)-C(17)-C(26)	1.0(2)	C(13)-C(12)-C(18)-C(111)	-16.8(5)
C(11)-C(12)-C(18)-C(111)	176.4(3)	C(13)-C(12)-C(18)-C(110)	101.0(4)
C(11)-C(12)-C(18)-C(110)	-65.8(4)	C(13)-C(12)-C(18)-C(19)	-137.9(4)

Table 4. (continued)

C(11)-C(12)-C(18)-C(19)	55.3(5)	C(13)-C(12)-C(116)-C(119)	172.1(13)
C(11)-C(12)-C(116)-C(119)	-14.1(18)	C(13)-C(12)-C(116)-C(118)	55.8(14)
C(11)-C(12)-C(116)-C(118)	-130.4(12)	C(13)-C(12)-C(116)-C(117)	-61.6(13)
C(11)-C(12)-C(116)-C(117)	112.2(13)	O(31)-Aℓ(1)-C(112)-C(113)	-169.15(19)
O(11)-Aℓ(1)-C(112)-C(113)	-79.7(2)	C(114)-Aℓ(1)-C(112)-C(113)	56.0(2)
Aℓ(3)-Aℓ(1)-C(112)-C(113)	-123.2(2)	O(31)-Aℓ(1)-C(114)-C(115)	-104.8(2)
O(11)-Aℓ(1)-C(114)-C(115)	164.3(2)	C(112)-Aℓ(1)-C(114)-C(115)	33.3(3)
Aℓ(3)-Aℓ(1)-C(114)-C(115)	-147.7(2)	O(41)-Aℓ(2)-O(21)-C(21)	151.21(19)
C(214)-Aℓ(2)-O(21)-C(21)	24.2(2)	C(212)-Aℓ(2)-O(21)-C(21)	-108.6(2)
Aℓ(4)-Aℓ(2)-O(21)-C(21)	164.4(2)	O(41)-Aℓ(2)-O(21)-Aℓ(4)	-13.20(6)
C(214)-Aℓ(2)-O(21)-Aℓ(4)	-140.24(9)	C(212)-Aℓ(2)-O(21)-Aℓ(4)	86.95(14)
O(41)-Aℓ(4)-O(21)-C(21)	-154.11(15)	C(414)-Aℓ(4)-O(21)-C(21)	-42.82(19)
C(412)-Aℓ(4)-O(21)-C(21)	88.64(17)	Aℓ(2)-Aℓ(4)-O(21)-C(21)	-167.53(18)
O(41)-Aℓ(4)-O(21)-Aℓ(2)	13.42(7)	C(414)-Aℓ(4)-O(21)-Aℓ(2)	124.72(12)
C(412)-Aℓ(4)-O(21)-Aℓ(2)	-103.83(12)	Aℓ(2)-O(21)-C(21)-C(26)	-88.9(2)
Aℓ(4)-O(21)-C(21)-C(26)	72.9(2)	Aℓ(2)-O(21)-C(21)-C(22)	94.5(2)
Aℓ(4)-O(21)-C(21)-C(22)	-103.6(2)	C(26)-C(21)-C(22)-C(23)	-9.6(3)
O(21)-C(21)-C(22)-C(23)	166.9(2)	C(26)-C(21)-C(22)-C(216)	168.8(7)
O(21)-C(21)-C(22)-C(216)	-14.8(7)	C(26)-C(21)-C(22)-C(28)	161.0(5)
O(21)-C(21)-C(22)-C(28)	-22.5(5)	C(21)-C(22)-C(23)-C(24)	3.0(4)
C(216)-C(22)-C(23)-C(24)	-175.5(6)	C(28)-C(22)-C(23)-C(24)	-168.7(4)
C(22)-C(23)-C(24)-C(25)	4.2(4)	C(22)-C(23)-C(24)-Br(2)	176.5(5)
C(23)-C(24)-C(25)-C(26)	-4.8(4)	Br(2)-C(24)-C(25)-C(26)	-176.6(5)
C(23)-C(24)-C(25)-C(15)	175.0(2)	Br(2)-C(24)-C(25)-C(15)	3.1(6)
C(14)-C(15)-C(25)-C(24)	4.5(4)	C(16)-C(15)-C(25)-C(24)	-176.1(2)
C(14)-C(15)-C(25)-C(26)	-175.7(2)	C(16)-C(15)-C(25)-C(26)	3.7(3)
C(22)-C(21)-C(26)-C(25)	9.2(3)	O(21)-C(21)-C(26)-C(25)	-167.39(18)
C(22)-C(21)-C(26)-C(17)	-169.0(2)	O(21)-C(21)-C(26)-C(17)	14.4(3)
C(24)-C(25)-C(26)-C(21)	-1.8(3)	C(15)-C(25)-C(26)-C(21)	178.43(19)
C(24)-C(25)-C(26)-C(17)	176.8(2)	C(15)-C(25)-C(26)-C(17)	-3.0(2)
C(16)-C(17)-C(26)-C(21)	179.6(2)	C(16)-C(17)-C(26)-C(25)	1.3(2)
C(21)-C(22)-C(28)-C(211)	-120.9(5)	C(23)-C(22)-C(28)-C(211)	49.8(7)
C(21)-C(22)-C(28)-C(210)	121.5(6)	C(23)-C(22)-C(28)-C(210)	-67.8(7)
C(21)-C(22)-C(28)-C(29)	-2.9(9)	C(23)-C(22)-C(28)-C(29)	167.8(5)
C(21)-C(22)-C(216)-C(219)	-69.2(10)	C(23)-C(22)-C(216)-C(219)	109.1(7)
C(21)-C(22)-C(216)-C(218)	173.9(7)	C(23)-C(22)-C(216)-C(218)	-7.7(12)
C(21)-C(22)-C(216)-C(217)	49.3(12)	C(23)-C(22)-C(216)-C(217)	-132.4(8)
O(21)-Aℓ(2)-C(212)-C(213)	109.1(3)	O(41)-Aℓ(2)-C(212)-C(213)	-164.0(3)
C(214)-Aℓ(2)-C(212)-C(213)	-23.0(3)	Aℓ(4)-Aℓ(2)-C(212)-C(213)	154.7(3)
O(21)-Aℓ(2)-C(214)-C(215)	158.87(19)	O(41)-Aℓ(2)-C(214)-C(215)	68.8(2)

Table 4. (continued)

C(212)-Aℓ(2)-C(214)-C(215)	-60.1(2)	Aℓ(4)-Aℓ(2)-C(214)-C(215)	122.81(18)
O(11)-Aℓ(1)-O(31)-C(31)	152.47(17)	C(114)-Aℓ(1)-O(31)-C(31)	34.97(19)
C(112)-Aℓ(1)-O(31)-C(31)	-100.70(18)	Aℓ(3)-Aℓ(1)-O(31)-C(31)	164.86(19)
O(11)-Aℓ(1)-O(31)-Aℓ(3)	-12.39(6)	C(114)-Aℓ(1)-O(31)-Aℓ(3)	-129.90(9)
C(112)-Aℓ(1)-O(31)-Aℓ(3)	94.44(11)	O(11)-Aℓ(3)-O(31)-C(31)	-154.19(15)
C(314)-Aℓ(3)-O(31)-C(31)	-45.98(18)	C(312)-Aℓ(3)-O(31)-C(31)	86.80(17)
Aℓ(1)-Aℓ(3)-O(31)-C(31)	-166.69(17)	O(11)-Aℓ(3)-O(31)-Aℓ(1)	12.50(6)
C(314)-Aℓ(3)-O(31)-Aℓ(1)	120.71(11)	C(312)-Aℓ(3)-O(31)-Aℓ(1)	-106.51(11)
Aℓ(1)-O(31)-C(31)-C(36)	-94.5(2)	Aℓ(3)-O(31)-C(31)-C(36)	67.0(2)
Aℓ(1)-O(31)-C(31)-C(32)	87.6(2)	Aℓ(3)-O(31)-C(31)-C(32)	-110.8(2)
C(36)-C(31)-C(32)-C(33)	-5.6(3)	O(31)-C(31)-C(32)-C(33)	172.1(2)
C(36)-C(31)-C(32)-C(38)	166.4(2)	O(31)-C(31)-C(32)-C(38)	-15.8(3)
C(31)-C(32)-C(33)-C(34)	0.1(4)	C(38)-C(32)-C(33)-C(34)	-172.7(3)
C(32)-C(33)-C(34)-C(35)	2.9(4)	C(32)-C(33)-C(34)-Br(3)	-169.4(15)
C(33)-C(34)-C(35)-C(36)	-0.4(4)	Br(3)-C(34)-C(35)-C(36)	171.8(15)
C(33)-C(34)-C(35)-C(45)	179.8(2)	Br(3)-C(34)-C(35)-C(45)	-8.0(16)
C(32)-C(31)-C(36)-C(35)	8.1(3)	O(31)-C(31)-C(36)-C(35)	-169.76(18)
C(32)-C(31)-C(36)-C(37)	-171.0(2)	O(31)-C(31)-C(36)-C(37)	11.2(3)
C(34)-C(35)-C(36)-C(31)	-5.0(3)	C(45)-C(35)-C(36)-C(31)	174.79(19)
C(34)-C(35)-C(36)-C(37)	174.2(2)	C(45)-C(35)-C(36)-C(37)	-6.0(2)
C(31)-C(36)-C(37)-C(46)	-176.9(2)	C(35)-C(36)-C(37)-C(46)	3.9(2)
C(33)-C(32)-C(38)-C(310)	-134.9(3)	C(31)-C(32)-C(38)-C(310)	53.0(3)
C(33)-C(32)-C(38)-C(39)	103.6(3)	C(31)-C(32)-C(38)-C(39)	-68.4(3)
C(33)-C(32)-C(38)-C(311)	-13.2(3)	C(31)-C(32)-C(38)-C(311)	174.8(3)
O(11)-Aℓ(3)-C(312)-C(313)	-166.30(19)	O(31)-Aℓ(3)-C(312)-C(313)	-77.8(2)
C(314)-Aℓ(3)-C(312)-C(313)	59.8(2)	Aℓ(1)-Aℓ(3)-C(312)-C(313)	-120.5(2)
O(11)-Aℓ(3)-C(314)-C(315)	-100.5(3)	O(31)-Aℓ(3)-C(314)-C(315)	168.9(3)
C(312)-Aℓ(3)-C(314)-C(315)	38.0(3)	Aℓ(1)-Aℓ(3)-C(314)-C(315)	-141.8(3)
O(21)-Aℓ(4)-O(41)-C(41)	157.6(2)	C(414)-Aℓ(4)-O(41)-C(41)	37.4(2)
C(412)-Aℓ(4)-O(41)-C(41)	-98.1(2)	Aℓ(2)-Aℓ(4)-O(41)-C(41)	170.7(2)
O(21)-Aℓ(4)-O(41)-Aℓ(2)	-13.14(6)	C(414)-Aℓ(4)-O(41)-Aℓ(2)	-133.35(11)
C(412)-Aℓ(4)-O(41)-Aℓ(2)	91.15(16)	O(21)-Aℓ(2)-O(41)-C(41)	-160.10(14)
C(214)-Aℓ(2)-O(41)-C(41)	-55.78(17)	C(212)-Aℓ(2)-O(41)-C(41)	75.07(17)
Aℓ(4)-Aℓ(2)-O(41)-C(41)	-173.41(17)	O(21)-Aℓ(2)-O(41)-Aℓ(4)	13.30(7)
C(214)-Aℓ(2)-O(41)-Aℓ(4)	117.63(11)	C(212)-Aℓ(2)-O(41)-Aℓ(4)	-111.53(12)
Aℓ(4)-O(41)-C(41)-C(46)	-102.0(2)	Aℓ(2)-O(41)-C(41)-C(46)	67.6(2)
Aℓ(4)-O(41)-C(41)-C(42)	80.2(3)	Aℓ(2)-O(41)-C(41)-C(42)	-110.3(2)
C(46)-C(41)-C(42)-C(43)	-9.6(3)	O(41)-C(41)-C(42)-C(43)	168.1(2)
C(46)-C(41)-C(42)-C(48)	163.7(2)	O(41)-C(41)-C(42)-C(48)	-18.5(3)
C(41)-C(42)-C(43)-C(44)	2.2(4)	C(48)-C(42)-C(43)-C(44)	-171.5(2)

Table 4. (continued)

C(42)-C(43)-C(44)-C(45)	4.3(4)	C(42)-C(43)-C(44)-Br(4)	177.8(3)
C(43)-C(44)-C(45)-C(46)	-3.6(4)	Br(4)-C(44)-C(45)-C(46)	-176.7(3)
C(43)-C(44)-C(45)-C(35)	171.5(2)	Br(4)-C(44)-C(45)-C(35)	-1.6(5)
C(34)-C(35)-C(45)-C(44)	10.0(4)	C(36)-C(35)-C(45)-C(44)	-169.8(2)
C(34)-C(35)-C(45)-C(46)	-174.5(3)	C(36)-C(35)-C(45)-C(46)	5.7(3)
O(41)-C(41)-C(46)-C(45)	-167.28(18)	C(42)-C(41)-C(46)-C(45)	10.6(3)
O(41)-C(41)-C(46)-C(37)	16.7(3)	C(42)-C(41)-C(46)-C(37)	-165.4(2)
C(44)-C(45)-C(46)-C(41)	-3.8(3)	C(35)-C(45)-C(46)-C(41)	-179.87(19)
C(44)-C(45)-C(46)-C(37)	172.9(2)	C(35)-C(45)-C(46)-C(37)	-3.1(2)
C(36)-C(37)-C(46)-C(41)	175.9(2)	C(36)-C(37)-C(46)-C(45)	-0.4(2)
C(43)-C(42)-C(48)-C(49)	-125.3(3)	C(41)-C(42)-C(48)-C(49)	61.6(3)
C(43)-C(42)-C(48)-C(410)	111.3(3)	C(41)-C(42)-C(48)-C(410)	-61.9(3)
C(43)-C(42)-C(48)-C(411)	-4.4(3)	C(41)-C(42)-C(48)-C(411)	-177.6(2)
O(41)-Aℓ(4)-C(412)-C(413)	-179.2(3)	O(21)-Aℓ(4)-C(412)-C(413)	-91.9(3)
C(414)-Aℓ(4)-C(412)-C(413)	44.7(4)	Aℓ(2)-Aℓ(4)-C(412)-C(413)	-134.2(3)
O(41)-Aℓ(4)-C(414)-C(415)	145.7(2)	O(21)-Aℓ(4)-C(414)-C(415)	53.8(3)
C(412)-Aℓ(4)-C(414)-C(415)	-75.8(3)	Aℓ(2)-Aℓ(4)-C(414)-C(415)	102.7(3)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($\mathring{A}^2 \times 10^2$) for $(C_{58}H_{88}A\ell_4O_4)_{0.88}(C_{58}H_{87}A\ell_4O_4Br)_{0.12}$.

ATOM	X	Y	Z	U_{iso}
H(13)	0.4855	-0.1054	0.3380	6.6
H(14)[a]	0.5812	-0.1034	0.4493	6.3
H(17A)	0.6746	0.2260	0.3100	4.1
H(17B)	0.7859	0.1637	0.2854	4.1
H(19A)[e]	0.4330	0.0214	0.0671	8.9
H(19B)[e]	0.5501	-0.0308	0.1012	8.9
H(19C)[e]	0.5201	0.0831	0.0807	8.9
H(11A)[e]	0.3272	0.0951	0.2511	10.1
H(11B)[e]	0.2984	0.1041	0.1581	10.1
H(11C)[e]	0.3897	0.1598	0.1750	10.1
H(11D)[e]	0.3641	-0.0867	0.2760	12.0
H(11E)[e]	0.4390	-0.1301	0.2088	12.0
H(11F)[e]	0.3247	-0.0637	0.1835	12.0
H(11G)[f]	0.4719	-0.1536	0.1957	12.7
H(11H)[f]	0.5867	-0.1188	0.1637	12.7
H(11I)[f]	0.4911	-0.0981	0.1005	12.7
H(11J)[f]	0.3476	-0.0617	0.2667	14.2
H(11K)[f]	0.2986	-0.0128	0.1774	14.2
H(11L)[f]	0.3225	0.0523	0.2338	14.2
H(11M)[f]	0.3776	0.0828	0.0798	13.4
H(11N)[f]	0.5011	0.0474	0.0536	13.4
H(11O)[f]	0.4746	0.1288	0.1019	13.4
H(11P)	0.6861	0.0522	0.0090	5.6
H(11Q)	0.8143	0.0490	-0.0130	5.6
H(11R)	0.7758	-0.1090	0.0500	11.8
H(11S)	0.7248	-0.0773	0.1308	11.8
H(11T)	0.8526	-0.0809	0.1078	11.8
H(11U)	0.9120	0.1645	0.1695	6.1
H(11V)	0.8939	0.0571	0.2126	6.1
H(11W)	1.0691	0.0581	0.1463	11.4
H(11X)	1.0168	0.1140	0.0593	11.4
H(11Y)	0.9986	0.0062	0.1025	11.4
H(23)	0.8126	-0.0107	0.6305	5.4

Tbale 5. (continued)

H(24)[b]	0.6943	-0.0639	0.5600	5.6
H(29A)[g]	1.0247	0.1988	0.4914	11.0
H(29B)[g]	1.0604	0.2066	0.5781	11.0
H(29C)[g]	0.9505	0.2697	0.5384	11.0
H(21A)[g]	0.9406	0.1569	0.7055	12.0
H(21B)[g]	0.8535	0.0881	0.7079	12.0
H(21C)[g]	0.8256	0.2000	0.6639	12.0
H(21D)[g]	1.0520	0.0222	0.5612	9.7
H(21E)[g]	0.9856	-0.0176	0.6461	9.7
H(21F)[g]	1.0774	0.0468	0.6440	9.7
H(21G)[h]	0.8331	0.2495	0.6329	9.7
H(21H)[h]	0.8963	0.2834	0.5453	9.7
H(21I)[h]	0.9622	0.2486	0.6287	9.7
H(21J)[h]	0.8590	0.0763	0.7116	13.2
H(21K)[h]	0.9862	0.0826	0.7093	13.2
H(21L)[h]	0.9469	0.0012	0.6778	13.2
H(21M)[h]	1.0888	0.1297	0.5738	11.7
H(21N)[h]	1.0266	0.1619	0.4888	11.7
H(21O)[h]	1.0444	0.0520	0.5406	11.7
H(21P)	1.0428	0.4494	0.3514	8.0
H(21Q)	1.0237	0.3923	0.4456	8.0
H(21R)	1.2115	0.3749	0.4089	14.7
H(21S)	1.1920	0.3293	0.3363	14.7
H(21T)	1.1729	0.2724	0.4311	14.7
H(21U)	1.0611	0.1853	0.3241	5.4
H(21V)	0.9523	0.2026	0.2753	5.4
H(21W)	1.1014	0.2280	0.1804	10.1
H(21X)	1.1288	0.3089	0.2188	10.1
H(21Y)	1.0194	0.3267	0.1699	10.1
H(33)	0.8606	0.4759	-0.1529	6.0
H(34)[c]	0.8774	0.5736	-0.0684	6.1
H(37A)	0.8353	0.3168	0.1942	4.0
H(37B)	0.7081	0.3637	0.1896	4.0
H(39A)	0.9077	0.1819	-0.1410	9.1
H(39B)	0.8892	0.1860	-0.0465	9.1
H(39C)	0.9694	0.2501	-0.1079	9.1
H(31A)	0.7077	0.2264	-0.1683	9.0
H(31B)	0.6380	0.3170	-0.1430	9.0
H(31C)	0.6837	0.2239	-0.0726	9.0
H(31D)	0.8315	0.3210	-0.2556	11.3

Table 5. (continued)

H(31E)	0.9003	0.3840	-0.2223	11.3
H(31F)	0.7723	0.4179	-0.2351	11.3
H(31G)	0.5043	0.2381	-0.0258	7.1
H(31H)	0.3997	0.2635	0.0317	7.1
H(31I)	0.4107	0.3966	-0.0896	12.4
H(31J)	0.5298	0.4043	-0.0660	12.4
H(31K)	0.4255	0.4296	-0.0087	12.4
H(31L)	0.5447	0.3214	0.2280	6.4
H(31M)	0.5299	0.4120	0.1494	6.4
H(31N)	0.3656	0.4018	0.2281	19.1
H(31O)	0.3646	0.2974	0.2173	19.1
H(31P)	0.3498	0.3885	0.1387	19.1
H(43)	0.8445	0.7146	0.1698	5.6
H(44)[d]	0.8707	0.6633	0.0491	5.6
H(49A)	0.8399	0.6169	0.4448	9.1
H(49B)	0.9374	0.5922	0.3817	9.1
H(49C)	0.8543	0.5181	0.4197	9.1
H(41A)	0.6442	0.6547	0.3991	10.1
H(41B)	0.6559	0.5597	0.3685	10.1
H(41C)	0.6209	0.6620	0.3053	10.1
H(41D)	0.7774	0.7675	0.3515	10.1
H(41E)	0.7459	0.7768	0.2590	10.1
H(41F)	0.8711	0.7514	0.2830	10.1
H(41G)	0.7861	0.3886	0.5467	9.3
H(41H)	0.6907	0.4756	0.5131	9.3
H(41I)	0.6340	0.3780	0.6404	18.9
H(41J)	0.6543	0.2877	0.6025	18.9
H(41K)	0.5590	0.3747	0.5690	18.9
H(41L)	0.5237	0.4289	0.3904	7.0
H(41M)	0.5747	0.3702	0.3261	7.0
H(41N)	0.4307	0.3016	0.4031	13.1
H(41O)	0.4899	0.2860	0.4876	13.1
H(41P)	0.5410	0.2270	0.4227	13.1

a: Occ. = 0.97
b: Occ. = 0.97
c: Occ. = 0.99
d: Occ. = 0.95
e: Occ. = 0.768(6)
f: Occ. = 0.232(6)
g: Occ. = 0.591(5)
h: Occ. = 0.409(5)

Table 6. Anisotropic parameters ($Å^2 \times 10^2$) for $(C_{58}H_{88}A\ell_4O_4)_{0.88}(C_{58}H_{87}A\ell_4O_4Br)_{0.12}$.

The anisotropic thermal parameters are the coefficients of the expression:

$$T = \exp[-2\pi^2(U_{11}a^{*2}h^2+...+ 2U_{12}a^*b^*hk+...)].$$

ATOM	U11	U22	U33	U23	U13	U12
Br(1)	9.5(8)	6.4(6)	8.0(7)	-0.6(5)	0.1(6)	-3.3(6)
Br(2)	8.8(7)	5.8(5)	4.4(4)	-0.2(4)	-0.6(4)	-3.4(5)
Br(3)	10.(3)	7.(2)	5.6(17)	-1.5(15)	0.2(16)	-2.8(18)
Br(4)	10.2(5)	4.5(3)	5.5(3)	-1.1(2)	0.2(3)	-2.9(3)
Aℓ(1)	3.79(3)	3.26(3)	3.24(3)	-1.15(2)	0.09(2)	-0.82(2)
Aℓ(2)	4.10(3)	4.09(3)	3.63(3)	-1.15(3)	-0.26(2)	-1.44(3)
Aℓ(3)	3.28(3)	4.08(3)	3.99(3)	-1.23(3)	-0.29(2)	-0.73(2)
Aℓ(4)	5.02(4)	4.34(4)	3.48(3)	-1.68(3)	0.72(3)	-1.41(3)
O(11)	3.65(7)	3.73(7)	3.18(7)	-0.96(6)	0.22(5)	-1.42(6)
C(11)	3.74(10)	3.67(10)	3.43(10)	-1.09(8)	0.37(8)	-1.38(8)
C(12)	4.57(12)	4.85(12)	4.22(12)	-1.49(10)	0.39(9)	-2.42(10)
C(13)	6.60(16)	5.38(14)	5.29(14)	-1.28(11)	0.64(12)	-3.89(13)
C(14)	6.71(16)	5.10(14)	4.26(13)	-0.41(10)	0.42(11)	-3.21(12)
C(15)	4.48(11)	3.83(11)	3.60(11)	-0.97(8)	0.48(9)	-1.66(9)
C(16)	3.62(10)	3.41(10)	3.38(10)	-1.08(8)	0.51(8)	-1.27(8)
C(17)	3.84(10)	3.60(10)	3.02(9)	-0.95(8)	0.12(8)	-1.38(8)
C(18)	5.0(2)	6.3(3)	4.5(2)	-2.18(15)	0.41(15)	-3.24(19)
C(19)	6.4(3)	8.7(4)	4.3(2)	-3.0(2)	-0.04(19)	-3.3(2)
C(110)	5.1(2)	9.7(3)	5.8(2)	-2.5(2)	-0.16(16)	-1.70(19)
C(111)	10.0(4)	9.7(4)	6.4(3)	-2.2(3)	-0.1(2)	-7.1(3)
C(116)	5.0(2)	6.3(3)	4.5(2)	-2.18(15)	0.41(15)	-3.24(19)
C(117)	10.4(12)	6.5(9)	10.2(12)	-3.9(8)	-2.3(9)	-2.4(8)
C(118)	7.3(11)	16.(2)	7.7(10)	-5.9(14)	0.0(8)	-4.2(12)
C(119)	9.1(16)	13.(2)	5.5(9)	-0.3(13)	-0.5(10)	-8.1(15)
C(112)	5.68(14)	3.84(11)	5.00(13)	-2.01(10)	1.01(10)	-1.60(10)
C(113)	9.7(2)	3.68(14)	10.2(3)	-1.68(15)	-0.2(2)	-1.34(15)
C(114)	4.26(12)	6.45(15)	4.55(13)	-2.06(11)	-0.39(10)	0.05(11)
C(115)	4.93(16)	11.0(3)	6.87(19)	-3.82(18)	-0.08(14)	0.91(16)
O(21)	4.61(8)	3.58(7)	3.31(7)	-0.93(6)	-0.07(6)	-1.48(6)
C(21)	4.17(11)	3.60(10)	3.09(10)	-0.94(8)	0.28(8)	-1.12(8)

Tbale 6. (continued)

C(22)	5.07(12)	4.29(12)	2.92(10)	-1.07(8)	0.16(8)	-1.20(9)
C(23)	5.89(14)	4.70(13)	2.92(10)	-0.61(9)	0.12(9)	-1.44(10)
C(24)	6.08(14)	4.38(12)	3.49(11)	-0.50(9)	0.65(10)	-2.02(11)
C(25)	4.29(11)	4.09(11)	3.31(10)	-0.97(8)	0.50(8)	-1.46(9)
C(26)	3.94(10)	3.59(10)	2.97(9)	-0.85(8)	0.26(8)	-1.13(8)
C(28)	4.9(3)	4.96(18)	3.27(11)	-1.22(12)	-0.31(14)	-1.00(17)
C(29)	7.6(4)	7.8(4)	6.5(3)	1.0(3)	-3.2(3)	-4.2(3)
C(210)	7.0(3)	13.4(6)	5.9(3)	-6.3(4)	0.6(3)	-2.5(4)
C(211)	6.0(3)	7.1(3)	6.4(3)	-2.1(3)	-2.1(2)	0.1(2)
C(216)	4.9(3)	4.96(18)	3.27(11)	-1.22(12)	-0.31(14)	-1.00(17)
C(217)	8.6(5)	6.3(4)	5.5(4)	-3.1(3)	-2.9(4)	-0.3(4)
C(218)	11.0(8)	10.1(7)	5.1(4)	0.5(5)	-3.9(5)	-3.5(6)
C(219)	4.5(4)	11.7(8)	9.1(6)	-6.3(6)	-0.3(4)	-0.8(4)
C(212)	5.50(16)	7.13(19)	8.6(2)	-3.57(16)	-1.61(14)	-1.50(14)
C(213)	6.1(2)	16.1(4)	9.6(3)	-6.4(3)	-0.29(18)	-3.2(2)
C(214)	4.16(12)	5.44(14)	4.19(12)	-1.56(10)	-0.01(9)	-1.23(10)
C(215)	5.72(16)	9.5(2)	5.25(16)	-2.12(15)	1.23(12)	-2.63(15)
O(31)	3.57(7)	3.15(7)	3.25(7)	-0.99(5)	0.12(5)	-1.22(5)
C(31)	3.41(10)	2.99(9)	3.31(10)	-0.83(7)	-0.08(7)	-1.02(7)
C(32)	4.90(12)	3.85(11)	3.19(10)	-1.08(8)	0.10(8)	-1.33(9)
C(33)	7.58(17)	4.69(13)	3.22(11)	-0.90(9)	0.69(10)	-2.66(12)
C(34)	7.56(17)	4.41(12)	3.77(12)	-0.85(10)	0.41(11)	-3.05(12)
C(35)	4.70(12)	3.59(10)	3.54(10)	-1.01(8)	-0.14(8)	-1.55(9)
C(36)	3.38(10)	3.42(10)	3.12(10)	-0.96(8)	-0.07(7)	-1.01(8)
C(37)	4.14(10)	3.24(10)	3.01(10)	-1.15(8)	-0.04(8)	-1.31(8)
C(38)	6.51(15)	4.35(12)	3.36(11)	-1.51(9)	0.46(10)	-1.72(11)
C(39)	6.55(17)	5.09(15)	6.91(17)	-2.52(13)	1.47(13)	-1.45(12)
C(310)	7.49(18)	6.85(17)	4.93(14)	-2.82(13)	-0.64(13)	-2.39(14)
C(311)	13.5(3)	6.39(18)	3.76(14)	-2.33(13)	1.39(16)	-3.74(19)
C(312)	4.35(13)	7.67(19)	5.88(16)	-1.60(14)	-1.37(11)	-1.23(12)
C(313)	7.1(2)	8.9(2)	7.3(2)	-0.45(18)	-2.38(16)	1.10(18)
C(314)	4.46(13)	5.81(15)	5.89(15)	-2.37(12)	-0.35(11)	0.38(11)
C(315)	4.83(19)	20.5(6)	15.6(4)	-11.3(4)	1.2(2)	0.2(3)
O(41)	4.52(8)	3.35(7)	3.18(7)	-1.05(6)	0.09(6)	-1.23(6)
C(41)	3.73(10)	3.44(10)	3.39(10)	-1.00(8)	0.18(8)	-1.16(8)
C(42)	4.55(12)	3.60(11)	4.26(11)	-1.66(9)	0.07(9)	-1.43(9)
C(43)	6.41(15)	3.45(11)	4.75(13)	-1.42(9)	0.05(11)	-2.06(10)
C(44)	6.68(15)	3.79(11)	4.11(12)	-0.93(9)	0.10(10)	-2.38(11)
C(45)	4.55(11)	3.55(10)	3.69(11)	-1.19(8)	0.01(8)	-1.57(9)
C(46)	3.67(10)	3.07(10)	3.62(10)	-1.10(8)	-0.19(8)	-1.08(8)

Table 6. (continued)

C(48)	6.30(15)	4.22(12)	4.98(13)	-2.45(10)	0.39(11)	-1.55(11)
C(49)	8.7(2)	5.63(15)	5.16(15)	-2.89(12)	-0.58(13)	-1.90(14)
C(410)	7.07(19)	6.42(17)	7.43(19)	-3.55(15)	1.61(15)	-1.04(14)
C(411)	10.0(2)	4.47(14)	6.88(18)	-3.14(13)	0.50(16)	-2.03(14)
C(412)	11.6(3)	8.7(2)	4.47(15)	-3.41(15)	2.08(16)	-4.0(2)
C(413)	10.3(3)	21.9(6)	5.5(2)	-4.7(3)	2.3(2)	-2.2(3)
C(414)	4.80(14)	6.23(16)	6.87(17)	-2.56(13)	0.68(12)	-1.18(12)
C(415)	6.03(19)	9.1(2)	12.1(3)	-4.5(2)	2.95(19)	-2.46(17)

Table 7. Distances to the weighted least-squares planes for $(C_{58}H_{88}A\ell_4O_4)_{0.88}(C_{58}H_{87}\text{-}A\ell_4O_4Br)_{0.12}$.

Plane no. 1

*	0.048	(0.002)	C(11)
*	-0.033	(0.002)	C(12)
*	-0.005	(0.002)	C(13)
*	0.029	(0.002)	C(14)
*	-0.014	(0.002)	C(15)
*	-0.025	(0.002)	C(16)
	0.235	(0.003)	O(11)
	-0.158	(0.003)	C(17)
	-0.422	(0.006)	C(18)
	-0.011	(0.016)	C(116)
	0.256	(0.015)	Br(1)

Rms deviation of fitted atoms = 0.029

Plane no. 2

*	-0.058	(0.002)	C(21)
*	0.037	(0.002)	C(22)
*	0.012	(0.002)	C(23)
*	-0.040	(0.002)	C(24)
*	0.020	(0.002)	C(25)
*	0.030	(0.001)	C(26)
	-0.317	(0.003)	O(21)
	0.180	(0.003)	C(17)
	0.370	(0.010)	C(28)
	0.198	(0.015)	C(216)
	0.035	(0.013)	Br(2)

Rms deviation of fitted atoms = 0.036

Angle to previous plane (with approximate esd) = 6.21 (0.16)

Table 7. (continued)

Plane no.3

*	-0.039 (0.001)	C(31)
*	0.012 (0.002)	C(32)
*	0.018 (0.002)	C(33)
*	-0.020 (0.002)	C(34)
*	-0.007 (0.002)	C(35)
*	0.037 (0.001)	C(36)
	-0.215 (0.003)	O(31)
	0.187 (0.004)	C(37)
	0.233 (0.004)	C(38)
	-0.297 (0.041)	Br(3)

Rms deviation of fitted atoms = 0.025

Plane no. 4

*	0.061 (0.001)	C(41)
*	-0.033 (0.002)	C(42)
*	-0.017 (0.002)	C(43)
*	0.039 (0.002)	C(44)
*	-0.011 (0.002)	C(45)
*	-0.040 (0.001)	C(46)
	0.302 (0.003)	O(41)
	-0.268 (0.003)	C(37)
	-0.295 (0.004)	C(48)
	-0.010 (0.008)	Br(4)

Rms deviation of fitted atoms = 0.037

Angle to previous plane (with approximate esd) = 11.87 (0.10)

Plane no. 5

*	-0.019 (0.001)	C(15)
*	0.011 (0.001)	C(16)
*	0.001 (0.001)	C(17)
*	0.019 (0.001)	C(25)
*	-0.012 (0.001)	C(26)

Rms deviation of fitted atoms = 0.014

Table 7. (continued)

Plane no. 6

*	0.034 (0.001)	C(35)
*	-0.029 (0.001)	C(36)
*	0.013 (0.001)	C(37)
*	-0.025 (0.001)	C(45)
*	0.007 (0.001)	C(46)

Rms deviation of fitted atoms = 0.024

Angle to previous plane (with approximate esd) = 24.80 (0.12)

Plane no. 7

*	0.120 (0.002)	C(11)
*	-0.037 (0.002)	C(12)
*	-0.068 (0.002)	C(13)
*	-0.022 (0.002)	C(14)
*	0.009 (0.002)	C(15)
*	0.061 (0.002)	C(16)
*	0.001 (0.002)	C(17)
*	-0.128 (0.002)	C(21)
*	0.051 (0.002)	C(22)
*	0.082 (0.002)	C(23)
*	0.008 (0.002)	C(24)
*	-0.015 (0.002)	C(25)
*	-0.064 (0.002)	C(26)
	0.370 (0.002)	O(11)
	-0.448 (0.002)	O(21)
	-0.448 (0.005)	C(18)
	-0.041 (0.015)	C(116)
	0.419 (0.010)	C(28)
	0.244 (0.015)	C(216)
	0.117 (0.015)	Br(1)
	0.167 (0.012)	Br(2)

Rms deviation of fitted atoms = 0.065

Table 7. (continued)

Plane no. 8

*	-0.194 (0.002)	C(31)
*	-0.072 (0.002)	C(32)
*	0.077 (0.002)	C(33)
*	0.110 (0.002)	C(34)
*	0.052 (0.002)	C(35)
*	-0.048 (0.002)	C(36)
*	0.050 (0.002)	C(37)
*	0.139 (0.002)	C(41)
*	-0.109 (0.002)	C(42)
*	-0.161 (0.002)	C(43)
*	-0.030 (0.002)	C(44)
*	0.071 (0.002)	C(45)
*	0.116 (0.002)	C(46)
	-0.512 (0.002)	O(31)
	0.460 (0.002)	O(41)
	0.084 (0.003)	C(38)
	-0.464 (0.003)	C(48)
	0.017 (0.041)	Br(3)
	-0.185 (0.008)	Br(4)

Rms deviation of fitted atoms = 0.106

Angle to previous plane (with approximate esd) = 30.31 (0.06)

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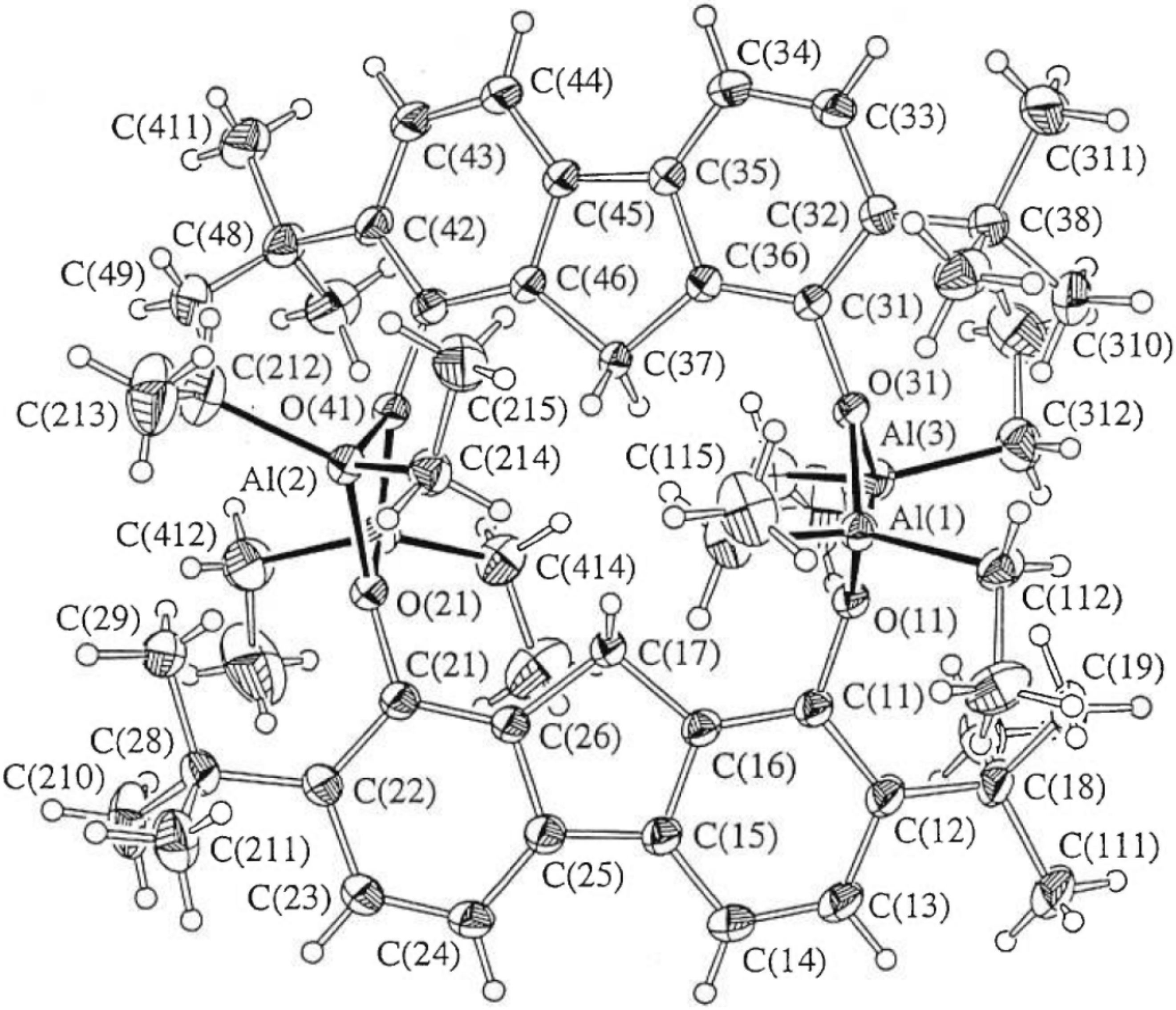
* indicates atoms used to define plane



ORTEP view of $(C_{58}H_{88}A\ell_4O_4)_{0.88}(C_{58}H_{87}A\ell_4O_4Br)_{0.12}$

with the numbering scheme adopted. Ellipsoids drawn at

40% probality level. Hydrogens represented by sphere of arbitrary size.

Discussion of structure determination and refinement procedure

A crystal of the compound was attached to a glass fiber and transferred rapidly under a cold stream of nitrogen to a Nonius CAD-4 system equipped with a low temperature gas-stream cryostat for data collection at 225(2)K.

The structure was solved by direct methods using SHELXS96 (Sheldrick, 1990) and difmap synthesis using NRCVAX (Gabe et al, 1989) and SHELXL96 (Sheldrick, 1996). All non-hydrogen atoms are treated as anisotropic, hydrogen atoms isotropic. Hydrogen atoms were placed in ideal positions and refined as riding atoms with different C-H distances for different types of carbon hydrogen. The isotropic displacement factors, U_{iso}, were adjusted to 50% (methyl) and 20% (others) higher value of the bonded carbon atom.

Finally, 2 reflections which were badly corrected for absorption were rejected in the last cycles prior to final convergence.

2 small holes remained in this structure accounting for a total of 3 electrons and 2 x 18.3Å^3 of the volume of the cell. Those residuals, as well as necessary very minor occupancies disorder that should have been included at positions C(215) and C(415) due to close contacts to bromine residuals (occ. = 0.03 and 0.01), were not taken into account in the proposed final model.

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