Université de Montréal

Synthesis, Properties and Characterization of N-Alkyl Substituted β-Diketiminato Copper(I) Complexes

Par

Paul Okechukwu Oguadinma

Département de chimie

Faculté des arts et des sciences

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Présenté par :
Paul Okechukwu Oguadinma

A été évaluée par un jury composé des personnes suivantes :

Davit Zargarian, président rapporteur
Frank Schaper, directeur de recherche
Garry Hanan, membre de jury
Sean Barry, examinateur externe
Silva Carlos, représentant du doyen de la Faculté

Abstract

The ligand *nacnac*^{xyl}H (xyl = $C_6Me_2H_3$) and the N-alkyl substituted diketimine ligands (*nacnac*$^{CH(Me)Ph}$H, *nacnac*^{Bn}H and *nacnac*^{iPr}H) have been prepared in good yields except *nacnac*^{iPr}H (23%) using a one-step procedure with the help of a Dean-Stark apparatus. Reaction of *S*,*S*-*nacnac*$^{CH(Me)Ph}$H and *nacnac*^{Bn}H with *n*BuLi in THF gave *S*,*S*-*nacnac*$^{CH(Me)Ph}$Li(THF) and *nacnac*^{Bn}Li(THF). Attempts to brominate these THF adducts with N-bromosuccinimide gave instead the β-carbon substituted succinimido ligands *S*,*S*-^{succ}*nacnac*$^{CH(Me)Ph}$H and ^{succ}*nacnac*^{Bn}H (succ = succinimido). Chlorination with N-chlorosuccinimide, afforded the desired product albeit with significant amounts of impurities.

Reaction of these ligands with CuO*t*Bu (or MesCu and catalytic amounts of CuO*t*Bu, Mes = $C_6Me_3H_2$) in the presence of Lewis bases gave (*nacnac*^{xyl}Cu)$_2$(μ-toluene), *nacnac*^{xyl}CuCNC_6H_3(Me)$_2$, *nacnac*$^{CH(Me)Ph}$CuL (L = PPh_3, PMe_3, CNC_6H_3(Me)$_2$, DMAP, lutidine, Py, MeCN), *nacnac*^{Bn}CuL (L = PPh_3, CNC_6H_3(Me)$_2$, styrene, *trans*-stilbene, phenylvinylether, acrylonitrile, diphenylacetylene), *nacnac*^{iPr}CuL (L = PPh_3, CNC_6H_3(Me)$_2$, MeCN) and ^{succ}*nacnac*$^{CH(Me)Ph}$CuL (PPh_3, CNC_6H_3(Me)$_2$, pyridine). All complexes are yellow and sensitive to air and moisture. There was no reaction between the copper precursors and the N-alkyl substituted ligands in the absence of strong Lewis bases.

NMR studies of the complex (*nacnac*^{xyl}Cu)$_2$(μ-toluene) in C_6D_6, showed no toluene adduct but an equilibrium mixture of (*nacnac*^{xyl}Cu)$_2$(μ-C_6D_6) and *nacnac*^{xyl}Cu(C_6D_6) in a ratio of 2:1. While addition of up to 50 equiv of either toluene or THF did not cause any significant change in the ^{1}H NMR spectrum, addition of 2 equiv MeCN gave instantaneously the *nacnac*^{xyl}Cu(MeCN) complex. In addition, (*nacnac*^{xylyl}Cu)$_2$(μ-C_6D_6) did not coordinate or react with N_2O even after heating at 60 ^oC for thirteen days.

In the presence of DPA (diphenylacetylene), reaction of *nacnac*^{Bn}H with CuO*t*Bu yields the bridged dimer (*nacnac*^{Bn}Cu)$_2$(μ-DPA). Addition of excess DPA (10-12 equiv) converts the bridged dimer to the terminally bound complex *nacnac*^{Bn}CuDPA. *Nacnac*^{R}H (R = CH(Me)Ph and *i*-Pr) did not form complexes with olefins or with DPA. Similar

reactivity was observed in *nacnac*$^{CH(Me)Ph}$Cu(NCMe) and *nacnac*$^{i\text{-}Pr}$Cu(NCMe) complexes. While the terminally bound MeCN complex was isolated and characterized, equilibrium in solution led us to suspect the formation of a bridged acetonitrile adduct.

Reactivity and comparative studies were performed with several copper complexes. Morpholine did not react with *nacnac*^{Bn}Cu(acrylonitrile) while free acrylonitrile does. Olefin exchange experiment showed that acrylonitrile (an electron withdrawing olefin) binds stronger than the other olefins examined, showing the importance of π-backbonding relative to σ-donation. π-Backbonding is, however, still low when compared other structurally characterized transition metal styrene complexes. Complexes *nacnac*$^{CH(Me)Ph}$CuL (L = PPh_3 and MeCN) have been employed in catalytic cyclopropanation of styrene and the conjugate addition of $ZnEt_2$ to 2-cyclohexenone, but results indicate that the diketimine ligand is lost before it enters the catalytic cycle. Hence, there was no chiral induction.

Four-coordinate copper(I) complexes of the form *nacnac*^{R}Cu(phen) (R = Bn, CH(Me)Ph and Phen = 1,10-phenanthroline, 2-Mes-1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline (dmp) and 2,9-diphenyl-1,10-phenanthroline (dpp)) were also prepared. The complexes are intensely blue in colour and intramolecular π-stacking interactions between one of the phenyl rings of *nacnac* ligand with the phenanthroline were observed in the solid state structures. UV-vis absorption measurements were performed in toluene and the MLCT bands are red-shifted relative to those of bisphenanthroline copper complexes. All compounds are emissive in the solid state, but 1,10-phenanthroline and 2-Mes-1,10-phenanthroline complexes do not emit in solution.

To buttress the π-stacking interactions, the new ligands *nacnac*^{R}H (R = $CH_2C_6H_2(OMe)_3$, $CH_2C_6F_5$) and their respective copper complexes with dmp and dpp were prepared. For the sake of comparison, *nacnac*$^{i\text{Bu}}$Cu(dmp) was prepared. While the dmp complexes showed enhanced π-π intramolecular interactions with both phenyl substituents of the diketimine ligand and the phenanthroline, dpp revealed no such interactions. The perfluorinated complex showed a significant blue-shift in absorption and emission spectra when compared to the other complexes, while the isobutyl substituted complex displayed

red-shifted transitions. While luminescence intensities and lifetimes were low, reduced Stoke shifts and comparable sharp luminescence peaks indicate reduced distortions in the excited state.

Key words: copper, β-diketimine, chiral *nacnac*, π back-bonding, π-π intramolecular interactions, X-ray.

Résumé

Le ligand *nacnac*^{xyl}H (xyl = $C_6Me_2H_3$) et les ligands dikétimines N-alkyle substitués (*nacnac*$^{CH(Me)Ph}$H, *nacnac*^{Bn}H and *nacnac*^{iPr}H) ont été préparés avec de bons rendements à l'exception du *nacnac*^{iPr}H (23%) en utilisant un protocole en une étape et à l'aide d'un montage Dean-Stark. La réaction du *S,S*-*nacnac*$^{CH(Me)Ph}$H et du *nacnac*^{Bn}H avec le *n*BuLi dans le THF conduit au *S,S*-*nacnac*$^{CH(Me)Ph}$Li(THF) et au *nacnac*^{Bn}Li(THF). Les tentatives de bromation de ces composés par le N-bromosuccinimide conduisent plutôt aux ligands *S,S*-^{succ}*nacnac*$^{CH(Me)Ph}$H et ^{succ}*nacnac*^{Bn}H (succ = succinimido) substitués par un groupement succinimido sur le carbone β. La chloration par le N-chlorosuccinimide conduit au produit désiré, mais avec des impuretés.

La réaction de ces ligands avec le CuO*t*Bu (ou bien MesCu, où Mes = $C_6Me_3H_2$, et une quantité catalytique de CuO*t*Bu) en présence de bases de Lewis donne les (*nacnac*^{xyl}Cu)$_2$(μ-toluène), *nacnac*^{xyl}CuCN$C_6H_3(Me)_2$, *nacnac*$^{CH(Me)Ph}$CuL (L = PPh_3, PMe_3, $CNC_6H_3(Me)_2$, DMAP, lutidine, Py, MeCN), *nacnac*^{Bn}CuL (L = PPh_3, $CNC_6H_3(Me)_2$, styrène, *trans*-stilbene, phenylvinylether, acrylonitrile, diphenylacetylène), *nacnac*^{iPr}CuL (L = PPh_3, $CNC_6H_3(Me)_2$, MeCN) et le ^{succ}*nacnac*$^{CH(Me)Ph}$CuL (PPh_3, $CNC_6H_3(Me)_2$, pyridine). Tous ces complexes sont jaunes et sensibles à l'air et à l'humidité. En l'absence de fortes bases de Lewis, on n'observe pas de réaction entre les précurseurs de cuivre et les ligands N-alkyle substitués.

Les études RMN des complexes dans le C_6D_6 ne présentent pas de complexe de toluène mais un mélange à l'équilibre du (*nacnac*^{xyl}Cu)$_2$(μ-C_6D_6) et *nacnac*^{xyl}Cu(C_6D_6) dans une proportion de 2 pour 1. Alors que l'addition de plus de cinquante équivalents soit de THF, soit de toluène n'induit aucun changement des spectres RMN, l'addition de 2 équivalents de MeCN conduit instantanément au complexe *nacnac*^{xyl}Cu(MeCN). De plus, le (*nacnac*^{xylyl}Cu)$_2$(μ-C_6D_6) ne se coordone ni ne réagit avec le N_2O, même après avoir été chauffé à 60°C pendant treize jours.

En présence de DPA (diphenylacétylène), la réaction du *nacnac*^{Bn}H avec le CuO*t*Bu conduit au dimère ponté (*nacnac*^{Bn}Cu)$_2$(μ-DPA). L'addition d'un excès de DPA (10-12

équivalents) transforme le dimère ponté en complexe lié en position terminale *nacnac*^{Bn}CuDPA. Les *nacnac*^{R}H (R = CH(Me)Ph et *i*-Pr) ne forment pas de complexe ni avec les oléfines ni avec le DPA. Une réactivité similaire a été observée avec les complexes de *nacnac*$^{CH(Me)Ph}$Cu(NCMe) et *nacnac*$^{i\text{-}Pr}$Cu(NCMe). Tandis que le complexe lié en position terminale par MeCN a été isolé et caractérisé, l'équilibre en solution nous laisse suspecter la formation d'un complexe d'acétonitrile ponté.

Des études de réactivité comparatives ont été menées sur quelques complexes de cuivre. La Morpholine ne réagit pas avec le *nacnac*^{Bn}Cu(acrylonitrile) contrairement à l'acrylonitrile libre. L'expérience de l'échange d'oléfine montre que l'acrylonitrile (une oléfine électro-attractrice) se lie plus fortement que les autres oléfines, mettant ainsi en évidence l'importance de la rétrodonation π face à la donation σ. La rétrodonation π est cependant faible comparée aux autres complexes de styrène structurellement caractérisés. Les complexes *nacnac*$^{CH(Me)Ph}$CuL (L = PPh_3 et MeCN) ont été employés dans la cyclopropanation catalytique du styrène et dans l'addition conjuguée du $ZnEt_2$ sur la 2-cyclohexénone, mais les résultats indiquent que le ligand dikétimine est éliminé avant son entrée dans le cycle catalytique. Par conséquent, il n'y a pas d'induction chirale.

Les complexes tétra coordinées de cuivre avec les *nacnac*^{R}Cu(phen) (R = Bn, CH(Me)Ph et Phen = 1,10-phenanthroline, 2-Mes-1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline (dmp) et 2,9-diphenyl-1,10-phenanthroline (dpp)) ont été synthétisés. Ces complexes sont d'une intense couleur bleue et des interactions d'empilement π entre l'un des cycles phényle des ligands *nacnac* et la phénanthroline ont été observées dans les structures à l'état solide. Les mesures en absorption UV-visible ont été effectuées dans le toluène et les bandes MLCT sont déplacées vers le rouge par rapport à celles des complexes de cuivre et bisphénanthroline. Tous ces composés émettent à l'état solide mais les complexes 1,10-phenanthroline et 2-Mes-1,10-phenanthroline n'émettent pas en solution.

Pour renforcer les interactions d'empilement π, les nouveaux ligands *nacnac*^{R}H (R = $CH_2C_6H_2(OMe)_3$, $CH_2C_6F_5$) et leurs complexes de cuivre respectifs ont été préparés avec du dmp et dpp. Afin de permettre la comparaison, le *nacnac*$^{i\text{Bu}}$Cu(dmp) a été synthétisé. Alors que les complexes dmp montrent une augmentation des interactions intramoléculaires

π-π avec les substituants phényle du ligand dikétimine et de la phénanthroline, les complexes dpp ne révèlent pas de telles interactions. Les complexes perfluorés montrent, en absorption et en émission, un déplacement significatif vers le bleu, alors que les complexes substitués par un groupements isobutyle présentent des transitions déplacées vers le rouge. Alors que les intensités de luminescence et les durées de vie sont faibles, les déplacements réduits de Stokes et les pics étroits de luminescence comparables indiquent une réduction des distorsions de l'état excité.

Mots clés: cuivre, β-dikétimine, *nacnac* chirale, rétrodonation π, interactions intramoléculaires π-π, rayons-X.

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Abbreviations

Å	Armstrong
acac	$(CH_3C(O))_2CH^-$
*i*Bu	isobutyl ($CH_2CH(CH_3)_2$)
*n*Bu	*n*-butyl (C_4H_9)
*t*Bu	*tert*-butyl ($C(CH_3)_3$)
bp	boiling point
bm	broad (multiplet)
Bn	benzyl
bs	broad (singlet)
^oC	degrees centigrade
cm^{-1}	inverse centimeter
Cp	cyclopentadienyl (η^5-C_5H_5)
δ	chemical shift (in ppm)
d	doublet
DCM	dichloromethane
dd	doublet of doublets
deg	degree
dipp	2,6-diisopropylphenyl
equiv.	equivalents
Et	ethyl
FWHM	full width at half maximum
g	gram
GC	Gas chromatography
GFC	Supercritical Fluid Chromatography

h	hour
HMQC	heteronuclear multi-quantum correlation
J	coupling constant (in NMR)
L	neutral ligand
LLCT	ligand-ligand charge transfer
Me	methyl
min	minute
mL	millilitre
MLCT	metal-ligand charge transfer
MS	mass spectrometry
MW	molecular weight
nm	nanometer
NMR	nuclear magnetic resonance
ppm	part per milliom
Ph	phenyl
*i*Pr	isopropyl
q	quadruplet (NMR)
R	alkyl group
s	singlet
s	second
succ	succinimido
tol	tolyl
TsOH	*para*-toluene sulfonic acid
t	triplet
xyl	2,6-dimethlphenyl
λ	wavelength

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Introduction

1.1 Application of copper in organic synthesis

Copper is one of the oldest metals known to man occurring in the same group of the periodic table as silver and gold. It occurs freely in nature as well as in mineral forms.[1] Copper is a relatively cheap metal, although increase in its consumption over the last couple of years has prompted a steady rise in its price until the global economic meltdown.[2] Copper is a good conductor of heat and electricity, ductile and malleable, making it useful in electronics and telecommunication. Its physical properties can be enhanced by combining it with other metals to form alloys. In biological systems, copper mediates processes such as electron transfer, metal management, oxygen transport (haemocynin) and, sometimes, it is involved in catalytic activivities.[3] A notable example is the enzyme nitrous oxide reductase (N_2OR), whose active site contains a tetranuclear copper center bridged by a sulfur atom. This enzyme catalyses the two electron reduction of N_2O to atmospheric nitrogen.[4]

Copper occurs mostly in the 0, +I and +II oxidation states. Copper(I) with d^{10} electronic configuration usually forms colourless, air- and moisture-sensitive compounds which may disproportionate to give copper(II) and copper(0) species. Copper(II) compounds, on the other hand, have d^9 electronic configuration. They are usually characterized by their blue or green colour and show more stability in air than copper(I) compounds. Copper(III) compounds have been postulated as intermediates in catalytic cycles but only few have been isolated.[5]

Copper catalysed cyclopropanation of olefins. Cyclopropanes are three-membered ring cycloalkanes which occur as components in some natural products.[6] Synthetic derivatives of cyclopropanes have been widely used as pesticides.[7] In the presence of a diazo compound, copper compounds promote the formation of cyclopropanes from olefins. Recently, synthetic efforts have been based on reacting the olefin and the carbene

asymmetrically. A major development was the use of chiral Schiff-base copper complex (Figure 1.1) by Nozaki in the mid 60s to perform the reaction.[8]

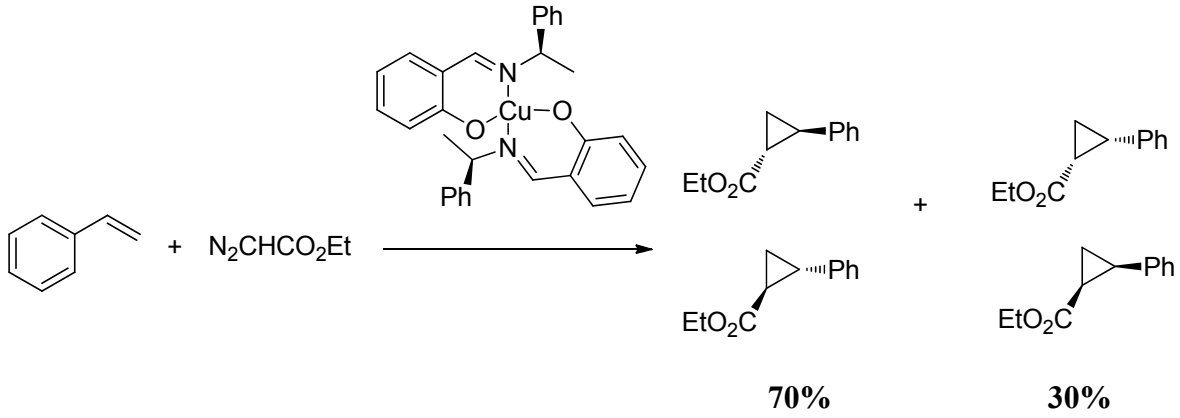
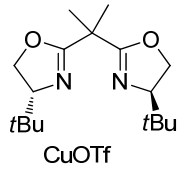
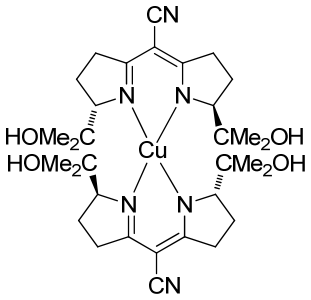


Figure 1.1: Copper catalysed cyclopropanationation of olefin.[8]

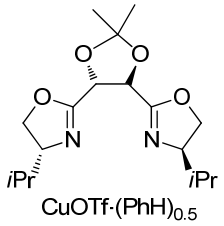
A 70:30 diastereomeric ratio was obtained with only 6% ee, on which Aratani *et al*. improved later by modifying the salicyaldimine ligand.[9] Since then, many chiral ligands have been developed which show very high activities and enantioselectivities (Figure 1.2).



dr: 94:6 (N_2CHCOOBHT)
99% ee (*trans*),
Evans, 1991



dr: 73:27 (N_2CHCOO-*D*-menthyl)
97% ee (*trans*), 95% ee (*cis*)
Pfaltz, 1986



dr: 85:15 (N_2CHCOO-*L*-menthyl)
89% ee (*trans*), 89% ee (*cis*)
Knight, 1996

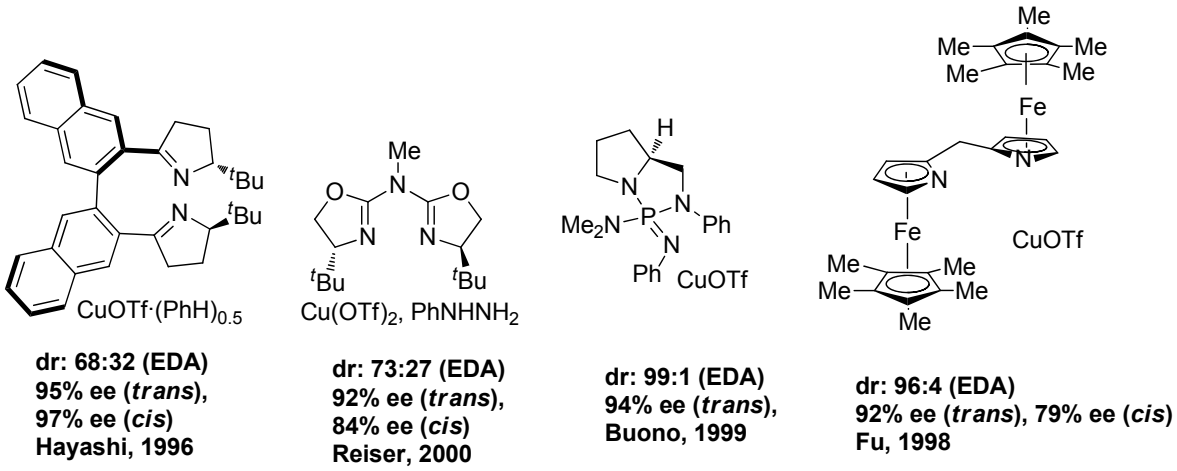


Figure 1.2: Chiral catalyst used in copper catalyzed cyclopropanation of styrene.

Though most copper catalysts used are in +2 oxidation state, the active species is Cu(I), generated *in situ* as a copper carbene 'M=CR_2' intermediate. An example of such a compound was recently isolated and it proved to be active in cyclopropanation.[10] Coordination of the olefin to the carbene is then followed by formation of a four-membered metallacycle which undergoes reductive elimination to yield the organic products (Figure 1.3).

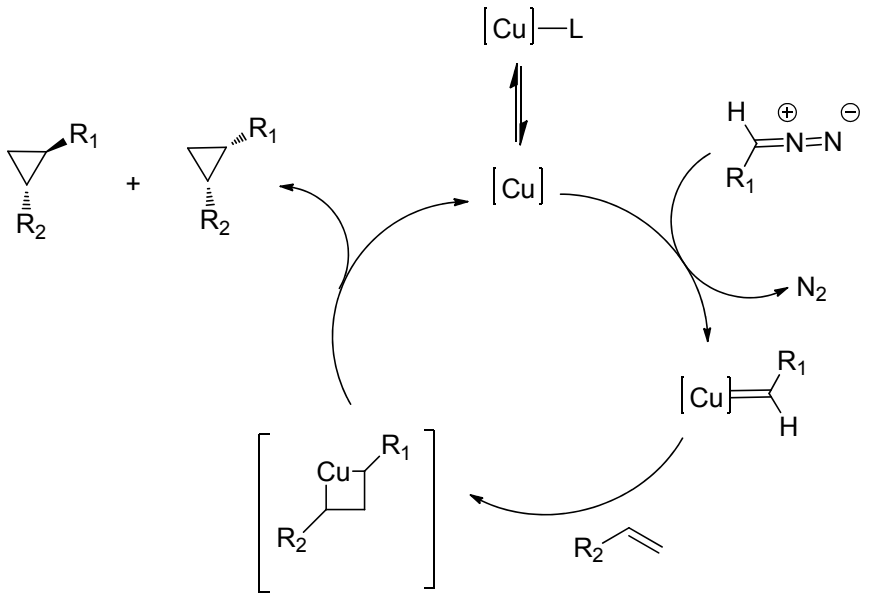


Figure 1.3: Proposed mechanism for copper catalysed cyclopropanations.

Aziridination. Aziridines, like cyclopropanes, are 3-membered rings in which one of the carbon atoms is replaced by a nitrogen atom. Such strained compounds are formed from the reaction of nitrenes with olefins (Figure 1.4). The aziridine units occur as components of natural products, such as in mitomycin which is known to have anti tumour and antibiotic activities.[11]

Copper-catalysed aziridination was developed by Kwartz and Khan after they observed that copper powder catalyses the decomposition of benzenesulfonyl azide into benzenesulfonamide.[12] Major developments include the use of PhINTs [*N*-(*p*-toluensulfonyliminophenyl) iodinane] as nitrene source.[13] Recently, aziridination has been performed using copper β-diketiminato complexes.[14]

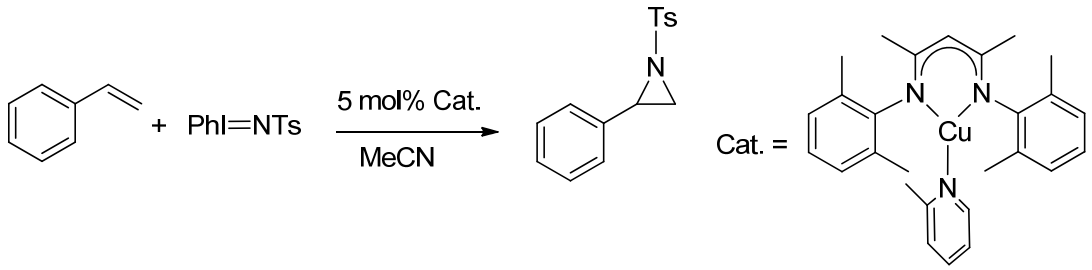


Figure 1.4: Copper catalysed aziridination of styrene.[14]

Conjugate addition reaction. Conjugate addition of alkyl substituents to α,β-unsaturated carbonyl compounds (Michael acceptors) is a C-C bond forming reaction which is regioselective in the presence of copper source, favouring the 1,4-addition product over the 1,2-product.[15] First introduced by Kharash in 1941,[16] the reaction has broad synthetic potential. It is employed, for example, in the synthesis of bioactive β_2-amino acids.[17] The reaction was first performed stoichiometrically using organocuprates.[18] Today, Grignard and dialkylzinc reagents are also used as nucleophiles in the presence of catalytic amounts of a copper source.

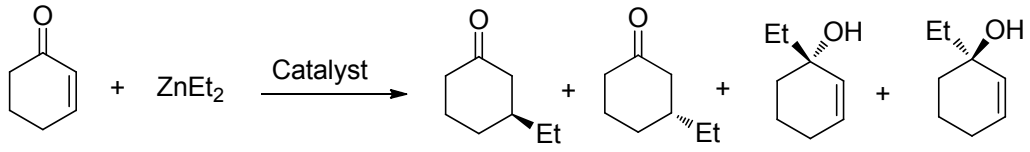


Figure 1.5: Conjugate addition of $ZnEt_2$ to 2-cyclohexenone.

A mechanism for the copper catalysed conjugate addition of $ZnEt_2$ to enones was proposed by Feringa *et al*. (Figure 1.6).[19] Transmetallation between the copper species and organozinc reagent followed by coordination of copper and zinc to the soft and hard part of the enone respectively, yields a π-complex. Such species have been characterized by employing rapid injection NMR techniques.[20] Alkyl group transfer to the enone moiety and acid work-up affords the organic product.

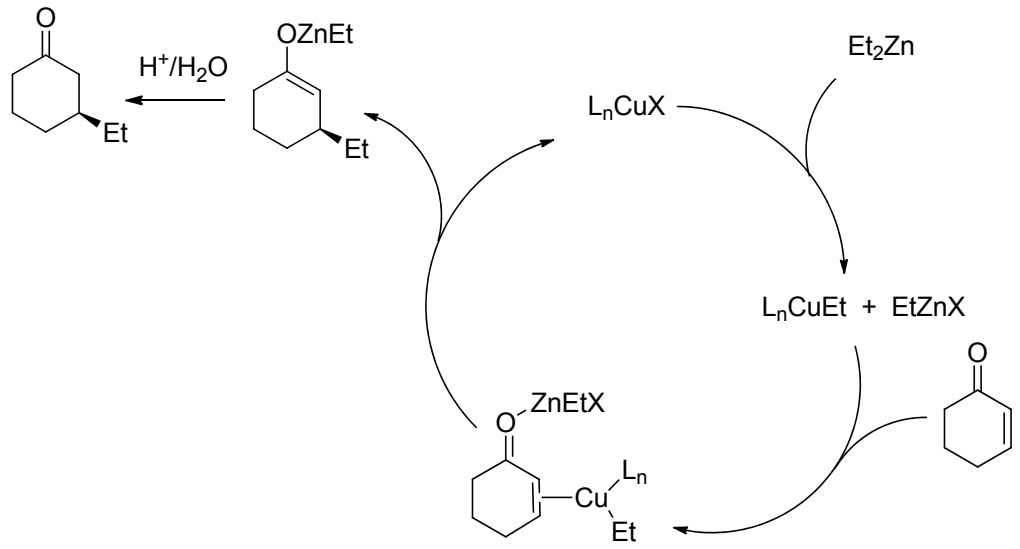


Figure 1.6: Proposed mechanism for copper catalysed conjugate addition reaction.

Ullmann reaction. The Ullmann reaction, otherwise known as Ullmann coupling, is another C-C bond-forming reaction leading to the formation of biaryls in the presence of stoichiometric amounts of copper. Such aryl units are common in natural products[21] and are used as monomers for the synthesis of conductive polymers.[22] It is a heterogeneous reaction that works well for both inter- and intramolecular substrates and tolerates functional groups such as nitro-, aldehyde and even esters.[23] The original protocol as reported by Ullmann in 1901 involved harsh reaction conditions and works well with electron deficient aryl halides leading mostly to symmetrical products.[24]

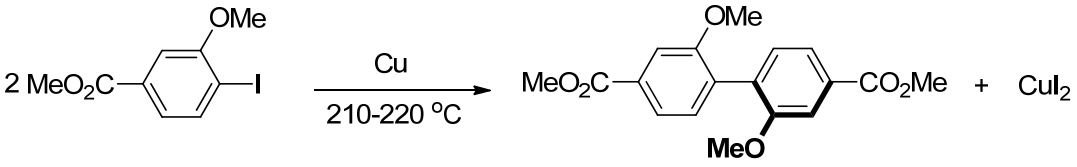


Figure 1.7: Example of Ullmann the reaction.[24]

Over the years, progress has been made in modifying and widening of the scope of the reaction. For example, Ziegler et al.[25] have performed the reaction at ambient temperature with a modified copper source to obtain unsymmetrical biaryls while, Hassan

et al.[26] replaced copper with catalytic amounts of $Pd(OAc)_2$ in the presence of isopropanol as reducing agent. Despite these developments, other coupling schemes such as Heck and Sonogashira reactions are preferred due to their much wider scope.

A simple mechanism for the reaction is depicted below (Figure 1.8). The aryl halide undergoes oxidative addition with copper followed by comproportionation to afford aryl copper which then undergoes a second oxidative addition with another aryl halide. Reductive elimination of the Cu(III) species affords the biaryl.

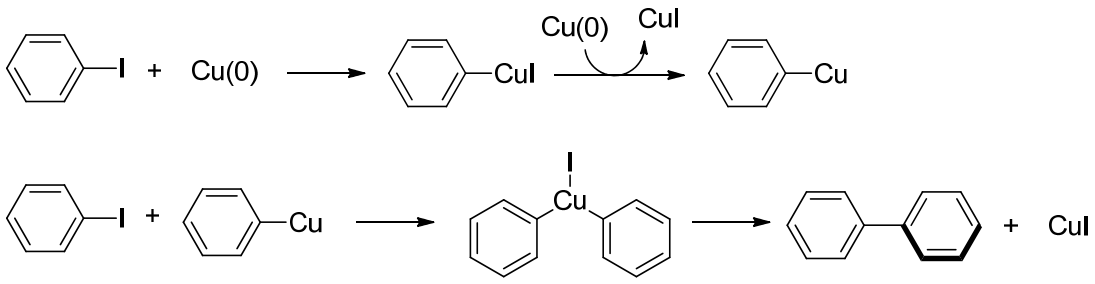


Figure 1.8: Mechanism of Ullmann coupling.

1.2 β-Diketimine ligands

1.2.1 General background

Organometallic chemistry has witnessed a steady growth and the synthesis of cheap, easily synthesized, innocent and tunable ligands has been vital to this development. β-Diketimines (*N,N'*-diaryl-2-amino-4-iminopent-2-ene or *N,N'*-dialkyl-2-amino-4-iminopent-2-ene) cleary fit this description. The coordination chemistry of β-diketiminates or *nacnac*[27] was first officially reported in 1968 by McGeachin[28] and Holm.[29] Since then, their coordination chemistry has evolved with strong emphasis on the *N*-aryl substituted β-diketimines. This can partly be ascribed to Brookhart's discovery in the mid 90s, that late transition metal complexes of α-diimine ligands with bulky *N*-substituents, namely 2,6-diisopropyl (dipp), are active in olefin polymerization and even tolerate polar substrates,[30] which was one of the limitations of the well known Ziegler-Natta catalysts.[31] In 1997, Feldman *et al*. prepared *nacnac*^{dipp}H as an anionic version of this α-diimine ligand.[32]

Although its performance in olefin polymerization was not outstanding, the electronic and steric influence of the *N*-substituents on the metal was so remarkable that it was employed subsequently in biochemistry to model the active sites of metalloproteins.[33] In the following years, new β-diketimine ligands were prepared with varying steric and electronic properties including some with only hydrogen atoms on the α-carbon atoms.[34]

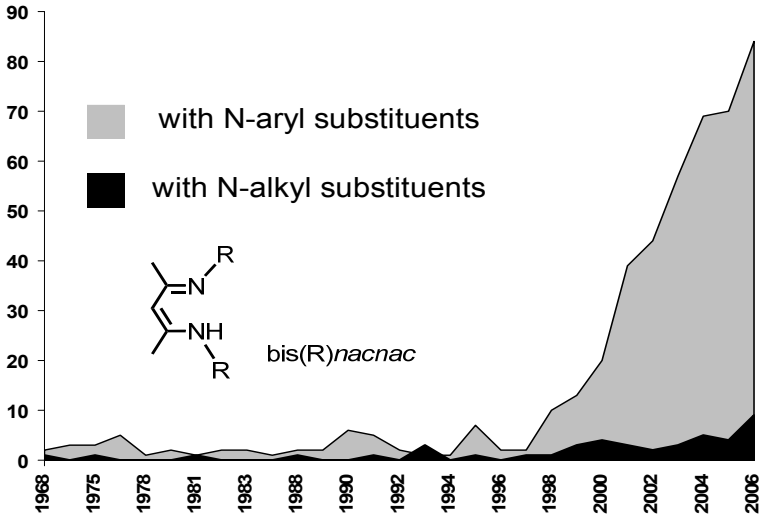
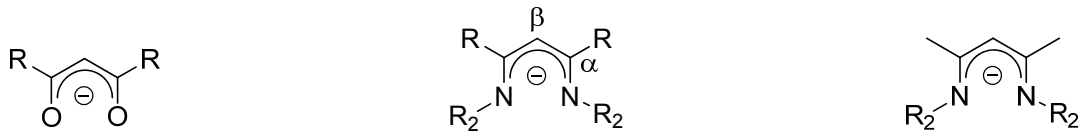


Figure 1.9: Publications featuring the β-diketimine ligands.

1.2.2 Description of β-diketimines

Like cyclopentadienyls (Cp) and trispyrazoylborates (Tp), β-diketimines are monoanionic multidentate ligands.[35] They are derived from 1,3-diones. The carbon atoms attached to the nitrogen atoms are labeled α-carbons while the one between the imino groups is often referred to as the β carbon. The sub-group with Me groups on the α carbon atoms are commonly called *nacnac* since they are the nitrogen equivalent of acetyacetonate (*acac*) (Figure 1.10, **A**). In the literature, the term β-diketiminates (**B**) and *nacnac* (**C**) are often used interchangeably.



A **B** **C**

Figure 1.10: Differentiation among 1,3-diketonate (**A**), β-diketiminates (**B**) and *nacnac* (**C**).

Some major differences exist between acetyacetonates and β-diketimines. For example, in solution, *acac*H exists as an equilibrium mixture of keto and enol forms. The analogous β-diketimine ligands do not show such equilibrium behaviour and only the enamine forms were reported. The appearance of only one resonance for α-CH_3 in a ratio of 6:1 with respect to the β-H indicates rapid tautomeric interconversion of the enamine forms (Figure 1.11) which averages out to the resonance form E (Figure 1.11).[29] Form F, the open conformation is mostly observed when R = H or for protonated salts.

D **E** **F**

Figure 1.11: Tautomerism in *nacnac*H (**D**), resonance form (**E**), and open conformation (**F**).

1.2.3 Properties of β-diketimines

Tunable steric and electronic properties. The electronic and the steric properties of the β-diketimines can be easily modified by varying the substituents of the nitrogen atoms. Such changes influence the preparation and the reactivity of the ligand. Variation in steric demands can lead to drastic geometric changes. For example, $(nacnac^{Ph})_2Co$ is tetrahedral while the sterically less demanding $(nacnac^{H})_2Co$ is square planar.[28,36]

Electronic and steric properties can also be varied by changing the substituents on the β-diketimine backbone, which might influence its conformation, the coordination number and nuclearity of its metal complexes. β-Diketimines with unsubstituted α-carbon atoms may adopt the W- or open conformation in the solid state depending on the substituents on the β-carbon atom (Figure 1.11 F).[34] Bulky groups on the backbone interact sterically with the *N*-substituents. This pushes the *N*-substituents towards the metal in its complexes, reducing the possibility for the metal to attain a high coordination number. The group of Holland used this strategy to generate three-coordinate Fe(I) precursors for the activation of molecular nitrogen.[37]

Good spectator ligands. Like cyclopentadienyl ligands, β-diketimines are good spectator ligands by virtue of the strong bonds formed by the metal ion and the chelating nitrogen atoms.[34] Such a characteristic is very important in catalysis. However, their non-innocent behavior should not be over-emphasized as there are some examples where β-diketiminates are transformed. Mostly, these are related to the high electron density on the central β-carbon atom in the ligand backbone. Yokota *et al*. have described, for example, the oxidative degradation of $(nacnac^{Ar})_2M$ (M = Cu(II), Zn(II) and Ar = 2,6-$C_6H_3(Me)_2$)[38] while Hitchcock *et al*. have shown in certain β-diketiminato lanthanoid complexes that the methyl substituent on the ligand backbone can be deprotonated.[39]

Stabilization of complexes in unusual oxidation states or coordination numbers. The β-diketimine ligand framework stabilizes complexes with unusal oxidation states and or unsaturated coordination geometries, such as three-coordinate Fe(I),[37] Fe(II),[37] Ni(I),[40] Cu(II)[33] and Zn(I)[41] complexes. They have also been applied in main group chemistry and notable examples are *nacnac* complexes of Al(I),[42] Ga(I)[43] and Mg(I).[44] These complexes serve as electron reservoirs and as powerful reducing agents.

Variable bonding modes. β-Diketimines show diverse binding to metal centers. Most metals bind through the two nitrogen atoms (Figure 1.12, A). Some early transition metal ions, due to electron deficiency, can increase their hapticity by involving all NCCCN atoms

in bonding (Figure 1.12, B). In this case, *nacnac* becomes a 6-electron donor as opposed to 4 when the bonding is solely by the nitrogen atoms. Such complexes are usually characterized by out-of-plane disposition of the metal ion and the β-carbon of the *nacnac* ligand, leading to a pseudo-boat conformation with a short β-carbon-metal bond. Examples include the complexes (*nacnac*)$ZrCl_3$ and (*nacnac*)$Zr(Cp)Cl_2$ reported by Lappert and Collins, respectively.[45,46] The coordination mode C has been observed in some lanthanoid complexes.[39] The bonding mode D is very rare. Feldman *et al*. while attempting to synthesize the complex *nacnac*$^{dipp}Pd(MeCN)_2BF_4$ as catalyst for olefin polymerization, serendipituously prepared a new complex with one Pd atom bonding to the nitrogen atoms and another bonding to the β-carbon of the *nacnac* backbone.[32] Another example is the mixed metal complex $\{[LiOEt_2][(nacnac^{dipp}CuI)]\}_2$ prepared by reacting *nacnac*$^{dipp}Li(OEt_2$ with CuI.[47]

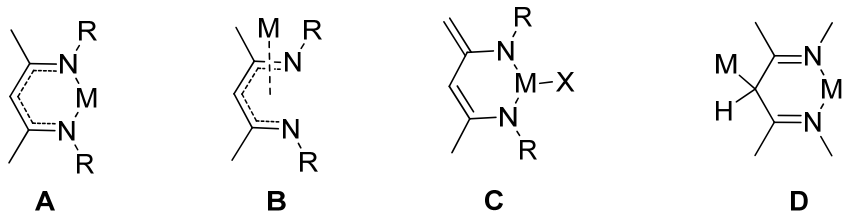


Figure 1.12: Different coordination modes of *nacnac* ligands.

Economic and straightforward synthesis. Some supporting ligands such as semicorrins[48] and the bisoxazoline ligands[49] structurally resemble *nacnac* ligands. Despite the structural similarity, their syntheses require cumbersome multi-step procedures. On the other hand, most β-diketimines are easily prepared from cheap commercially available starting materials in one to three steps. Most compounds are solids, generally pack well in their lattices and are easily purified by crystallization.[37]

1.2.4 Synthesis of the diketimine ligands

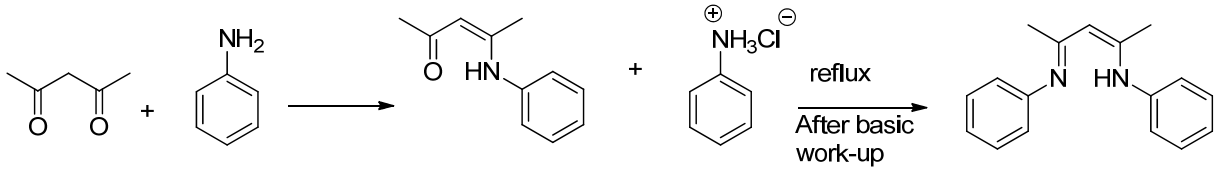
Double condensation of *acac*H with two equiv of a primary amine gives the diketimine. While the first condensation proceeds smoothly even in the absence of

activating agents, the second requires the activation of the carbonyl carbon for which several methods exist.

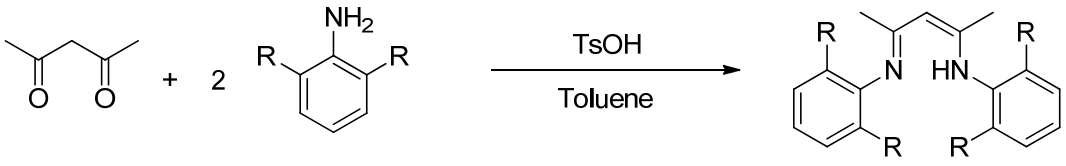
***N*-aryl substituted β-diketimines.** The earliest protocol employed two steps by first forming the mono-condensation product and subsequently refluxing it with the salt of the amine to propel the second condensation (Figure 1.13).[29] In recent literature, most *N*-aryl β-diketimines are prepared by a one-step procedure using *p*-TsOH in refluxing toluene with the help of a Dean-Stark apparatus.[50] The driving force for the reaction is the azeotropic removal of water. HCl in refluxing ethanol is an alternative.[32]

Less often observed is the use of $TiCl_4$[51] as activating reagent, which is mostly used for the synthesis of α-carbon fluorinated β-diketimines. The major draw-back of this method is the requirement of excess amine. Fluorinated β-diketimines are also prepared by employing the Aza-Witting reaction.[52] Another method which has been rarely used is the Knorr and Weiss method. It is a four-step synthesis, suitable for the preparation of very bulky β-diketimines.[53]

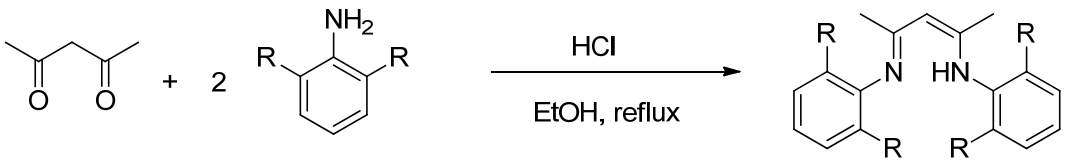
By using the amine salt



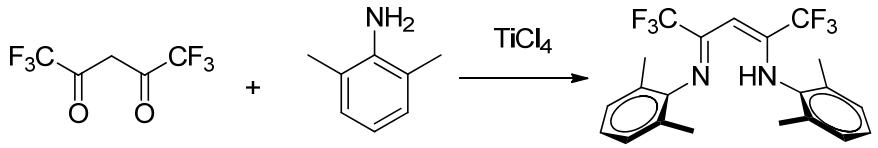
By using Dean Stark apparatus



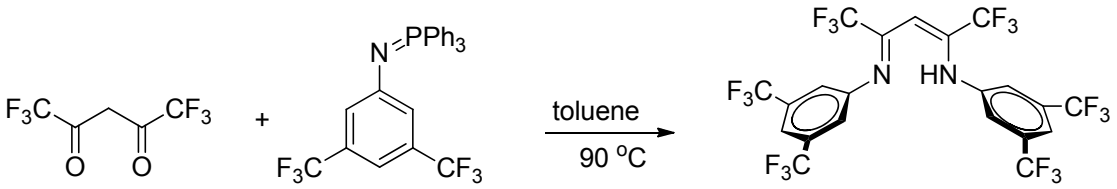
By using ethanolic HCl



By using $TiCl_4$



Aza-Wittig method



Knorr and Weiss method

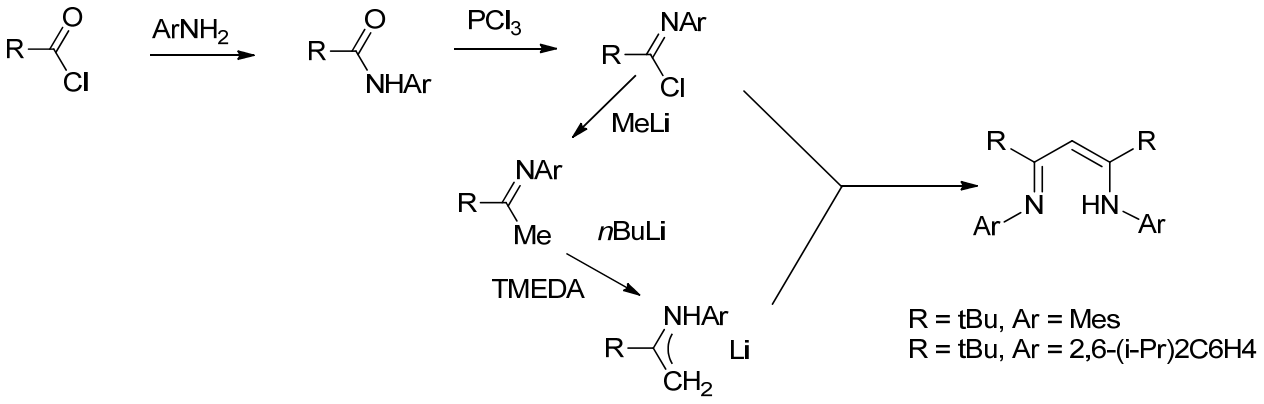
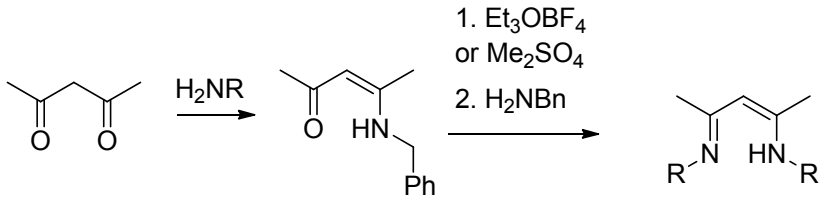


Figure 1.13: Methods to prepare *N*-aryl substituted β-diketimines.

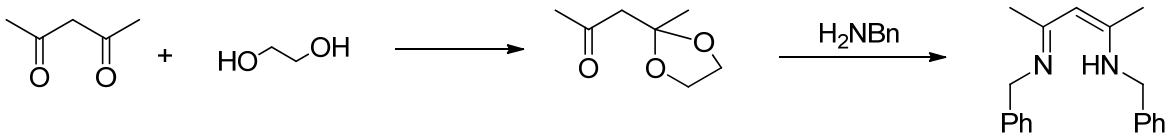
***N*-alkyl substituted β-diketimines.** Prior to this work, aliphatic *N*-substituted diketimine ligands were prepared only by multi-step procedures. The first step is always the preparation of the enaminoketone. The second step involves the use of Meerwein salt as the activating agent. Yields of this reaction are generally below 60%.[28] The air-and moisture

sensitive nature of the Meerwein salt, coupled with its toxicity makes this method not suitable for multigram synthesis. Recently, Bradley *et al*. have employed Me_2SO_4 as activating agent which gave improved yields.[54] Isolated reports describe the reaction of acetyacetone monoketal with the appropriate amine[55,56] or refluxing the enaminoketone in MeI,[57] but these methods have not been generalized. The latter method does not involve the addition of a second equiv of amine and its mechanism has not been clarified.

Using Meerwein salt or Me_2SO_4



From the monoketal



Using MeI

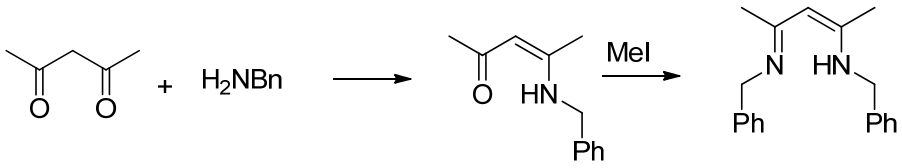


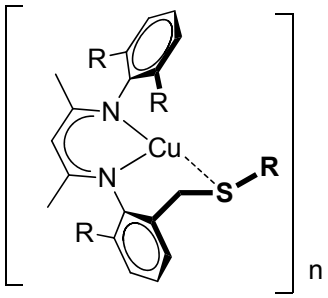
Figure 1.14: Different methods for the preparation of *N*-alkyl substituted β-diketimines.

1.3 β-Diketiminato copper(I) complexes

1.3.1 *N*-Aryl substituted β-diketiminato copper(I) complexes

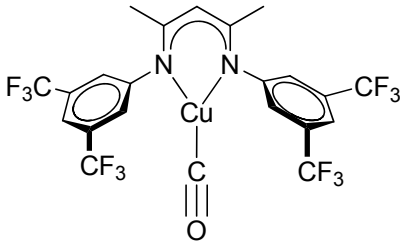
β-Diketiminato compounds are now known for almost all elements in the periodic table. For copper, initial coordination chemistry was based on Cu(II) complexes.[28,29,53,58] Copper(I) *nacnac* complexes were first reported in 2001 and used in the activation of

dioxygen.[59] Since then, more Cu(I) complexes have been prepared as models for the active sites of metalloproteins (Figure 1.15, A), in particular by Tolman's group. For example, Lee *et al*. prepared the mixed Cu(I)/Cu(II) *nacnac*^{dipp}CuSC(Ph)$_2$CH$_2$C$_6$H$_4$NCu*nacnac*^{dipp} as model of the histidine-cysteine bridged copper array nitrite oxide reductase,[60] while Aboelella *et al*. synthesized a Cu(I) thioether β-diketiminato complex to investigate the role of the methionine ligand in copper monooxygenases.[61] A mixed Cu^{I}-Ge^{II} complex has been used for reactivity studies to probe the lability of the Cu-Ge bond.[62] Laiter *et al*. also prepared a series of fluorinated *nacnac* complexes to investigate the effects of electron withdrawing substituents on the complexes and their use in intramolecular aerobic hydroxylation (Figure 1.15, B).[51] Copper *nacnac* complexes have also been applied in organic transformations. Isolated Cu(I) carbene (Figure 1.15, C)[63] and nitrene complexes have been successfully employed in cyclopropanation, aziridination and in C-H bond amination.[64] Complexes lacking α-carbon substituents are also known with various substituents on the β-carbon. These complexes adopt open or close conformation, depending on the *N*-substituent and the substituent on the central carbon atom of the diketimine backbone, forming oligomers and in some cases, polymers which could find application in supramolecular chemistry (Figure 1.15, D).[34]



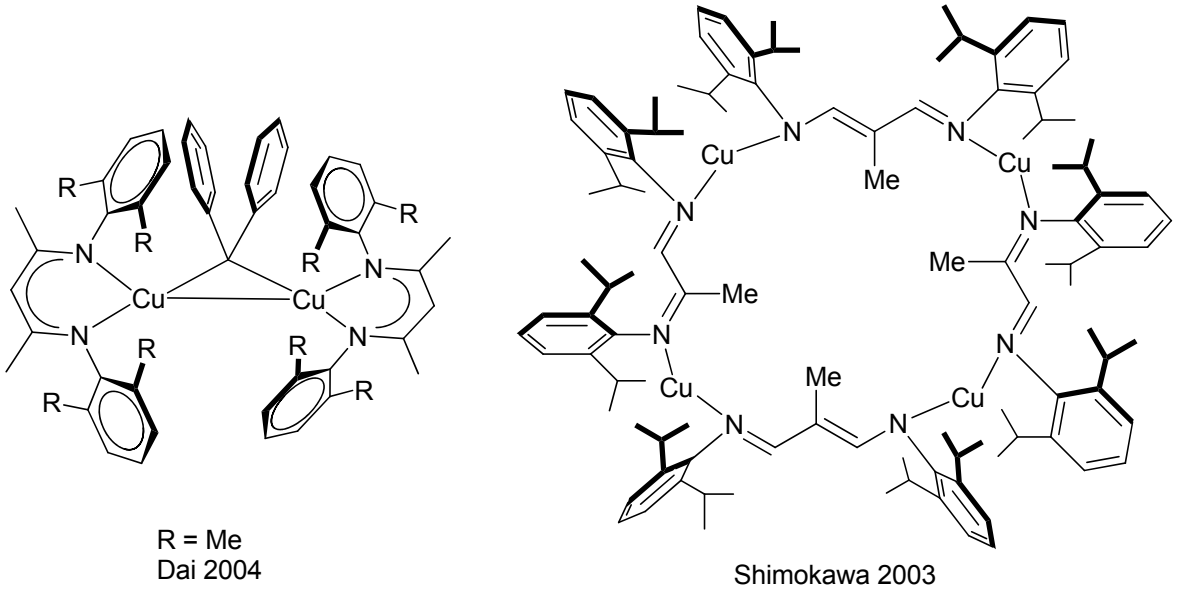
R = iPr, R = Me or Ph
Aboelella 2006

A



Laiter 2003

B



C **D**

Figure 1.15: Examples of copper(I) diketiminato complexes.

1.3.2 Preparation Copper(I) diketiminato complexes

Salt metathesis. β-Diketiminate copper(I) complexes are mostly prepared by reacting *nacnac*Li or *nacnac*Tl with a suitable copper(I) source which include $Cu(NCCH_3)_4PF_6$,[34] CuX (X = Br,[63] I[65]), $Cu(NCCH_3)_4CF_3SO_3$.[66] A major problem with these copper salts is their insolubility in common organic solvents. Also, simple reaction of *nacnac*Li with CuX does not often proceed to the desired product.[46] $CuBr{\cdot}SMe_2$ has been employed as a more soluble copper precursor.[59]

Protonation with the free ligand. In 2005, Dai *et al*. performed the cupration of *nacnac* ligand using Cu*O*t*Bu*[63] directly with the protonated ligand, which afforded better yields than the reaction of *nacnac*Tl with $CuBr{\cdot}SMe_2$. MesCu[51] and $(Me_3SiCH_2Cu)_4$[61,67] have also been used. This method has the advantage that the copper salts are soluble in most organic solvents and that the only by-products are volatile and can easily be removed.

1.3.3 *N*-Alkyl β-diketiminato copper(I) complexes.

Unlike the *N*-aryl β-diketiminates, which are known for almost all elements in the periodic table, the *N*-alkyl β-diketiminates are less common. Copper complexes with simple *N*- alkyl substituents were employed in CVD and ALD applications.[68,69] However, most of the complexes used for this purpose are in the +2 oxidation state. Copper(I) complexes with simple *N*-alkyl substituents such as Me and Et tend to be unstable and disproportionate to afford copper(II) species.[68] However, in 2006, Park *et al*. reported copper(I) complexes with simple *N*-alkyl substituents supported by vinyltrimethylsilylane which were employed in CVD studies.[70,71] In the same year, Thompson *et al*. prepared the *nacnac*^{iBu}Cu($Me_3SiCCSiMe_3$) and used it to to demonstrate the influence of ancillary ligands on π backbonding.[72] In 2009, Arri *et al*. reported the synthesis of a *nacnac*$^{i Pr}$Cu-germylene complex.[73]

1.4 Research objective

The coordination chemistry of the β-diketiminate ligand is broad, but mostly limited to the *N*-aryl substituted ligands. For copper(I), only three articles and one patent report *N*-alkyl substituted complexes,[70-73] one of them appeared in the literature while this work was in progress.

The objective of this research is to explore the chemistry of *N*-alkyl β-diketimines with emphasis on their copper(I) complexes. A preliminary, but essential part of the work will explore the influence of the *N*-alkyl substituents on complex synthesis and stability. Afterwards, the *N*-alkyl substituted copper diketiminato complexes will be investigated to take advantage of changes introduced by the the *N*-alkyl substituents, namely: higher basicity, the option to introduce chirality and the changes in the steric environment due to an sp^3-hybridized atom as the *N*-substituent.

In more detail:

- In chapter two, complexes with *N*-xylyl substituents are prepared as potential biomimetic models for N_2O reductase. This is the only chapter not dealing with *N*-alkyl substituents and it stands somehow isolated from the rest of the work.

- In the third chapter, the first chiral β-diketimine is prepared and subsequently used to prepare the respective copper(I) complexes. Their application in the catalytic cyclopropanation of styrene and 1,4-conjugate addition of $ZnEt_2$ to 2-cyclohexenone will be discussed in chapter four.
- In chapter five, copper(I) complexes with *N*-*i*Pr substituents are prepared to investigate whether the lack of reactivity in the presence of olefins is peculiar to β-diketiminates with *N*-*sec*-alkyl substituents.
- Chapters six and seven discuss *nacnac* copper(I) complexes with an *N*-Bn substituent. Their π backbonding characteristics will be discussed in chapter six while the ability of the Bn substituents to form intramolecular π stacking interactions found application in the synthesis of luminescent copper complexes (chapter 7).

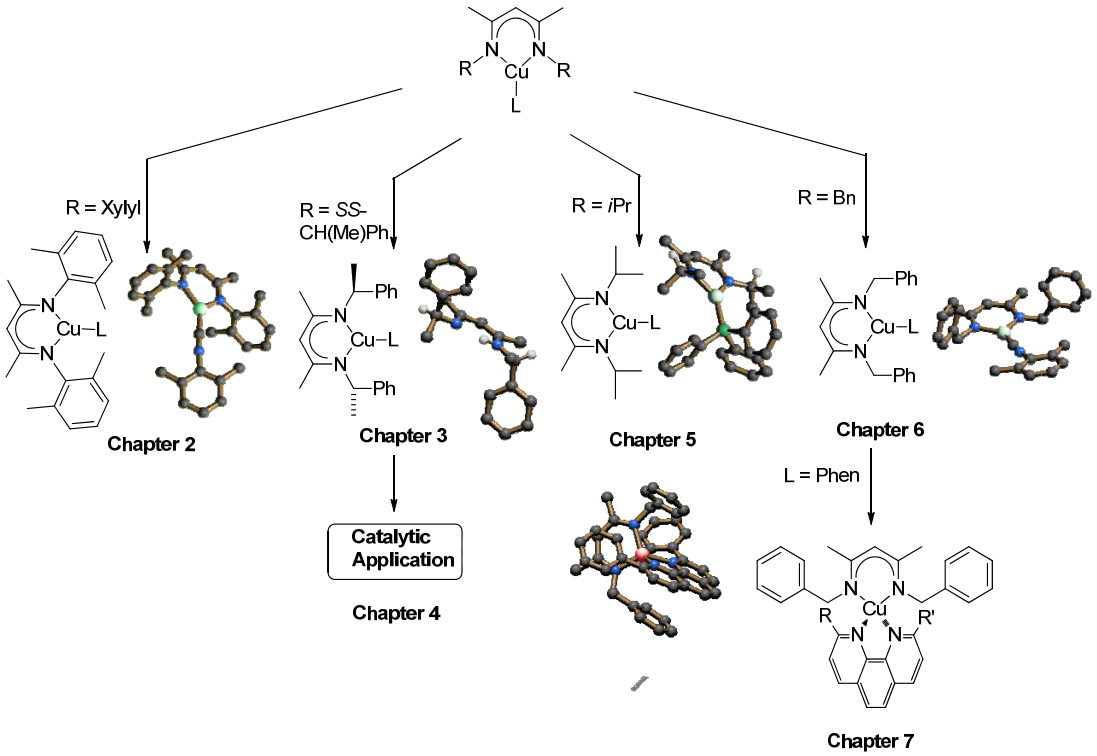


Figure 1.16: Working plan

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Chapter 2

Syntheses and structures of bis(2,6-xylyl-*nacnac*) copper(I) complexes

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Paul O. Oguadinma and Frank Schaper

Département de chimie, Université de Montréal, Montréal, Québec, H3C 3J7, Canada.

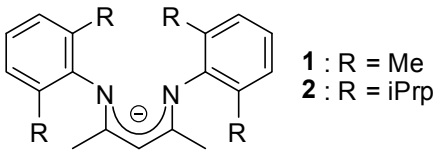
Abstract

The copper(I) complex {(bis-2,6-dimethylphenyl-penta-2,3-diiminato)Cu}$_2$(μ-toluene), **3** has been prepared and its reactivity with Lewis bases and nitrous oxide investigated. Complex **3** crystallizes as a toluene-bridged dimer and forms mono- and dinuclear benzene adducts in C_6D_6 solution. It does not coordinate excess THF, but reacts quantitatively with 2 equiv. of acetonitrile. Reaction with 2,6-xylyl isonitrile yields (bis-2,6-dimethylphenyl-penta-2,3-diiminato)Cu(2,6-xylyl isonitrile), **6**, (ν_{CN} = 2123 cm^{-1}), which was characterized by an X-ray diffraction study. Complex **3** does not react with nitrous oxide in either C_6D_6 solution (5 days at 50 °C) or in diethyl ether (13 days at ambient temperature).

1. Introduction

Nitrous oxide, N_2O, is able to oxidize unsaturated carbon-carbon bonds, albeit only at elevated pressures and temperatures [1-5], while reactions involving transition metal complexes as catalysts or reagents proceed under much milder conditions [6-17]. Although coordination of nitrous oxide to the metal center is probably involved in all of these reactions, very little is known about the coordination chemistry of nitrous oxide [18-24].

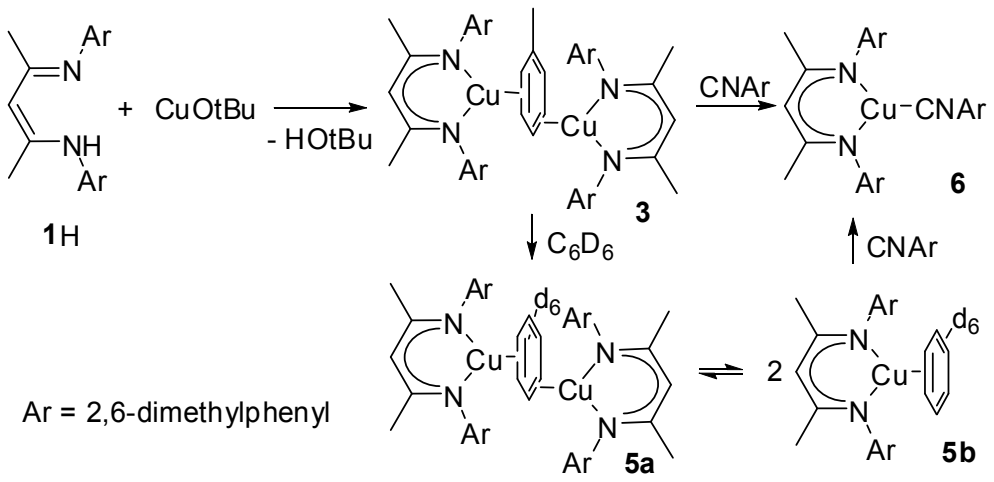
Recently, coordination of nitrous oxide to copper atoms has gathered additional interest. The crystal structure of the enzyme nitrous oxide reductase revealed a unprecedented Cu_4S-cluster as its active center for the reduction of nitrous oxide (Cu_Z) [25, 26], and a bridging coordination of nitrous oxide to two copper centers was proposed as an essential part of the reaction mechanism [27, 28]. We were interested in the reactivity of nitrous oxide with well defined mononuclear copper complexes, in particular with copper complexes containing an *N,N'*-substituted 2,4-pentane-diketiminato (= "*nacnac*") ligand (Scheme 2.1), which have been extensively studied as models for the activation of dioxygen in biological systems [29-34]. We report herein the synthesis and characterization of Cu(I) complexes carrying a bis(2,6-xylyl) *nacnac* ligand, which proved, however, unreactive towards nitrous oxide even at elevated temperatures and increased reaction times.



Scheme 2.1

2. Results and Discussion

2.1. Complex Synthesis. Several pathways have been described for the synthesis of (*nacnac*)Cu(I) complexes with varying ancillary substituents at the copper center [29, 35-39]. Given the poor coordinative ability of nitrous oxide, we considered it necessary to avoid strongly coordinating ancillary ligands such as acetonitrile or olefins, thus eliminating the often used $[Cu(NCMe)_4][OTf]$ salt as a possible starting material. Direct reactions of copper iodide with **1**Li(THF) or **2**Li(THF) failed in our hands to give the desired compound. We attempted to synthesize the desired Cu(I) complex *via* the corresponding Cu(II) compounds, but neither comproportionation of the corresponding Cu(II) complex **1**Cu(OAc) or **2**CuCl [40] with copper metal, nor reduction with a methyl Grignard reagent, employing the known instability of Cu(II) alkyls versus reductive elimination, were successful. We thus turned to a protonation route using Cu(O*t*Bu), introduced by Warren and coworkers as an economic and soluble starting material for the preparation of copper complexes [38]. Reaction of the protonated ligand **1**H with Cu(O*t*Bu) and recrystallisation from toluene/hexane yielded the toluene-bridged dimeric complex $(\mathbf{1}Cu)_2$(μ-toluene), **3**, in 90% yield (Scheme 2.2). The preparation of derivatives of **3**, i.e. $(\mathbf{1}Cu)_2$, lacking the bridging toluene molecule, as well as **1**Cu(L) complexes where L is a more strongly coordinating ligand such as olefin, phosphine, lutidine or acetonitrile has been reported previously [30, 35, 37, 41].



Scheme 2.2

In the absence of more strongly coordinating ligands, *nacnac* copper complexes form mono- or dinuclear complexes with the copper center coordinated either to an aromatic solvent or to the aromatic *N*-aryl substituent [36-38, 41, 42]. An X-ray diffraction study confirmed that here a toluene bridged dimer was obtained (Figure 2.1). Its structure is similar to the related compound {(bis-2,4,6-trimethylphenyl-nacnac)Cu}$_2$(μ-toluene), **4**, reported by Badiei et al. [38]. Complex **3** displays a trigonal coordination geometry around the copper atom. Bond distances in the ligand and to the metal centers are comparable to those found in similar compounds (Table II-1). As typically observed in *nacnac* copper olefin/arene complexes where rotation of the unsaturated ligand is possible, the coordinated double bond is co-planar with the mean plane of the *nacnac* copper fragment. Localisation of the double bonds in the bridging toluene molecule is evidenced by the alternation of the C-C distances in the aromatic ring. A comparable alternation was observed for **4**, while it is significantly less pronounced in complexes with non-bridging arenes (Table II-1). Coordination of C44-C45 and C46-C47 to the copper centers results in a significant elongation of these bond distances in comparison to the "isolated double bond" C48-C43 (1.405(3) and 1.404(3) Å, compared to 1.361(3) Å, respectively).

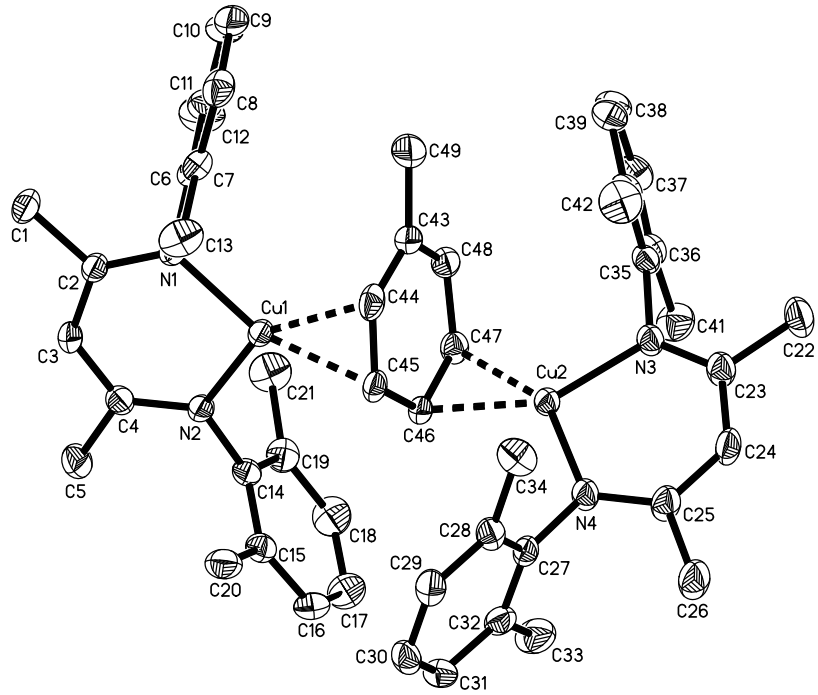


Figure 2.1: Crystal structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

Table II-1: Selected Bond Distances and Angles of **3**, **4** and Related Complexes

	3	**4** [a]	related complexes [b]
Cu-N [Å]	1.932(2) - 1.949(2)	1.922 - 1.942	1.903 - 1.969
Cu-$C_{arom.}$ [Å]	2.055(2) - 2.084(2)	2.027 - 2.078	2.047 - 2.119
C44-C45 [Å]	1.405(3)	1.402	1.380 - 1.402
C46-C47 [Å]	1.404(3)	1.400	
C43-C44 [Å]	1.437(3)	1.438	1.323 - 1.423
C45-C46 [Å]	1.440(3)	1.436	
C47-C48 [Å]	1.431(3)	1.435	
C48-C43 [Å]	1.361(3)	1.361	
N-Cu-N	98.9(1) - 100.1(1) °	98.8 - 99.0 °	99.2 - 100.7 °

[a] see ref. [38], [b] see ref. [36, 37, 41, 42]

^{1}H NMR spectra of **3** in C_6D_6 display two sets of signals corresponding to a C_{2v}-symmetric *nacnac* ligand. No signals for coordinated toluene were detected. In analogy to assignments made by Badiei et al. for **4**, which showed a comparable behaviour [38], we assign these two species to an equilibrium mixture of the benzene adducts {**1**Cu}$_2$(μ-C_6D_6), **5a**, and **1**Cu(η^2-C_6D_6), **5b** (Scheme 2.2). Irreversible loss of benzene and formation of a benzene-bridged dinuclear copper complex was also reported by Laitar *et al*., in this case using a fluorinated nacnac ligand [36]. The ratio of **5a** and **5b** remained unchanged upon addition of up to 50 equiv. of toluene, consistent with their assignment as benzene coordinated complexes. Upon dilution the NMR resonances observed at higher field diminishes and we thus assign this species to the dinuclear complex **5a**. An equilibrium constant K_{300K} = [**5b**]^2/[**5a**] = 130-220 M was found over a concentration range of 2-36 mM **3** in C_6D_6. As expected, no peaks originating from close contacts between the two species were observed in NOESY spectra of **3** in C_6D_6. Cross peaks due to chemical exchange indicate a reasonably fast interconversion at room temperature, in agreement with the fact that the original toluene adduct was never observed. This is in contrast to the behaviour described for **4**, where broadened signals of the original toluene adduct were observed to transform slowly, overnight, into the putative benzene adducts [38].

2.2. Reactivity towards different ligands. Addition of up to 50 equiv THF to a C_6D_6 solution of **3** failed to have any noticeable influence on its ^{1}H NMR spectrum. In contrast, formation of the putative complex **1**Cu(NCMe) was observed in the presence of 2 equiv. of acetonitrile, indicating as expected a strong coordination of this solvent to *nacnac* copper complexes. No attempt was undertaken to isolate **1**Cu(NCMe). Addition of 2,6-xylyl isonitrile to **3**/C_6D_6 led to immediate formation of a single product, which was assigned as **1**Cu{CN($Me_2C_6H_3$)}, **6**. This assignment was supported by direct synthesis of **6** and its crystal structure analysis. The structure of **6** displays the expected trigonal coordination of the copper center. The η^2-coordinated *nacnac* ligand is planar, bond distances indicate complete delocalisation of the double bonds in the ligand backbone and the copper atom is located in the mean ligand plane (∠(Cu1,N1,N2)(Cu1,N1,N2,C2-C4 = 7°). The structural features of **6** (Table II-2) are similar to those of analogous xylyl isonitrile complexes with

the bis-2,4,6-trimethylphenyl *nacnac* [38] or bis-2,6-diisopropylphenyl *nacnac* ligand [43]. Compound **6** resembles the former particularly in the symmetric placement of the isonitrile ligand (Δ(Cu-N) = 13 and 19 pm, Δ(C-Cu-N) = 6 and 9°, respectively), while the sterically more encumbered isopropyl substituted complex displays a more asymmetric coordination (Δ(Cu-N) = 34 pm, Δ(C-Cu-N) = 22°). The C-N distance (1.157(3) Å) and the N-C-C angle of the isonitrile (173.8(2)°) are in the middle of the range observed for metal complexes containing a κ-bound 2,6-xylyl isonitrile ligand (1.159(26) Å and 172(6)° [44]) and similar to that of the free ligand (1.160-1.161 Å [45]). The lack of significant back-bonding indicated by the structural data is substantiated by the stretching frequency ν_{CN} = 2123 cm^{-1} observed for solutions of **6** in toluene, which is higher than that of free isonitrile (ν_{CN} = 2119 cm^{-1}) [46].

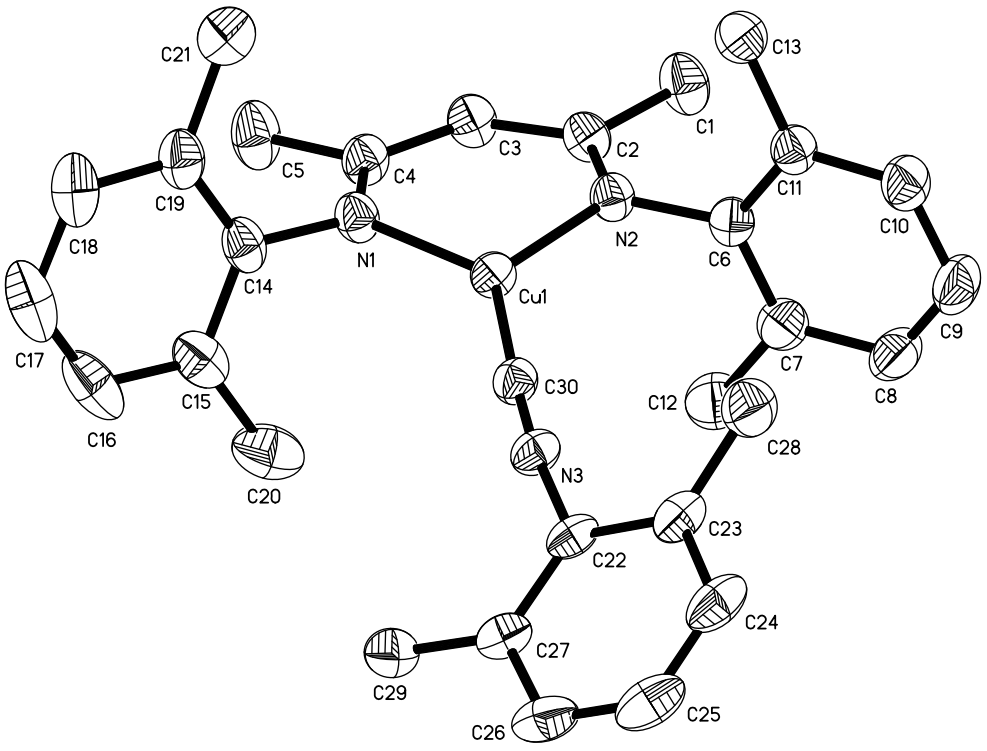


Figure 2.2: Crystal structure of **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

Table II-2

Selected Bond Distances and Angles of **6** and other N,N'-Bis-aryl-*nacnac* Copper (2,6-Xylyl Isonitrile) Complexes.

	Ar = 2,6-$Me_2C_6H_2$, **6**	Ar = 2,4,6-$Me_3C_6H_2$ [a]	Ar = 2,6-*i*$Prp_2C_6H_3$ [b]
Cu1 – N1	1.933(2) Å	1.926(2) Å	1.928(2) Å
Cu1 – N2	1.946(2) Å	1.945(1) Å	1.962(2) Å
Cu1 – C30	1.822(2) Å	1.814(2) Å	1.817(2) Å
C30 – N3	1.157(3) Å	1.159(2) Å	1.158(3) Å
C30–N3–C22	173.8(2)°	177.0(2)°	171.4(2)°
N1–Cu1–C30	134.0(1)°	135.5(1)°	141.8(1)°
N2–Cu1–C30	127.6(1)°	126.6(1)°	120.0(1)°
∠ nacnac, isonitrile [c]	35°	35°	45°

[a] see ref. [38], [b] see ref. [43], [c] ∠ (Cu1, N1, N2, C2-C5)(C22-C29)

2.3. Reactivity towards nitrous oxide. Solutions of **3** in C_6D_6 under 1 atm of N_2O at room temperature displayed no changes in their NMR spectra, indicating that nitrous oxide coordination does not occur to a visible extent under these conditions. More surprisingly, however, neither any noticeable decline in the concentration of **3** (or more precisely: in the concentrations of **5a** and **5b**, obtained upon dissolution of **3** in C_6D_6), nor any colour change was observed when a solution of **3** in C_6D_6 was kept for 5 days in presence of an excess of nitrous oxide (1 atm N_2O, exclusion of light, ambient temperature). After heating for 5 days at 60 °C, the concentration of **3** declined by 10-15%. Approximately the same ratio of decomposition was observed for the control experiment (nitrogen atmosphere) under identical conditions and we have to conclude that there is no evidence for the oxidation of **3** by nitrous oxide [47].

Given the fact that the benzene solvent displaces the bridging toluene in **3** and could not be replaced by added THF, we investigated reactions of **3** with N_2O in diethyl ether solution to minimize inhibition of nitrous oxide coordination by the solvent. Solutions of **3** in Et_2O ($3\cdot10^{-4}$ – $5\cdot10^{-3}$ M) under 1 atm of nitrous oxide (10-200 equiv) were kept under

exclusion of light at ambient temperatures for 6-13 days. No change of the yellowish colour was observed and UV/vis spectra, measured for less concentrated solutions, remained significantly different from those of solutions exposed to oxygen. In all experiments, spectral changes were comparable to those observed for control experiments under nitrogen atmosphere and exposure to dry oxygen resulted in an immediate colour change to dark brown even after prolonged storage under N_2O atmosphere. We have to conclude that **3** was not oxidised by N_2O in any measurable extend.

3. Conclusion

Nitrous oxide lived up to its reputation as a "poor" ligand in its failure to coordinate to *nacnac* copper complexes under the conditions examined here. Reactions of **1**Cu(L) with nitrous oxide in benzene or diethyl ether solutions, if they occurred at all, were too slow to be detected next to complex degradation (under nitrogen atmosphere and otherwise identical conditions appr. 1-3% per day). Further investigations, e. g. reactions of N_2O with dinuclear copper complexes, are necessary to determine if this lack of reactivity is related to the fact that coordination to two copper centers is an essential part of the proposed mechanism of nitrous oxide reduction in biological systems [28].

4. Experimental Section

4.1. General

All reactions were carried out under nitrogen atmosphere using Schlenk or glove box techniques. THF was distilled from sodium/benzophenone, all other solvents were dried by passage through activated aluminium oxide (MBraun SPS) and de-oxygenated by repeated extraction with nitrogen. C_6D_6 was distilled from Na and de-oxygenated by three freeze-pump-thaw cycles. **1**H [48], **2**H [49], and CuO^{t}Bu [50] were synthesized as reported. All other chemicals were obtained from commercial suppliers and used as received. NMR spectra were recorded on a Bruker ARX 400MHz spectrometer and referenced to residual solvent ($C_6D_5\underline{H}$: δ 7.15, $\underline{C}_6D_6$: δ 128.02). Elemental analyses were performed by the Laboratoire d'Analyse Elémentaire (Université de Montréal).

4.2. (*N,N′*-bis-2,6-$Me_2C_6H_3$-*nacnac*)Cu(OAc), ({1}Cu{OAc}) (2)

Following the procedure published for the analogous *N,N′*-dimesityl complex [51], **1**H (1.50 g, 4.9 mmol) was dissolved in a mixture of methanol and dichloromethane (4:1, 125 mL) and added drop-wise to a solution of $Cu(OAc)_2$ (0.17 g, 4.9 mmol) in the same solvent mixture. On addition the originally blue solution turned light-green, dark-green and finally black. After stirring for 1.5 h at ambient temperature, the solvent was evaporated and the obtained brown precipitate washed twice with water (30 mL) and dried under vacuum (1.3 g, 84%). Found: C, 64.72, H, 6.59, N, 6.84. Calc. for $C_{23}H_{28}N_2O_2Cu$: C, 64.56, H, 6.57, N, 6.81.

4.3. {(*N,N′*-bis-2,6-$Me_2C_6H_3$-*nacnac*)Cu}$_2$(μ-C_7H_8) (3)

To a mixture of **1**H (3.28 g, 7.45 mmol) and Cu*O*tBu (1.50 g, 7.50 mmol), toluene (20 mL) was added. After stirring for 2h, the yellow-brown solution was filtered through a pad of celite, concentrated to one fifth of its volume and layered with hexane (20 mL). Yellow crystals of **3** (2.7 g, 90%), formed after 2 days at room temperature. δ_H (C_6D_6): a mixture of a dinuclear, **5a**, and a mononuclear C_6D_6 adduct, **5b**, was observed in C_6D_6 solution (see text): **5b**: 6.95-7.10 (m, $C_{Ar}\underline{H}$), 4.77 (s, 1 H, C$\underline{H}$), 2.01 (s, 12 H, ArC$\underline{H}_3$), 1.63 (s, 6 H, C(N)C$\underline{H}_3$). **5a**: 7.10-6.95 (m, $C_{Ar}\underline{H}$), 4.74 (s, 2 H, CH), 1.89 (s, 24 H, ArC$\underline{H}_3$), 1.55 (s, 12 H, C(N)C$\underline{H}_3$). δ_C (C_6D_6): **5a**: 159.62, 150.7, 130.6, 128.2 (partially obscured by solvent), 123.3, 93.4, 22.9 (N=C$\underline{Me}$), 18.8 (Ar$\underline{Me}$). **5b**: 159.64, 150.6, 130.7, 128.2 (partially obscured by solvent), 123.2, 93.1, 23.2 (N=C$\underline{Me}$), 18.9 (Ar$\underline{Me}$). Found: C, 70.56; H, 6.94; N, 6.73. Calc. for $C_{49}H_{58}N_4Cu_2$: C, 70.70; H, 6.97; N, 6.71.

4.4. (*N,N′*-bis-2,6-$Me_2C_6H_3$-*nacnac*)Cu{CN(2,6-$Me_2C_6H_3$)} (6)

To a mixture of **3** (200 mg, 0.24 mmol) and 2,6-xylylisonitrile (33 mg, 0.25 mmol), toluene (1 mL) was added and the resulting yellow solution was stirred for 1h, layered with hexane (2 mL) and kept at -35 °C. Yellow crystals of **6** (124 mg, 52%) formed after 2 days. δ_H (C_6D_6) 6.41-7.16 (m, 9 H, $C_{Ar}\underline{H}$), 5.02 (s, 1 H, C$\underline{H}$), 2.42 (s, 12 H, ArC$\underline{H}_3$), 1.77 (s, 6 H), 1.63 (s, 6 H). δ_C (C_6D_6) 162.6, 162.5 (weak), 153.0, 134.9, 130.3, 128.4, 128.3, 127.5,

122.8, (one aromatic peak missing), 94.3, 22.4, 19.3, 18.0. Found: C, 71.92; H, 6.81; N, 8.43. Calc. for $C_{30}H_{34}N_3Cu$: C, 72.03; H, 6.86; N, 8.47.

4.5. Reaction of 3 with N_2O in C_6D_6 solution

The desired complex **3** (15 mg, 0.018 mmol) was dissolved in C_6D_6 (0.8 mL). C_6Me_6 was added as an internal standard. The ensuing yellow solution was transferred to a J. Young NMR tube. Two freeze-pump-thaw cycles were performed to remove N_2, and N_2O (2 mL, 1 atm, 0.08 mmol) was introduced to the evacuated tube after warming to room temperature. As a control, an identical solution was prepared without addition of N_2O. NMR tubes were kept either at room temperature or at 60 °C under exclusion of light and monitored by ^1H NMR at room temperature.

4.6. Reaction of 3 with N_2O in Et_2O solution

a) A 25 mL Schlenk flask was charged with **3** (50 mg, 0.06 mmol) and Et_2O (12 mL). After two freeze-pump-thaw cycles, N_2O (1 atm, 0.8 mmol) was introduced to the evacuated flask. For control experiments, an identical solution was left either under nitrogen atmosphere. The solutions were kept under exclusion of light for 5 days without any visible colour change. An immediate colour change to brown was observed on exposure to oxygen.

b) A 25 mL Schlenk flask was charged with 12 mL of a solution of **3** in Et_2O (10 mg in 40 mL). After freeze-pump-thaw cycles, 1 atm of either nitrogen or nitrous oxide was introduced to the flask. Solutions were stored at ambient temperature under exclusion of light for up to 13 days. UV/vis spectra were recorded in regular intervals in the region of 400-800 nm by placing the sealed Schlenk flask directly in the spectrometer. An immediate colour change to brown was observed on exposure to oxygen after the end of the measurement.

4.7. Reaction of 3 with Lewis bases in in C_6D_6 solution

A J. Young NMR tube was charged with **3** (15 mg, 0.018 mmol) and C_6D_6 (0.6-0.8 mL). The required amount of Lewis base (THF: 1.5-75 µL, 0.02-0.9 mmol; toluene: 1.9-95µL, 0.02-0.9 mmol; MeCN: 1.3 µL, 0.024 mmol) was added in several portions and ^1H

NMR spectra were recorded after each addition. No changes were observed in the case of toluene or THF addition. Addition of MeCN lead to the formation of a new compound, presumably **1**Cu(NCMe): δ_H (C_6D_6) 6.95-7.10 (m, 6 H, $C_{Ar}\underline{H}$), 4.81 (s, 1 H, C$\underline{H}$), 2.08 (s, 12 H, ArC$\underline{H}_3$), 1.65 (s, 6 H), 0.52 (s, 3 H, NCC$\underline{H}_3$).

4.8. X-ray diffraction studies

Crystals suitable for X-ray diffraction studies were obtained directly in the synthesis. Diffraction data were collected on Bruker/AXS Smart 6000 (4K) diffractometer (Mirror Montel 200-monochromated Cu Kα radiation, FR591 Rotating Anode). Cell refinement and data reduction were done using APEX2 [52]. Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97 [53]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropic on calculated positions using a riding model. Further experimental details are listed in Table 3.

Table II-3

Details of X-ray Diffraction Studies

	3	**6**
Formula	$C_{49}H_{58}N_4Cu_2$	$C_{30}H_{34}N_3Cu$
Mw (g/mol); F(000)	830.07; 3504	500.14; 1056
Crystal color and form	yellow bloc	yellow bloc
Crystal size (mm)	0.12 x 0.12 x 0.20	0.12 x 0.12 x 0.12
T (K); $d_{calcd.}$ (g/cm^3)	150; 1.295	150; 1.233
Crystal System	orthorhombic	monoclinic
Space Group	Pbca	$P2_1/c$
Unit Cell: a (Å)	21.0373(8)	12.8755(5)
b (Å)	14.8188(6)	11.3387(5)
c (Å)	27.3128(11)	19.2722(9)
β (°)		106.693(2)
V (Å^3); Z	8514.7(6); 8	2695.0(2); 4
θ range (°); completeness	3.2-71.9; 0.970	3.6-72.0; 0.944
Reflections : collected / independent; R_{int}	98923 / 8101; 0.0594	36248 / 4991; 0.036
μ (mm^{-1}); Abs. Corr.	1.510; multi-scan	1.293; multi-scan
R1(F); wR(F^2) [$I > 2\sigma(I)$]	0.0345; 0.0906	0.0369; 0.1103
R1(F); wR(F^2) (all data)	0.0478; 0.0944	0.0412; 0.1135
GoF(F^2)	0.953	1.101
Residual electron density	0.38 e$^-$/Å^3	0.25 e$^-$/Å^3

Acknowledgements

We thank F. Bélanger-Gariépy and Dr. M. Simard for their assistance in X-ray diffraction studies and Dr. T. H. Warren for helpful discussions. Funding for this research was provided by the Natural Sciences and Engineering Research Council of Canada and the Université de Montréal.

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Chapter 3

Bis-(2-phenyl-ethyl)-*nacnac*: A chiral diketiminate ligand and its copper complexes

Paul O. Oguadinma and Frank Schaper

Département de chimie, Université de Montréal, Montréal, Québec, H3C 3J7, Canada.

Abstract

The chiral diketiminate ligand bis-*N,N′*-(2-phenyl-ethyl)-2,4-diiminopentane, **1**H, was synthesized in good yields in a one step reaction from chiral amine and acetylacetone. Reaction of **1**Li(THF) with N-bromosuccinimide yielded the succinimide-substituted ligand **2**H. Copper complexes (**1**Cu(NCMe), **1**Cu(DMAP), **1**Cu(PPh_3), **1**Cu(2,6-xylyl isonitrile), **2**Cu(PPh_3), and **2**Cu(2,6-xylyl isonitrile)) were obtained by reaction of the ligand with a basic copper source in the presence of coordinating Lewis bases and, for the most part, characterized by X-ray diffraction studies. Compared to their more common analogues with aromatic substituents on N, **1** and **2** seem to be more basic (**1**>**2**) and sterically more demanding (**2**>**1**). Their copper complexes are less stable than those of aryl-substituted diketiminates and tend to decompose by disproportionation, most probably after dissociation of the coordinated Lewis base. Despite the rotational freedom around the N-R* bond, the complexes are sterically rigid, a necessary requirement for potential applications in enantioselective catalysis.

Introduction

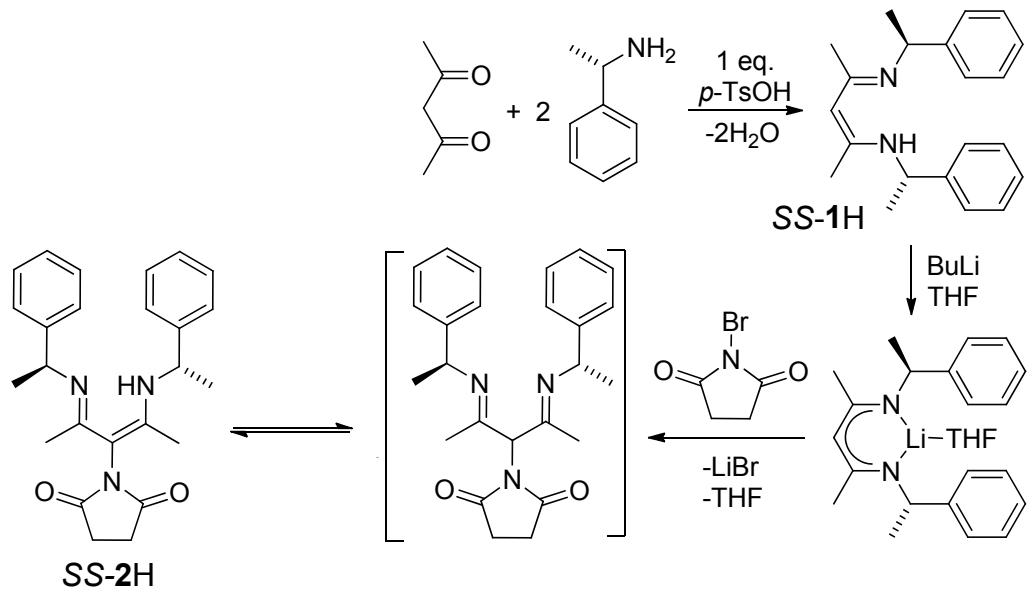
N,N′-substituted β-diketiminato ("*nacnac*")[1] ligands have been gaining increasing interest over the last decade, mainly due to their suitability as sterically crowded spectator ligands to stabilize coordinatively unsaturated metal centers and unusual oxidation states.[2] This rekindled interest in a ligand structure known since the 1960s is mainly due to Brookhart's seminal work on late metal complexes for olefin polymerization.[3] β-Diketiminates are the anionic equivalent of the *N,N′*-aryl substituted α-diimine ligands used there and research has focused, with only few exceptions, on *N,N′*-aryl substituted ligands, in particular *N,N′*-bis-2,6-diisopropyl-phenyl diketiminates. Copper(I) diketiminate complexes, for example, have been widely studied, in particular by the groups of Tolman[4, 5] and Warren,[6, 7] but only selected complexes investigated for Cu ALD carried diketiminate ligands with aliphatic substituents on nitrogen.[8] During previous work on biomimetic copper complexes,[9] we became interested in varying the ligand framework of *nacnac* complexes by switching from aromatic to aliphatic *N,N′*-substituents. In addition to drastically changing the steric environment around the metal center, aliphatic substituents would be a very economic way to introduce chirality into diketiminate ligands. We report

here the synthesis of *N,N'*-bis(2-phenylethyl)-*nacnac*H, **1H**, the first chiral *nacnac* ligand, and its copper complexes.

Results and Discussion

Ligand synthesis. Synthesis of β-diketimines with aliphatic *N*-substituents has been reported previously by a two step procedure.[10] Simple condensation of acetylacetone with a primary amine yielded the mono-substituted product, 4-ketimin-propan-2-one, which is normally obtained in its enamine form. Condensation with a second amine required activation of the ketone, most commonly by alkylation with Meerwein salt or other alkylating reagents.[10] To gain an economic and fast access to the required ligand, we investigated the possible one-step synthesis of aliphatic *nacnac* ligands. Following the synthetic protocol outlined for aryl-substituted diketimines,[11] double condensation of enantiomerically pure phenylethylamine and acetylacetone was achieved in the presence of 1 equiv. of *p*-toluenesulfonic acid under elimination of water with a Dean-Stark apparatus for 5 days. Chiral **1**H was obtained in 67-70% yield for *RR*- and *SS*-**1**H. While this work was in progress, Buch and Harder reported the synthesis of *SS*-**1**H in a two-step procedure *via* alkylation of the corresponding enaminoketone in 36% yield.[12] No metal complexes of this ligand were reported. Reaction of **1**Li(THF) with N-bromosuccinimide yielded the succinimide-substituted ligand **2**H, most probably by initial bromination at the central carbon atom followed by nucleophilic substitution of bromide by lithium succinimide.

Scheme 3.1



Crystals suitable for an X-ray diffraction study of *SS*-**1**H and *RR*-**2**H were obtained from ethanol at –20 °C (Figure 3.1, Table III-2). Ligand **1**H shows the expected planar conformation of an imine-enamine ligand. Bond lengths in previous solid state structures of 2-amino-4-imino-pent-2-enes[13-16] ranged from apparent delocalization ($\Delta_{C\text{-}C}$, $\Delta_{C\text{-}N}$ < 0.01 Å)[13] to clear bond alternation ($\Delta_{C\text{-}C}$ = 0.08 Å, $\Delta_{C\text{-}N}$ = 0.06 Å).[16] For **1**H, small differences in the C3-C2/C4 and C-N bond lengths ($\Delta_{C\text{-}C}$ = 0.02 Å, $\Delta_{C\text{-}N}$ = 0.02 Å) indicate an apparent delocalization (or better: disorder) of the double bonds. In agreement with this, inspection of the difference Fourier map yielded two maxima of electron density close to N1 and N2, which were assigned and refined as the disordered NH proton. Of special note is the orientation of the chiral *N*-substituent, which is rotated in a way as to orientate its hydrogen atom towards the methyl group of the ligand backbone. Ligand **2**H displays, as expected, the same general geometry (Figure 3.2, Table III-2), with the methine-hydrogen towards the ligand backbone. In contrast to **1**H, the double bonds are substantially localised as indicated by differences in the C3-C2/C4 and C-N bond lengths of $\Delta_{C\text{-}C}$ = 0.06 Å and $\Delta_{C\text{-}N}$ = 0.05 Å and H1A was consequently located bound to N1 only. The introduction of the succinimide substituent in the ligand backbone did not have any notable consequences on the overall geometry, as evidenced by virtually unchanged bond and torsion angles (Table III-2).

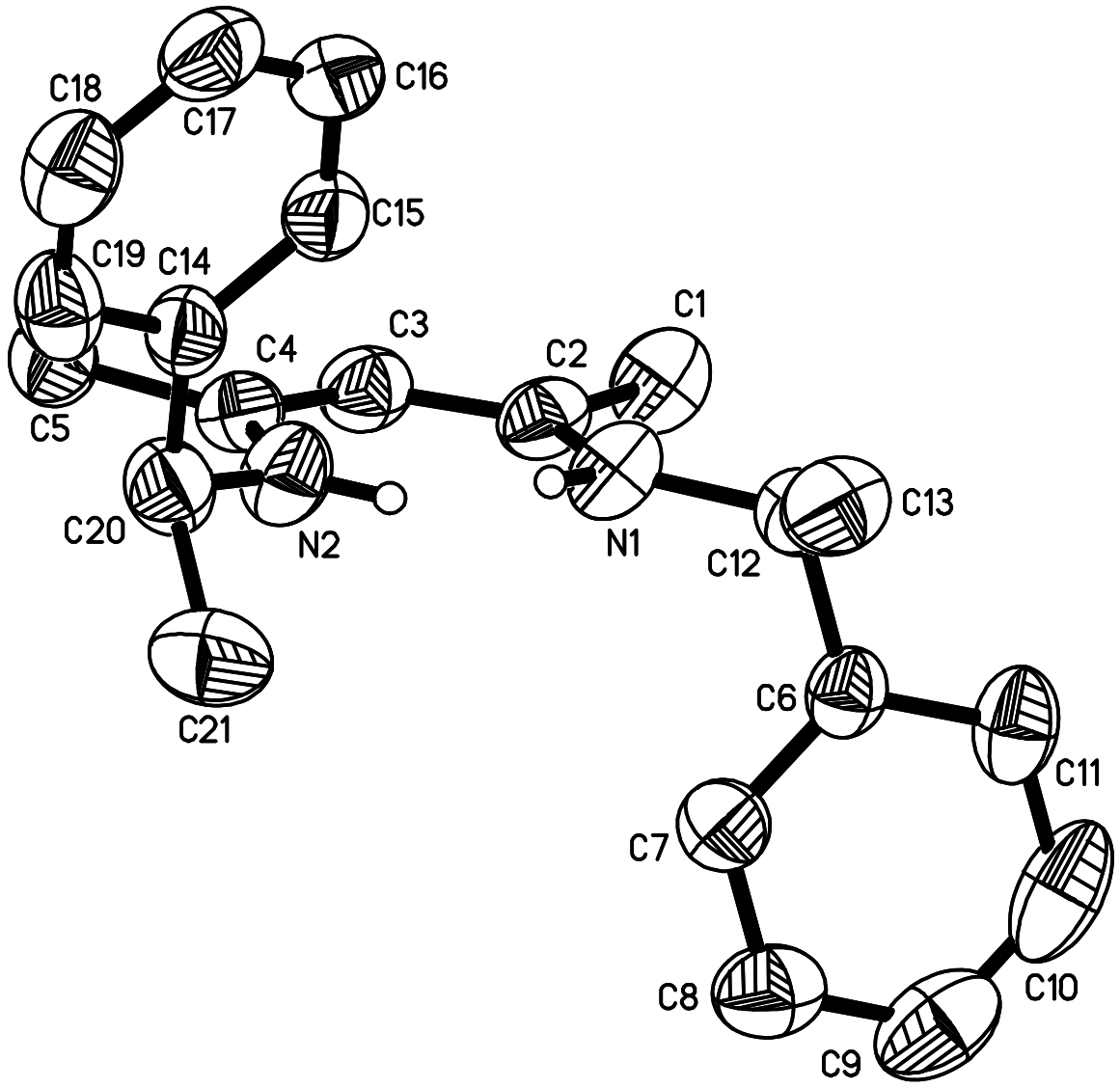


Figure 3.1: Crystal structure of *SS*-**1**H. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except the disordered NH, were omitted for clarity.

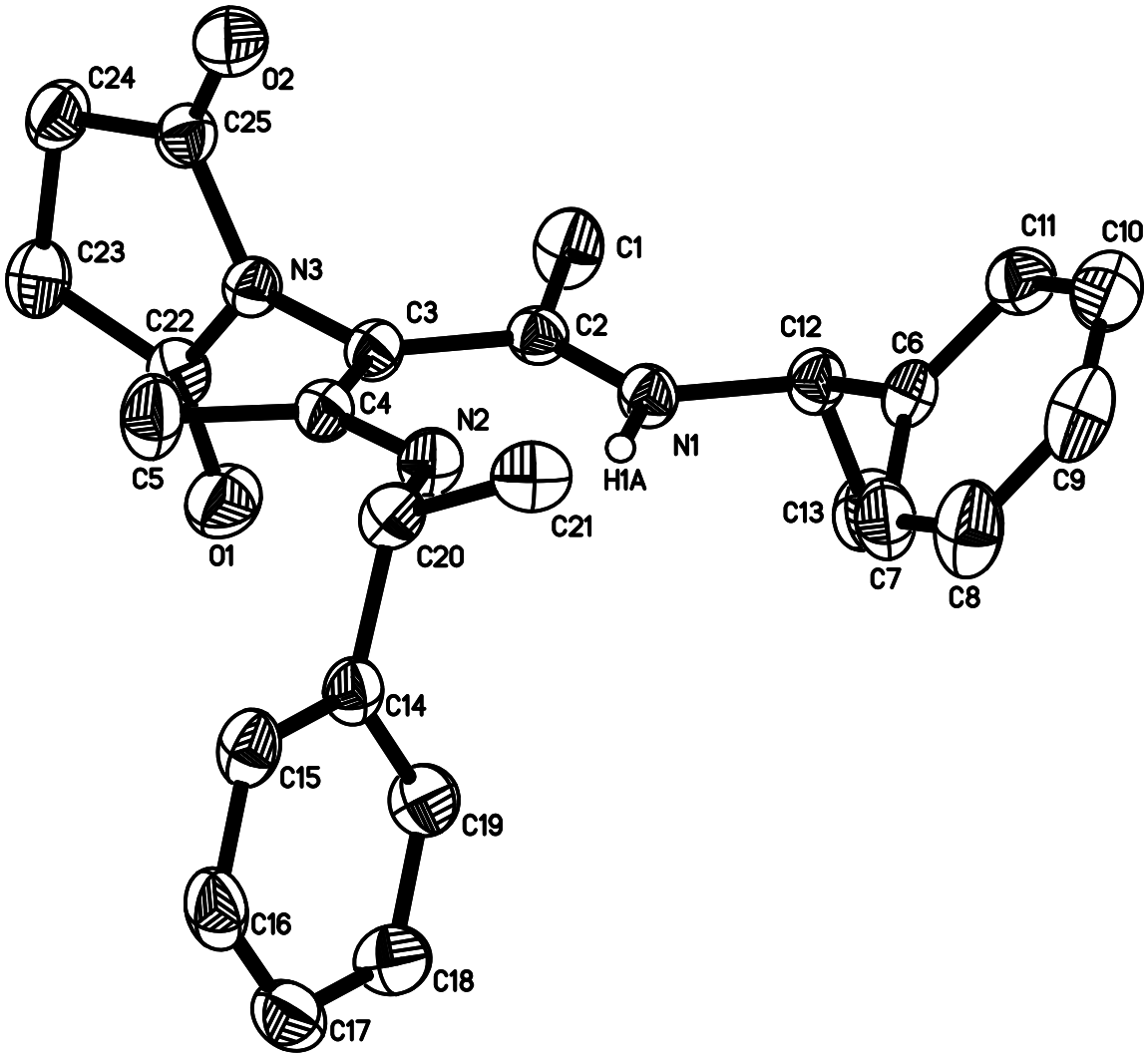
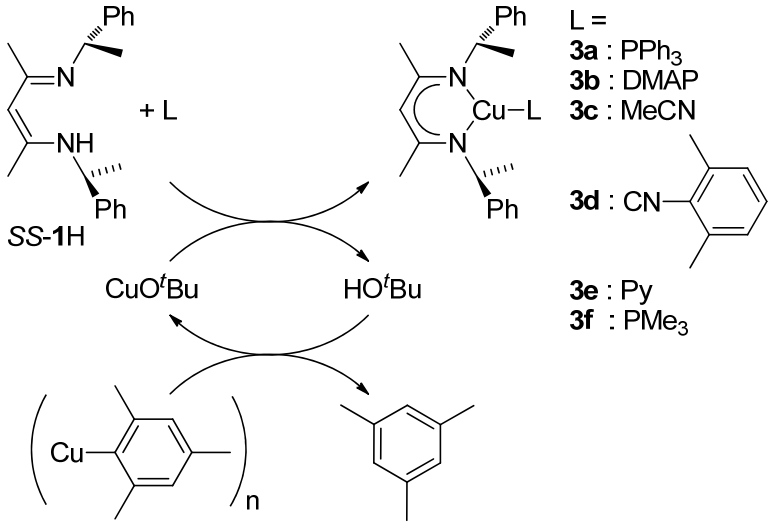


Figure 3.2: Crystal structure of *RR*-**2**H. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except NH, were omitted for clarity.

Complex syntheses. Protonation of CuO*t*Bu with *nacnac*H in aromatic solvents has proved to be a reliable route to *nacnac* copper complexes.[17] In contrast to aryl-substituted *nacnac* ligands, solutions of **1**H and CuO*t*Bu in benzene-d_6, however, displayed only signals associated with the starting material in its NMR spectra, even after several days at room temperature. Reactions with the stronger base CuMes (Mes = 2,4,6-trimethylphenyl) also did not lead to any deprotonation of **1**H. Reaction of CuO*t*Bu with **1**H in C_6D_6 can be achieved in the presence of coordinating ligands, such as PPh_3, to form the corresponding copper complex (**1**)Cu(PPh_3), **3a**, (*vide infra*) and *tert*-butanol (^{1}H NMR: δ 1.19 ppm).

Surprisingly, CuMes still remains inactive even in the presence of PPh_3, probably due to a kinetically hindered attack on the CuMes-pentamer.[18] CuMes could be employed as a copper source, however, in the presence of catalytic amounts of either *tert*-butanol or Cu*O*t*B*u. We propose a catalytic cycle, where Cu*O*t*B*u reacts with **1**H and is regenerated by reaction of *tert*-butanol with CuMes (Scheme 3.2). While no difference in reactivity between Cu*O*t*B*u and CuMes/Cu*O*t*B*u was observed in any reaction, we found that products obtained by reaction with CuMes/Cu*O*t*B*u were sometimes easier to isolate by crystallisation, probably due to the absence of large amounts of *tert*-butanol.

Scheme 3.2



Reaction of *SS*-**1**H with CuMes/Cu*O*t*B*u or with Cu*O*t*B*u in the presence of PPh_3, MeCN, *N,N'*-dimethylaminopyridine (DMAP) in toluene at room temperature yielded, after crystallization from toluene/hexane at –30 °C the corresponding ligand coordinated copper complexes *SS*-**3a-3c** in 65-80% yield (Scheme 3.2). While **3a & 3b** were stable in the presence of excess Lewis base, solutions of **3c** in benzene-d_6 start to visibly decompose after 15 min in the presence of excess MeCN. The lack of any NMR detectable decomposition products (apart from small amounts of **1**H) and the formation of a copper mirror indicate disproportionation as the most probable decomposition pathway. Analogous reactions in the presence of 2,6-xylyl isonitrile afforded after crystallization at –30 °C, on standing, or after evaporation of the volatiles only yellow precipitates, which were

insoluble in benzene or even DMSO. The same results were obtained in attempts to isolate **1**Cu($CNC_6Me_2H_3$), **3d**, from benzene-d_6 solutions, even after the NMR spectrum confirmed the formation of the copper complex. In one case, attempted crystallization of **3d** yielded a crystalline product, which was identified as $\{(2,6\text{-}Me_2C_6H_3\text{-}NC)Cu(O\textit{t}Bu)\}_4$ by X-ray crystallography (Figure 3.3). Since reactions were usually complete when followed via NMR, we believe this to be a minor or isolated occurrence and changing the order of reagent addition did not result in isolation of **3d**. Change of the solvent from toluene to ether finally allowed the isolation of **3d**, although we were not able to obtain crystals suitable for an X-ray structure determination. Reactions of the succinimide-substituted ligand *SS*-**2**H under analogous conditions in the presence of PPh_3 or 2,6-xylyl isonitrile yielded the Lewis-base coordinated complexes **2**Cu(PPh_3), **4a**, and **2**Cu($CNC_6Me_2H_3$), **4d**, respectively.

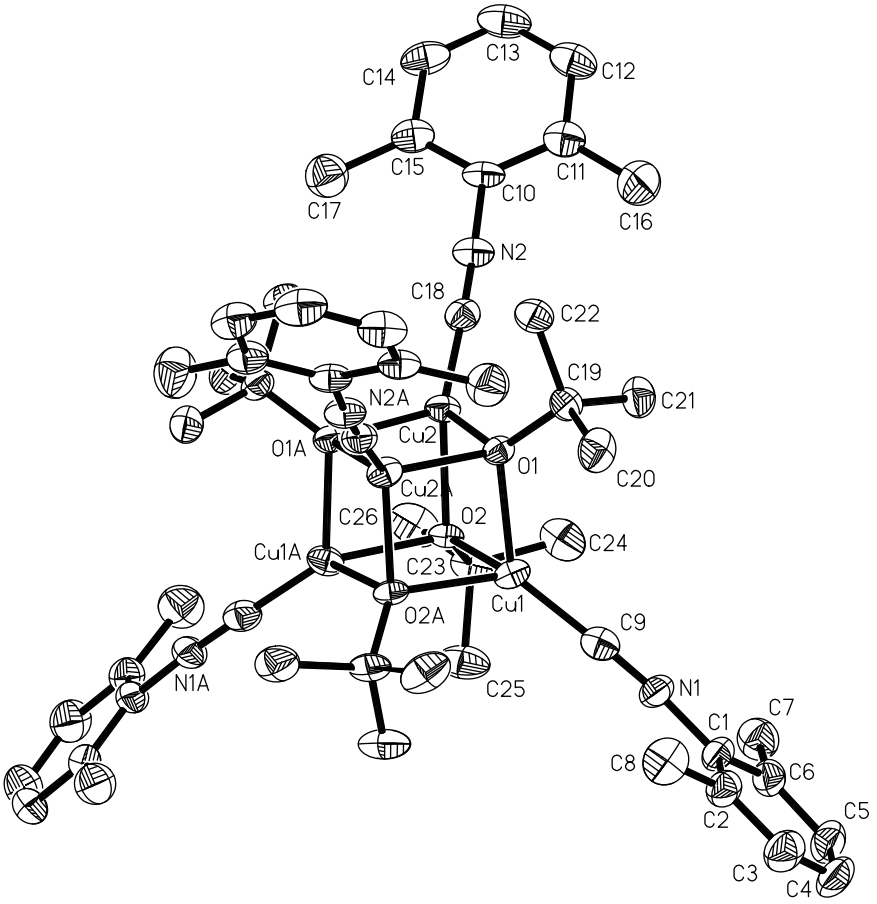


Figure 3.3: Crystal structure of $\{(2,6\text{-}Me_2C_6H_3\text{-}NC)Cu(O^tBu)\}_4$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

Since copper complexes **3** and **4** could not be obtained – in contrast to their aryl substituted analogues – in the absence of an additional Lewis base ligand, we decided to investigate the requirement of a coordinating Lewis base in more detail. Neither complex formation nor decomposition was observed in reactions of **1**H and either CuO*t*Bu or CuMes/CuO*t*Bu in benzene-d_6 in the presence of 1-hexene, styrene, diphenylacetylene, THF, acetone, or benzonitrile. The ^{1}H NMR spectra of the reaction mixtures contained only unreacted starting materials. In the presence of acetonitrile, signals for **1**Cu(NCMe), **3c**, were observed, but the reaction did not go to completion after 1 h, even when CuMes/CuO*t*Bu was employed as a copper source. After 1 h, the NMR spectra became difficult to interpret due to the instability of **3c**. Complete conversion to the complexes **3a, 3b & 3d** and the putative complexes **3e & 3f** were observed in the presence of PPh_3, DMAP, 2,6-xylylisocyanide, pyridine or PMe_3 (Scheme 3.2). The disappearance of signals for the starting materials was accompanied by the appearance of a new set of signals for the *nacnac* ligand which lacked a signal for the *N*-bonded proton and the formation of 2,4,6-mesitylene (^{1}H NMR: δ 2.15 ppm) and/or *tert*-butanol (δ 1.19 ppm).

Salt metathesis reactions of $[Cu(NCMe)_4][PF_6]$ with **1**Li(THF) in the presence of MeCN or excess of styrene did not yield any Cu(I) complex, but strongly coloured suspensions. In the presence of 2,6-xylyl isonitrile, the stable complex **3d** was obtained, albeit in lower yields than *via* the protonation route. On the other hand, protonation of CuO*t*Bu in the presence of styrene by the less sterically demanding *N,N′*-bis(benzyl)-*nacnac*H ligand cleanly generated the stable styrene complex (*nacnac*^{Bn})Cu(styrene).[19] The differences in reactivity towards the same Lewis base observed for electronically comparable, but sterically different diketiminate ligands indicate that activation of CuO*t*Bu by the Lewis base is not an essential step in the reaction mechanism. Identical results obtained using CuMes/CuO*t*Bu, in which *tert*-butanol is consistently removed from the reaction mixture, also rule out negative effects due to the presence of *tert*-butanol. Protonation of CuO*t*Bu thus seems to proceed whenever the resulting copper complex is of sufficient stability. Consequently, salt metathesis reactions in the presence of Lewis bases which have proved unreactive towards CuO*t*Bu led to decomposition.

When reactions of **2**H with CuMes/CuO*t*Bu or CuO*t*Bu in the presence of Lewis bases in benzene-d_6 were followed by NMR, no reaction was observed with 1-hexene,

styrene, acetone, or even acetonitrile (Scheme 3.3). In the presence of 1 equiv of pyridine, which yielded **3c** fast and quantitatively before, reaction of **2**H with CuO*t*Bu afforded the putative pyridine adduct **4e** only in 8% conversion (compared to unreacted **2**H). Further addition of 4 equiv pyridine increased the percentage of **4e** to 23%, while addition of 2 equiv *tert*-butanol decreased it back to 18%, which indicates reversible protonation between **2**H and *tert*-butanol in this case. Surprisingly, no reaction at all occurred, when CuO*t*Bu is replaced by the stronger base CuMes/CuO*t*Bu. This lack of reaction might have kinetic rather than thermodynamic reasons, i. e. deactivation of CuMes by pyridine coordination (c.f. Figure 3.3). Reactions with 2,6-xylyl isonitrile and triphenylphosphine as Lewis bases were complete as in the case of **1**H, but the reaction with triphenylphospine – fast in the case of **1**H – took several hours to reach completion. The succinimide-substituted ligand **2**H thus proved to be slightly less reactive in complex formation than **1**H (Table III-1).

Scheme 3.3

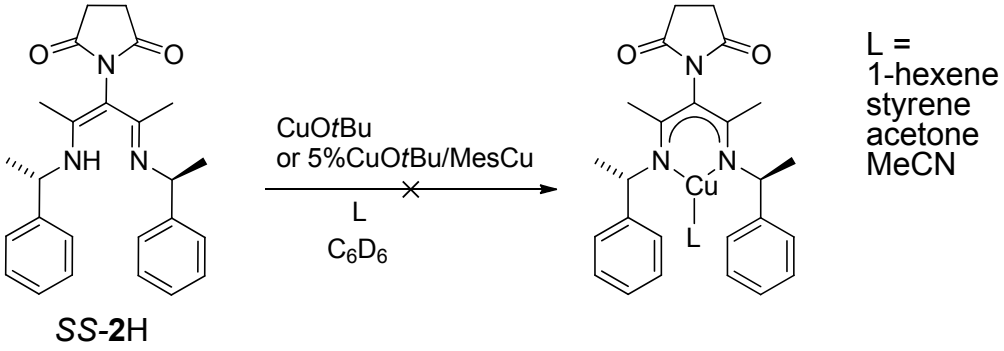


Table III-1: Relative Reactivities in the Formation of Complexes **3** and **4**.

L	**3**	**4**
hexene, styrene	none	none
MeCN	slow	none
Pyridine	fast, complete	partial reaction
PPh_3	fast, complete	slow, complete
$CNC_6Me_2H_3$	fast, complete	fast, complete

Dynamic processes in solution. The coordinated Lewis base in complexes **3a-3f** exchanges fast on the NMR time scale at room temperature with excess base present and only averaged signals of free and coordinated Lewis base were observed in their ^{1}H or ^{31}P NMR spectra. NMR spectra of **3a** in the presence of 5 equiv of $PMePh_2$ also displayed only two signals in the ^{31}P spectra: the PPh_3 signal, which was intermediate between that of **3a** and that of free PPh_3, and the signal of $PMePh_2$, displaced from the position of the free phosphine. Fast exchange of phosphine ligands was further confirmed by the ^{1}H NMR spectrum, which displayed only one set of signals for the *nacnac* ligand, slightly displaced from those in **3a**. Analogous observations were made when **3a** was reacted with 1 or 5 equiv. of 2,6-xylyl isonitrile: only one signal set was obtained for the *nacnac* ligand, intermediate between **3a** and **3d**, and averaged signals were observed for coordinated and free Lewis bases. ^{31}P spectra of benzene-d_6 solutions of **3a** in the absence of free phosphine did not show any change in the frequency of the coordinated PPh_3 ligand when measured at complex concentrations of 9-23 mM. Dissociation of the phosphine ligand from **3a** thus does not occur to a notable extent under these conditions. Taking into account that ligand exchange is fast on the NMR time scale even for strongly coordinating ligands such as isonitrile, we believe the ligand exchange to proceed by an associative mechanism.

Solutions of **3c** in C_6D_6 showed the presence of two signal sets, A & B, in a 2:1 ratio for the *nacnac* ligand. Only one signal was observed for MeCN, corresponding to 1 equiv acetonitrile per *nacnac*, as observed in the crystal structure. The ratio of A/B is independent from overall complex concentration. Addition of excess acetonitrile leads to exclusive formation of isomer A, which was assigned to **3c**. The nature of species B is not clear at the moment. Independence from overall concentration and dependence on MeCN concentration suggests an equilibrium between *nacnac*Cu(MeCN), **3c**, and (*nacnac*Cu)$_2$(μ-MeCN) + free MeCN, analogous to the one observed for *nacnac*^{Ar}Cu(C_6D_6) and (*nacnac*^{Ar}Cu)$_2$(μ-C_6D_6).[7, 9] IR-spectra of toluene solutions of **3c**, however, showed one resonance for ν_{CN} = 2254 cm^{-1}, which does not support a bridging acetonitrile coordination (free MeCN (toluene): ν_{CN} = 2259 cm^{-1}).

X-ray diffraction studies. Crystals suitable for an X-ray diffraction analysis of **3a-3c** and **4d** were obtained from toluene/hexane solutions at –30 °C. Complex **3c** displays a trigonal-

planar coordination geometry with the copper atom situated close to the mean plane of the ligand (Figure 3.4, Table III-2). The *nacnac* ligand is only very slightly distorted from the expected planar geometry (mean deviation of all atoms from the mean plane: 0.05 Å) and bond distances indicate the expected delocalization of the double bonds ($\Delta_{C\text{-}C}$ = 0.016 Å, $\Delta_{C\text{-}N}$ = 0.017 Å, Table III-2). Similar to the free ligand **1**H, the chiral *N*-substituent orients its hydrogen substituent towards the ligand backbone. The acetonitrile ligand is found in a slightly bent coordination (Cu1-N3-C22: 171.5(1)°) with geometrical data comparable to those of other *nacnac* copper acetonitrile complexes (Cu-N_{MeCN}: 1.866(3)-1.887(5) Å, C-N_{MeCN}: 1.122(8)-1.137(4) Å).[20] Introduction of a substituted alkyl group at the nitrogen had noticeable consequences on the ligand structure. The average C=N-C12/20 angle of 124.2±0.6° in **1**H is comparable to the corresponding angle found in diketimines with aromatic *N*-substituents (C=N-C_{Ar}: 124±3°). Upon coordination of diketiminates to copper, an *N*-aryl substituent is pushed towards the ligand backbone (C=N-C_{Ar}: 117-122°) with values for C_{Ar}-N-Cu of 114-122°.[21] Corresponding values of the averaged Me-N-C12/20 and the C12/20-N-Cu angles in **3c** (and as well as in **3a & 3b**, *vide infra*) are at the extremes of these ranges with 118.4±1.3° and 121.7±1.6°, respectively. In comparison to aryl substituents, the alkyl substituent is thus bent further away from the metal center towards the ligand backbone. Combined with the longer than average Cu-N distances of 1.945(1) and 1.963(1) Å in **3c** (average in *N*-Ar substituted Cu *nacnac* complexes: 1.94(3) Å),[21] this indicates that **1**H should be considered sterically more bulky, at least in the ligand mean plane, than *nacnac* ligands with *N*-aryl substituents, such as the widely employed bis(2,6-diisopropylphenyl) diketiminate. An increased steric bulk of diketiminate ligands with secondary alkyl substituents on N was confirmed by the calculation of the aperture accessible for coordination to copper in the N_2Cu-plane. While xylyl, mesityl and 2,6-bisisopropylphenyl substituted diketiminate copper complexes offered an aperture of 40-46°, a strongly reduced value of 13° was found for **1**Cu (see supplementary material).

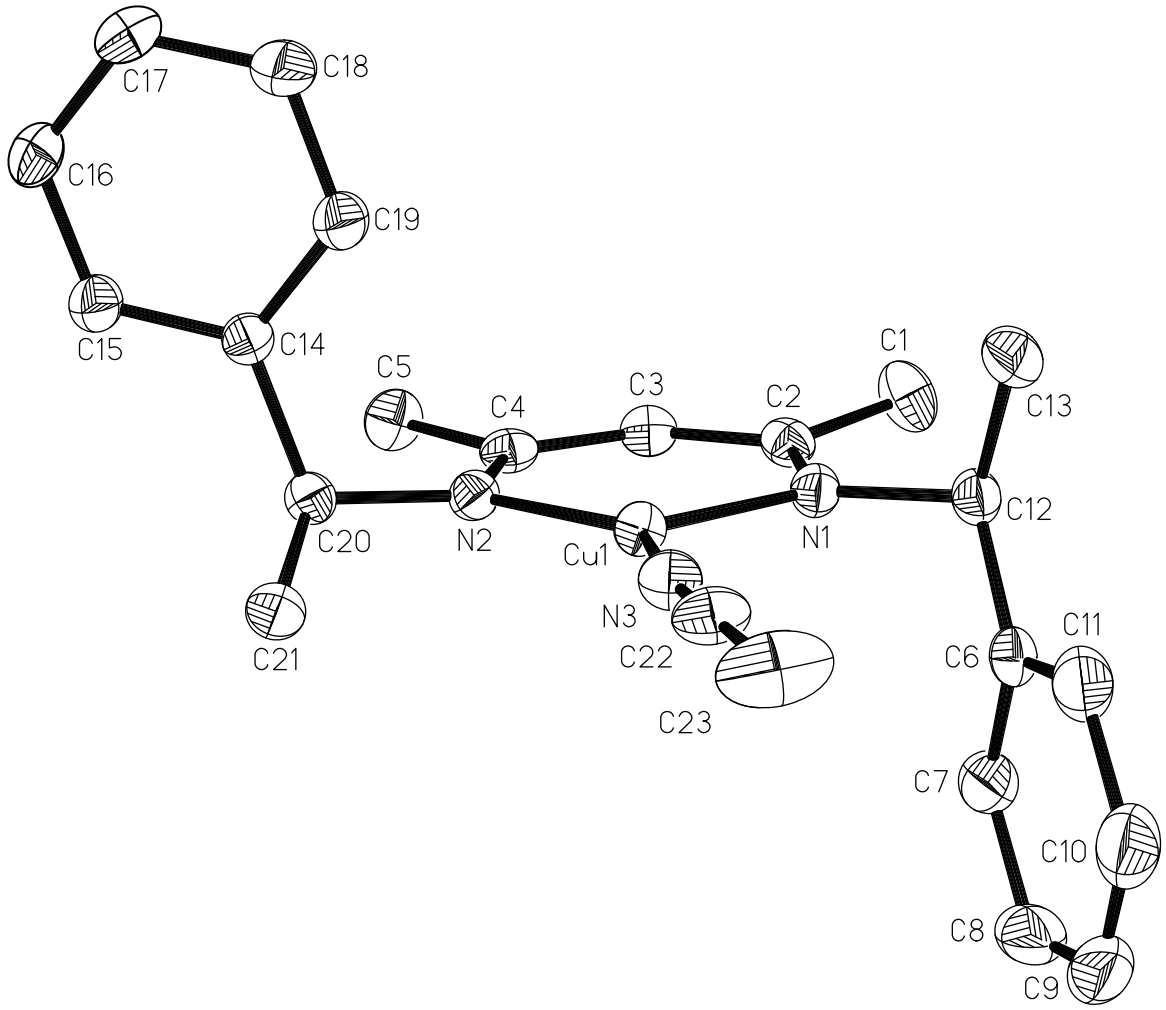


Figure 3.4: Crystal structure of *SS*-**3c**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

Table III-2: Selected bond distances [Å] and bond angles [deg] for *SS*-**1**H, *SS*-**2**H, *SS*-**3a-c**, and *SS*-**4d**.

	***SS*-1H**	***RR*-2H**	***SS*-3a**	***SS*-3b** [a]	***SS*-3c**	***SS*-4d**
N1-C2	1.335(3)	1.296(3)	1.326(2)	1.33±0.02	1.317(2)	1.329(4)
N2-C4	1.312(4)	1.348(3)	1.326(2)		1.334(2)	1.329(4)
C2-C3	1.393(4)	1.454(3)	1.406(2)	1.40±0.03	1.416(2)	1.416(4)
C3-C4	1.415(4)	1.385(3)	1.411(2)		1.400(2)	1.423(4)
N1-C12	1.455(2)	1.462(3)	1.473(2)	1.50±0.02	1.478(2)	1.474(4)
N2-C20	1.455(4)	1.469(3)	1.475(2)		1.476(2)	1.482(4)
Cu1-N1			1.972(1)	1.96±0.04	1.963(1)	1.930(3)
Cu1-N2			1.983(1)		1.945(1)	1.944(3)
Cu1-X [b]			2.195(1)	1.97±0.02	1.890(1)	1.813(4)
X - Y [b]			1.829-1.844		1.138(2)	1.172(4)
N1-Cu1-N2			97.79(5)	101.3±0.5	101.23(5)	98.09(11)
N1-Cu1-X [b]			129.85(4)	124 - 134	120.63(5)	130.73(13)
N2-Cu1-X [b]			130.37(4)		138.07(5)	130.75(14)
Tors. C=N-C_{Bn}-H [c]	34±10	34±2	15±12	17±29	14±26	11±1
complex bending [d]			25	4±2	5	3
C2-C3-C4	126.1(2)	125.4(2)	129.9(2)	133.7±1.8	131.1(1)	129.7(3)
Me-C-C3 [e]	118.5±0.9	119.3±2.1	114.8±0.4	116±1	114.7±0.4	118±1
C2/C4=N-C [f]	124.2±0.6	124.0±1.2	118.3±0.4	119±3	118.4±1.3	121±1
Cu-N-C12/20 [g]			121.5±0.3	122±3	121.7±1.6	115.8±0.6

Errors provided for averaged values indicate either the biggest deviation from the cited mean value or the highest 3σ, when the latter value was higher. [a] Averages of the geometrical data in all 4 independent molecules. [b] X, Y = P1, C22/C28/C34 (**3a**); N3/N6/N8/N11 (**3b**); N3, C22 (**3c**); C30, N3 (**4d**). [c] average of C2-N1-C12-H and C4-N2-C20-H. [d] angle between the least-square planes defined by C2-C4,N1,N2 and N1,N2,Cu1,X. [e] average of C1-C2-C3 and C5-C4-C3. [f] average of C2-N1-C12 and C4-CN2-C20. [g] average of Cu-N1-C12 and Cu-N2-C20.

While the *nacnac* ligand in **3a** retains the delocalization of the double bonds, coordination of triphenylphosphine instead of the sterically rather undemanding acetonitrile ligand to copper renders the ligand less planar (mean deviation: 0.09 Å) and significantly displaces the copper center from the ligand mean plane (Figure 3.5, bending angle in Table III-2). Despite this displacement, the phosphine is coordinated rather symmetrically (Δ(N-

Cu-P) = 0.5°) compared to the acetonitrile ligand in **3c** (Δ(N-Cu-P) = 17.5°), resulting in an overall higher symmetry of bond distances and angles in **3a**. Interaction of the sterically bulky phosphine and the substituents at the nitrogen atoms resulted in an elongation of Cu-N bond lengths by 0.02 Å and, consequently, a reduction of the N-Cu-N angle by 3°. Cu-N (1.972(1) & 1.983(1) Å) and Cu-P bond distances (2.195(1) Å) are longer and the out-of-plane coordination of the phosphine ligand (bending angle in Table III-2: 25°) is more pronounced than in (*N,N'*-Ar$_2$*nacnac*)Cu(PPh$_3$) complexes (Cu-N: 1.940(2)-1.964(2) Å, Cu-P: 2.158(1)-2.169(1) Å, complex bending: 4-17°),[5, 7, 15, 22] in agreement with an increased steric bulk introduced by the aliphatic substituent on N. It is noteworthy that, despite the steric demand of the phosphine ligand, the hydrogen atom of the 1-phenyl-ethyl substituent remains oriented towards the ligand backbone (see averaged torsion angle in Table III-2) and that averaged bond angles in the ligand did not change upon substitution of acetonitrile by phosphine (Me-C-C3: 114.8±0.4° (**3a**), 114.7±0.4° (**3c**); C-N-C12/22: 118.3±0.4° (**3a**), 118.4±1.3° (**3c**)). We conclude that the steric interaction of the *N*-substituent and the methyl groups of the ligand backbone governs the conformation of the chiral *nacnac* ligand and that its complexes will be sufficiently rigid to provide a controlled environment for potential applications.

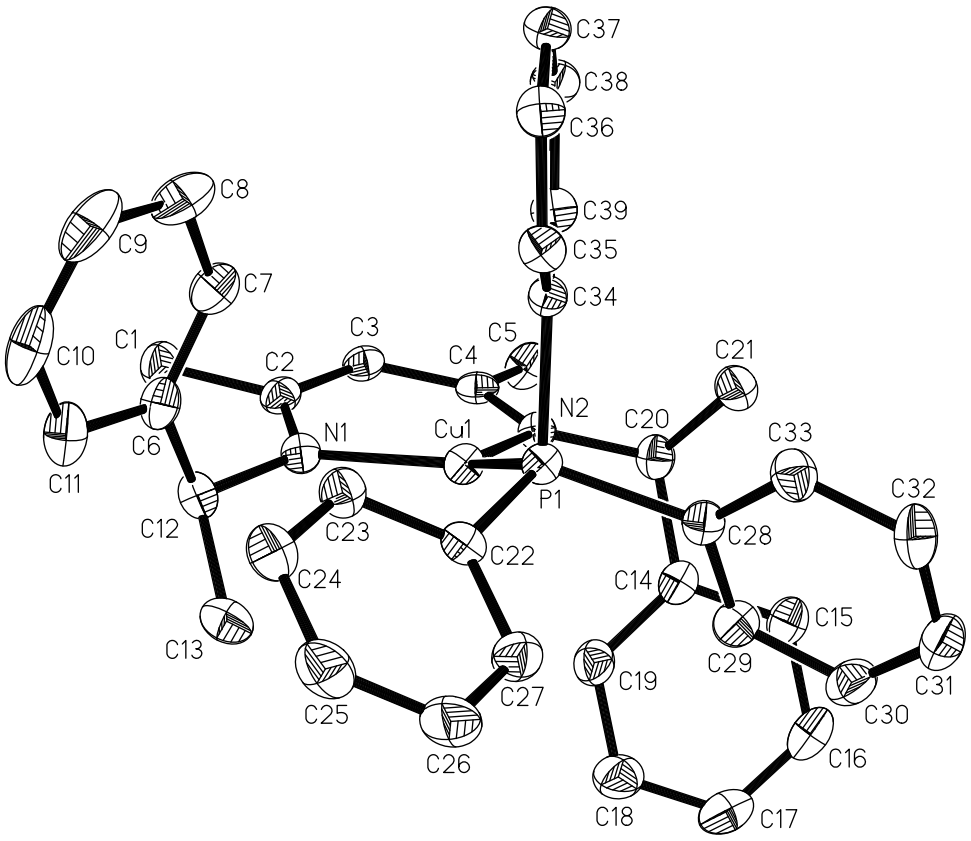


Figure 3.5: Crystal structure of *SS*-**3a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

The DMAP-coordinated complex *SS*-**3b** crystallizes with four independent molecules in the asymmetric unit, each with slightly different torsion angles (Figure 3.6). The structural data is of relatively low quality (due to the quality of the obtained single crystal) and only general structural features will be discussed (Table III-2). Coordination of DMAP is comparable to acetonitrile coordination in **3c** in the rather unsymmetrical binding of the DMAP ligand (Δ(N-Cu-N_{DMAP})= 2-10°). The in-plane coordination of the copper atom (c.f. complex bending angle of 4±2° in Table III-2) and the N1-Cu1-N2 angles (101.3±0.5°) are also strongly comparable to those found in **3c**.

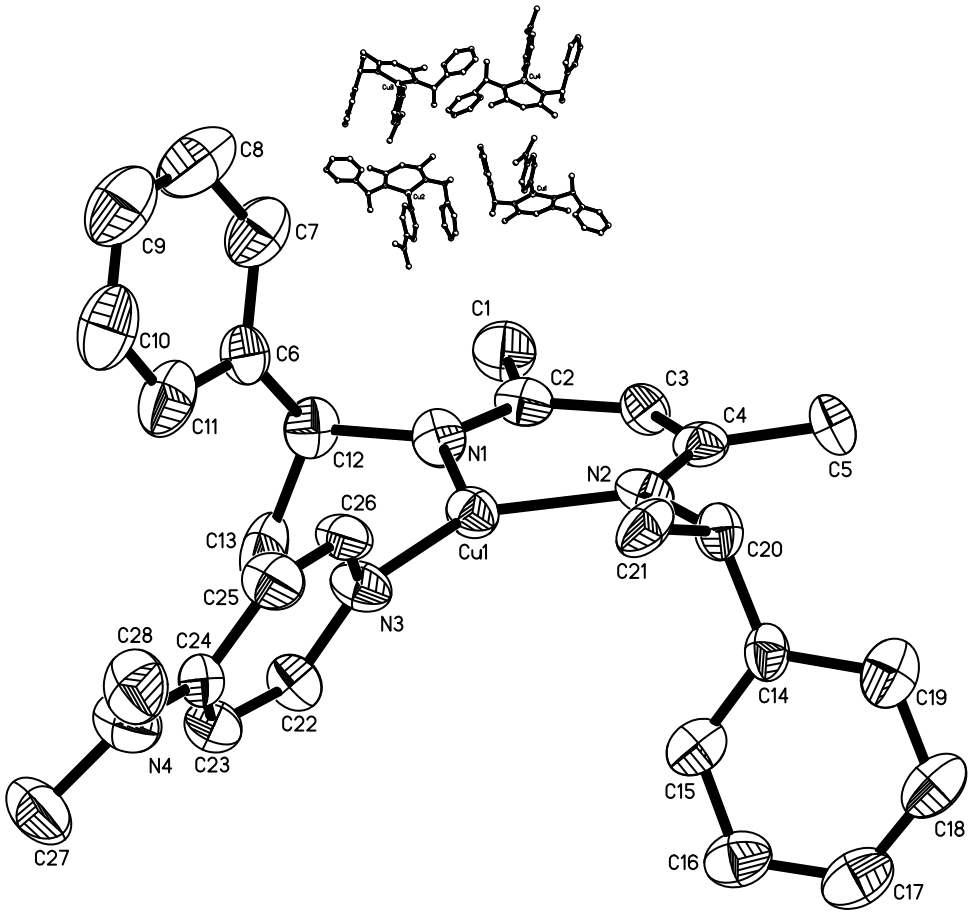


Figure 3.6: Crystal structure of *SS*-**3b**. Only one of 4 independent molecules is shown. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. The inset displays the orientation of the 4 independent molecules in the asymmetric unit.

The lack of strong steric interactions in **4d** (Figure 3.7, Table III-2) results again in a symmetrical coordination of the *nacnac* and the isonitrile ligand, with the copper atom in the mean plane of the complex. Cu-C and C-N distances of 1.813(4) and 1.172(4) Å, respectively, are at the extremes of the ranges observed in analogous copper 2,6-xylylisonitrile complexes with Ar_2*nacnac* ligands (Cu-C: 1.814(2)-1.822(2) Å, C-N: 1.157(3)-1.159(2) Å).[7, 9, 23] The observed reduced reactivity of **2**H with CuO*t*Bu to form copper complexes might be explained by an increased steric crowding of the expected copper complexes. Although no geometrical impact of the substitution at C3 was observed in the structures of the protonated ligands, it is notable in the geometry of the respective

copper complexes. Coordination of **1** or **2** to copper widens the C2-C3-C4 angle from 125.4(2)-126.1(2)° in **1**H and **2**H to 129.9(2)-135.6(6)° in **3a-3c** and **4d** and reduces the Me-C2/4-C3 angle by 3-4° in **3a-3c** (Table III-2). The presence of the succinimide substituent at C3, however, prevents this reduction in **4d** and the Me-C2/4-C3 angle remains practically unchanged. As a consequence, the alkyl substituents on the nitrogen atoms are pushed further into the copper coordination sphere in **4d**, evidenced by an increased average C2/4-N-C angle and a decreased average Cu-N-C12/20 bond angle compared to **3a-3c** (Table III-2), and thus indicating an increased steric crowding around the copper center in this complex.

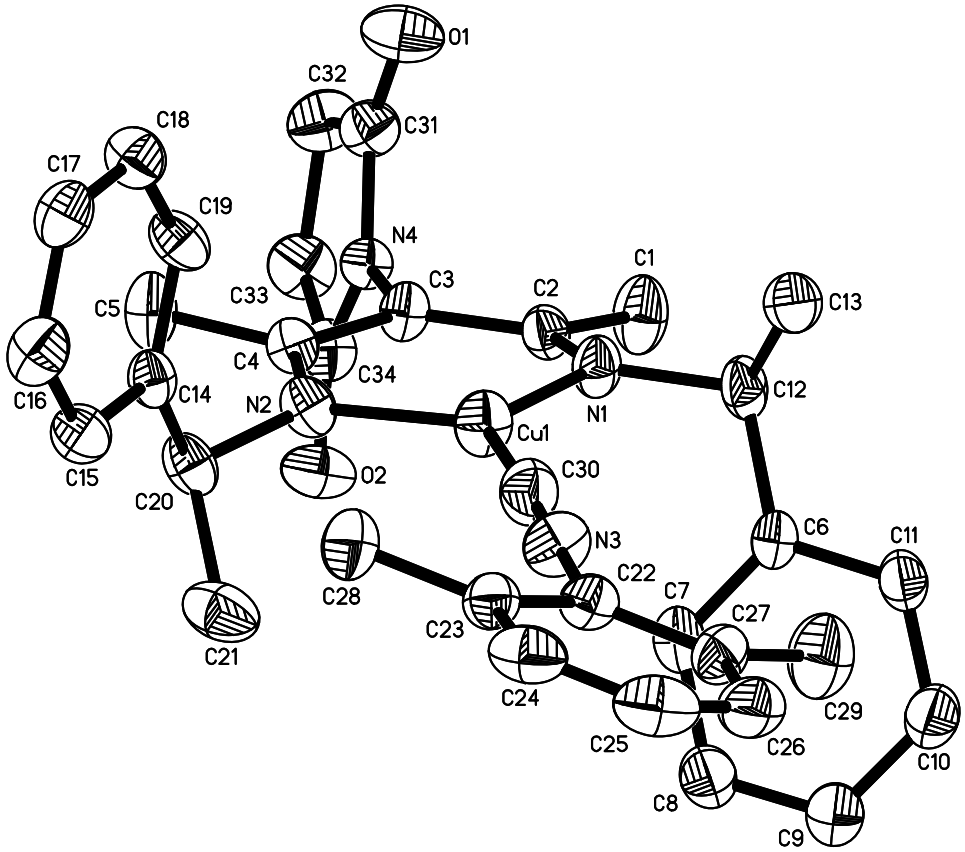


Figure 3.7: Crystal structure of *SS*-**4d**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

Spectroscopic properties: Despite the differences observed in reactivity with CuO*t*Bu, electronic influences of the aliphatic substituent in complexes **3** were subtle at best. The chemical displacement of the PPh_3 ligand in **3a** in its ^{31}P NMR spectra (δ = 3.9 ppm) is

intermediate between those of (*N,N'*-Ar$_2$*nacnac*)Cu(PPh$_3$) complexes (Ar = Me$_3$C$_6$H$_2$: 5.2 ppm,[7] Ar = Me$_2$C$_6$H$_3$: 5.4 ppm,[5] Ar = ^{i}Pr$_2$C$_6$H$_3$: 3.6 ppm[22]). The signal for the succinimide-substituted complex **4a** is observed at 3.6 ppm. Averaged P-C bond lengths in **3a** (Table III-2), which should mirror the amount of Cu back-donation into PPh$_3$,[24] are slightly longer (1.836 Å) than in complexes with *N*-Ar substituents (1.829-1.834 Å),[5, 7, 22] in agreement with increased back-donation in **3a**, but the differences are hardly significant. Clearer indications of the electronic differences can be observed in the isonitrile complexes **3d** and **4d**. The stretching frequency ν_{CN} = 2111 cm^{-1} of the isonitrile ligand in **3d** is lower than frequencies observed in 2,6-xylylisonitrile complexes with *N*-Ar substituted *nacnac* ligands (ν_{CN} = 2121-2126 cm^{-1}),[7, 9, 23] indicating an increased, but still weak back-donation (free isonitrile: ν_{CN} = 2119 cm^{-1}). Introduction of the succinimide substituent in **4d** displaced ν_{CN} by 6 cm^{-1} to 2117 cm^{-1}, in agreement with the expected electron withdrawing effect of this substituent.

Conclusions

Compared to its *N*-Ar substituted analogues, ligand **1**H is somewhat more basic, but sterically more demanding. Introduction of a succinimide substituent in **2**H slightly decreases its basicity, which is compensated by an increased steric crowding in complexes with **2**. The decreased stability of complexes **3** and **4** towards disproportionation, which correlates with their reduced reactivity towards CuO*t*Bu, seem to be of steric, rather than of electronic origin. While partial, slow conversion to the acetonitrile complex **3c** and complete conversion to a pyridine complex **3e** was observed with **1**H, no acetonitrile complex and only partial conversion to the pyridine complex **4e** was observed for the slightly less basic, but more bulky succinimide-substituted **2**H. Formation of the triphenylphosphine complex, which was fast in the case of **3a**, required several hours for **4a**. In further agreement with steric rather than electronic factors is the reported synthesis of stable vinyltrimethylsilane and bis(trimethylsilane)acetylene copper complexes of *nacnac* ligands with simple aliphatic *N*-substituents[8] and that of (*nacnac*^{Bn})Cu(styrene).[19] Overall, diketiminate ligands with chiral aliphatic substituents on nitrogen proved to be easily accessible and, at least in the case of **1**H and its derivatives, economically very attractive (< $10/g). Despite the rotational freedom around the N-C* bond, the ligand

appears to be sufficiently rigid, as evidenced by comparable torsion angles of the methylbenzyl substituent in all structurally characterized complexes. Taking further into account the increased sterical crowding of the metal center evidenced by the structural data, chiral diketimines such as **1**H might be interesting ligands for catalytic applications if the problem of complex stability in the absence of strongly coordinating ancillary ligands can be addressed. The effects of different ligand backbone substitutions on complex stability are currently under investigation.

Experimental Section.

All reactions were carried out under nitrogen atmosphere using Schlenk or glovebox techniques. THF was distilled from sodium/benzophenone. All other solvents were dried by passage through activated aluminum oxide (MBraun SPS) and de-oxygenated by repeated extraction with nitrogen. C_6D_6 was distilled from Na and de-oxygenated by three freeze-pump-thaw cycles. Cu*O*t*Bu*[25] and CuMes[26] were synthesized as reported. All other chemicals were obtained from commercial suppliers and used as received. NMR spectra were recorded on a Bruker ARX 400MHz spectrometer and referenced to residual solvent (C_6D_5H: δ 7.15, C_6D_6: δ 128.02) or external reference (^{31}P, 75% H_3PO_4). Elemental analyses were performed by the Laboratoire d'Analyse Elémentaire (Université de Montréal).

2-(*S*-2-phenylethyl)amino-4-(*S*-4-phenylethyl)imino-pent-2-ene, *SS*-1H Acetylacetone (2.6 mL, 25 mmol), *p*TsOH (4.7 g, 25 mmol) and *S*-Ph(Me)CHNH$_2$ (3.0 g, 25 mmol) were combined with toluene (250 mL). The resulting white suspension was refluxed for 3 h with the help of Dean-Stark apparatus to afford a yellow solution. After cooling to room temperature, a second equivalent of *S*-Ph(Me)CHNH$_2$ (3.0 g, 25 mmol) was added. The reaction mixture was then refluxed for 5 days. On cooling to room temperature, a brown precipitate appeared. The suspension was added to an aqueous KOH solution (5.0 g, 0.45 M) and stirred for 30 min. The phases were separated and the aqueous phase extracted twice with toluene (400 mL). The combined organic phases were dried over Na_2SO_4. Filtration and evaporation of the solvent gave a brown oil, which was dissolved in EtOH (10 mL). Colorless crystals formed at –20 °C after 1 day (5.2 g, 70%). ^1H NMR ($CDCl_3$

400MHz): δ 11.89 (bs, 1H, NH), 7.20-7.35 (m, 10H, Ph), 4.68 (q, 2H, *J* = 7 Hz, C*H*(Me)Ph), 4.48 (s, 1H, CH(C=N)$_2$), 1.82 (s, 6H, Me(C=N)), 1.49 (d, 6H, *J* = 7 Hz CH(*Me*)Ph). ^{13}C NMR ($CDCl_3$ 101 MHz): δ 159.7 (C=N), 146.9 (*ipso* Ph), 128.4 (*ortho* Ph), 126.3 (*para* CH(Me)*Ph*), 126.2 (*meta* Ph), 95.2 (*C*H(C=N)$_2$), 55.9 *C*H(Me)Ph), 25.8 (*Me*(C=N)), 19.5 (CH(*Me*)Ph). Anal. Calcd. for $C_{21}H_{26}N_2$: C, 82.31; H, 8.55; N, 9.15. Found: C, 81.67; H, 8.38; N, 9.14. Mp. 43.0-43.8 °C. $[\alpha]_D^{20}$ = +123(1)°·cm^2/g (c = 10^{-3} g/mL, toluene).

2-(*R*-2-phenylethyl)amino-4-(*R*-4-phenylethyl)imino-pent-2-ene, *RR*-1H Following the same procedure as for the *S*-enantiomer, *RR*-**1**H was obtained in 67% yield. Anal. Calcd. for $C_{21}H_{26}N_2$: C, 82.31; H, 8.55; N, 9.15. Found: C, 81.99; H, 8.68; N, 9.07. $[\alpha]_D^{20}$ = –123(1)°·cm^2/g (c = 10^{-3} g/mL, toluene).

2-(*S*-2-phenylethyl)amino-3-succinimido-4-(*S*-4-phenylethyl)imino-pent-2-ene, *SS*-2H. *n*-BuLi (1.5 mL, 2.9 M, 4.4 mmol) was added drop-wise over a period of 45 minutes at room temperature to a yellow solution of *SS*-**1**H (1.0 g, 3.3 mmol) in THF (50 mL). After stirring for 6 h, N-Bromosuccinimide (0.80 g, 4.5 mmol) was added and the resulting yellow suspension was heated for 24 h at 60 °C. The brown suspension obtained was cooled to room temperature, treated with 1,4-dioxane (1 mL) and stirred for a further 30 minutes. The mixture was filtered through a pad of celite, the solvent evaporated and the product extracted into toluene (50 mL). Evaporation of the solvent gave a brown solid (0.90 g, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 13.20 (bs, 1H, NH), 7.19-7.32 (m, 10H, Ph), 4.69 (q, 2H, *J* = 7 Hz, C*H(*Me)Ph), 2.76 (s, 4H, CH_2C(=O)), 1.58 (s, 6H, MeC(=N)). 1.50 (d, 6H, *J* = 7 Hz, CH*(Me)*Ph). ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 178.2 (C=O), 159.0 (C=N), 146.1 (*ipso* Ph), 128.5 (*ortho* Ph), 126.6 (*para* Ph), 126.1 (*meta* Ph), 105.1 (*C*(CN)$_2$ C), 56.3 (*C*HMePh), 28.0 (*Me*C(=N)), 25.7 (CH*Me*Ph), 14.5 (*C*H$_2$C(=O)). Anal. Calcd. for $C_{25}H_{33}N_3O_2$: C, 74.41; H, 7.24; N, 10.41. Found: C, 74.27; H, 7.27; N, 10.29. (Analogous reactions with *RR*-**1**Li(THF) gave *RR*-**2**H).

(*SS*-1)Cu(PPh$_3$), 3a. *SS*-**1**H (250 mg, 0.82 mmol), mesityl copper (150 mg, 0.83 mmol), CuO*t*Bu (11mg, 0.082 mmol) and PPh_3 (220 mg, 0.84 mmol) were dissolved in toluene (5

mL) to give a yellow-brown solution. After stirring for 1 h, the solution was concentrated to half its volume, layered with hexane (4 mL) and kept at –35ºC. Yellow crystals formed after 1 day (411 mg, 80%). ^{1}H NMR (C_6D_6, 400 MHz): δ 6.84-7.42 (m, 25H, CH(Me)*Ph* & P*Ph*$_3$), 5.01 (q, 2H, *J* = 7 Hz, C*H*(Me)Ph) , 4.84 (s, 1H, CH(C=N)$_2$), 2.00 (s, 6H, MeC(=N)), 1.36 (d, 6H, CH(*Me*)Ph, *J* = 7 Hz). ^{13}C NMR (C_6D_6, 101 MHz): δ 164.0 (CN), 148.3 (*ipso* CH(Me)*Ph*), 134.4 (d, J_{CP} = 4 Hz, *ortho* PPh$_3$), 129.4 (*ortho* or *meta* CH(Me)*Ph*), 128.5 (d, J_{CP} = 2Hz, *meta* PPh$_3$), 128.1, 127.1 (*ortho* or *meta* CH(Me)*Ph*), 125.7, 96.4 (*C*H(C=N)$_2$), 58.9 (*C*H(Me)Ph)., 25.4 (*Me*C(=N)), 23.7 (CH(*Me*)Ph). (*ipso* PPh$_3$ elusive). ^{31}P{^{1}H} NMR (C_6D_6, 75 MHz): δ 3.9. Anal. Calcd. for $C_{39}H_{40}N_2P_1Cu$: C, 74.20; H, 6.39; N, 4.44. Found C, 73.89; H, 6.52; N, 4.37.

(*SS*-1)Cu(DMAP), 3b. CuO*t*Bu (22 mg, 0.17 mmol), *SS*-**1**H (50 mg, 0.17 mmol), and DMAP (20 mg, 0.17 mmol) were dissolved in toluene (1 mL) to give a yellow solution. After stirring for 15 min, the solution was evaporated. The resulting yellow solid was suspended in toluene/hexane 1:1 (2 mL), filtered through a plug of celite and the filtrate kept at -30 C. Yellow crystals formed after 4 h (53 mg, 65%). ^{1}H NMR (C_6D_6 400 MHz, 298 K): δ 7.09–7.63 (m , 12H, CH(Me)*Ph* & *ortho* DMAP CH), 5.58 (bs, 2H, *meta* DMAP) 5.07 (q, 2H, *J* = 6 Hz C*H*(Me)Ph), 4.75 (s,1H, CH(C=N)$_2$), 2.15 (s, 6H, DMAP Me) 2.11 (s, 6H, MeC(=N)), 1.60 (d, 6H, *J* = 6 Hz CH(*Me*)Ph). ^{13}C NMR (C_6D_6 101 MHz, 298 K): δ 162.7 (C=N), 150.0 (*ortho* DMAP) 149.1 (*ipso* Ph), 128.1 (*meta* Ph), 127.2 (*ortho* Ph), 125.6 (*para* Ph), 106.9 (*meta* DMAP), 102.8 (*para* DMAP) 94.6 (*C*H(C=N)$_2$), 58.9 (*C*HMePh), 40.0 (DMAP Me), 26.2 (*MeC*(=N)), 23.1 (CH*Me*Ph). Anal. Calcd. for $C_{28}H_{35}N_4Cu$: C, 67.68; H, 7.36; N, 11.69. Found: C, 67.24; H, 7.13; N, 11.08.

(*SS*-1)Cu(NCMe), 3c. (1) Mesitylcopper (60 mg, 0.33 mmol), CuO*t*Bu (4 mg, 0.03 mmol) and *SS*-**1**H (100 mg, 0.33 mmol) were suspended in acetonitrile (3 mL). Toluene (3 mL) was added until a clear solution was obtained. The solution was stirred for 1 h, concentrated to half its volume and kept at -35°C. Yellow crystals formed after 1 day (98 mg, 72%). (2) *SS*-**1**H (167 mg, 0.60 mmol), CuO^{t}Bu (85 mg, 0.62 mmol) and MeCN (200 μL) were mixed in Et_2O (5 mL) to afford a yellow solution. The solution was kept at –35°C. Yellow crystals formed after 1 day (132 mg, 55%). ^{1}H NMR (C_6D_6, 400MHz, 298

K) δ 7.07-7.57 (m, 10H, CH(Me)*Ph*), 5.01 (q, 2H, *J* = 6 Hz C*H*(Me)Ph), 4.60 (s,1H, $CH(C=N)_2$), 2.02 (s, 6H, MeC(=N)), 1.78 (d, 6H, *J* = 6 Hz CH(*Me*)Ph), 0.73 (s, 3H, NCMe). ^{13}C NMR (C_6D_6 101 MHz): δ 163.1 (C=N), 147.6 (*ipso* Ph), 128.2 (*meta* Ph), 127.2 (*ortho* Ph), 125.8 (*para* Ph), 116.1 ($NCCH_3$) 95.1 ($CH(C=N)_2$), 59.2 (*C*H(Me)Ph), 27.3 (*MeC*(=N)), 23.0 (CH(*Me*) Ph), 0.2 ($NCCH_3$). Anal. Calcd. for $C_{23}H_{28}N_3Cu$: C, 67.37; H, 6.88; N, 10.25. Found: C, 67.14; H, 7.07; N, 10.11. IR (toluene): ν_{CN} = 2254 cm^{-1}.

In acetonitrile-free C_6D_6 solutions of **3c** a second isomer (B) is observed (see text): ^1H NMR (C_6D_6, 400MHz, 298 K) δ 7.05-7.59 (m, 10H, CH(Me)*Ph*), 4.92 (s,1H, $CH(C=N)_2$), 4.41 (q, 2H, *J* = 6 Hz C*H*(Me)Ph), 2.35 (bs, 6H, MeC(=N)), 1.45 (d, 6H, *J* = 6 Hz CH(*Me*)Ph), 0.50 (s, 3H, NCMe). ^{13}C NMR (C_6D_6, 101 MHz): δ 167.5 (C=N), 146.4 (*ipso* Ph), 128.6 (*meta* or *ortho* Ph), 127.1 (*ortho* or *meta* Ph), 126.7 (*para*Ph), 116.1 ($NCCH_3$) 95.1 ($CH(C=N)_2$), 59.2 (*C*H(Me)Ph), 30.4 (*Me*C(=N), 26.1 (CH(*Me*)Ph), 0.2 ($NCCH_3$).

(*SS*-1)Cu($CNC_6H_3Me_2$), 3d. *SS*-**1**H (100 mg, 33.0 μmol), $CNC_6H_3Me_2$ (43.0 mg, 33 μmol) and CuO*t*Bu (45 mg, 33 μmol) were dissolved in ether (10 mL) to afford a bright yellow solution. After stirring for 15 minutes, the solution was evaporated to give yellow brown oil (152 mg, 92%) (4 mL). ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 6.99-7.56 (m, 10H, CHMe(*Ph*)), 6.71 (t, 1H, *J* = 8Hz, *para* $C_6H_3Me_2$), 6.55 (d, 2H, *J* = 8Hz, *meta* $C_6H_3Me_2$), 5.03 (q, 2H, *J* = 7 Hz, C*H(*Me)Ph), 4.71 (s, 1H, $CH(C=N)_2$), 2.05 (s, 6H, C(=N)Me), 1.84 (s, 6H, $C_6H_3Me_2$) 1. 80 (d, 6H, *J* = 7 Hz, (CH*(Me)*Ph). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 163.3 (*C*=N), 149.0, 134.6, 128.2, 128.1, 127.9, 127.2, 125.9, 95.6 ($CH(C=N)_2$), 59.0 (*C*HMePh), 27.6 (C(=N)*Me*), 23.0 (CH*Me*Ph), 18.5 ($C_6H_3Me_2$). Two peaks were elusive. Anal. Calcd for $C_{30}H_{34}N_3Cu$: C, 72.04; H, 6.85; N, 8.40. Found: C, 71.81; H, 7.01; N, 8.13. IR (toluene): ν_{CN} = 2114 cm^{-1}.

(*SS*-2)CuPPh_3, **4a.** *SS*-**2**H (126 mg, 0.31 mmol), CuO*t*Bu (42 mg, 0.31 mmol) and PPh_3 (78 mg, 0.30 mmol) were dissolved in toluene (3 mL) to give a brown solution. After stirring for 15 min, the solution was evaporated. Addition of ether (6 mL) to the resulting brown oil gave a light brown precipitate. Decantation, washing with ether (6 mL) and

drying yielded 100 mg, (47%) of an off-white powder. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.07-7.61 (m, 25H, CH(Me)*Ph* & P*Ph*$_3$), 5.01 (q, 2H, *J* = 7 Hz C*H*(Me)Ph), 2.09 (s, 4H, $CH_2C(=O)$), 1.90 (s, 6H, C(=N)Me), 1.54 (d, 6H, *J* = 7 Hz, CH(*Me*)Ph). ^{13}C NMR (C_6D_6, 101 MHz, 298 K) δ 178.4 (C=O), 163.1 (C=N), 147.5 (*ipso* CH(Me)*Ph*), 134.2 (d, *J* = 14 Hz, *ortho* PPh_3), 129.5 (*ortho* or *meta* CH(Me)*Ph*), 128.7 (d, *J* = 9 Hz, *meta* PPh_3), 127.1 (*ortho* or *meta* CH(Me)*Ph*), 126.0, 98.3 (*C*H(C=N)$_2$), 59.3 (*C*H(Me)Ph), 28.0 (*C*H_2C(=O)), 24.8 (*Me*C(=N)), 17.7 (CH(*Me*)Ph). Two signals missing. ^{31}P{^{1}H} NMR (C_6D_6, 75 MHz, 298K): δ 3.6. Anal. Calcd. for $C_{43}H_{43}N_3O_2PCu$: C, 70.91; H, 5.95; N, 5.77. Found C, 70.26; H, 5.99; N, 5.69.

(*SS*-2)CuCN(2,6-Me$_2$C$_6$H$_3$), 4d. *SS*-**2**H (100 mg, 25.0 μmol), 2,6-xylyl isonitrile (32.0 mg, 25 μmol) and CuO*t*Bu (40 mg, 27 μmol) were dissolved in toluene (4 mL) to afford a dark-brown solution. After stirring for 15 minutes, the solution was layered with hexane (4 mL). Dark-yellow crystals formed after 2 days (68 mg, 47%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 6.94-7.48 (m, 10H, CHMe*Ph*), 6.69 (t, 1H, *J* = 8 Hz, *para* $C_6H_3Me_2$), 6.52 (d, 2H, *J* = 8 Hz, *meta* $C_6H_3Me_2$), 5.00 (q, 2H, *J* = 7 Hz, C*H*(Me)Ph), 2.01 (s, 4H, $CH_2C(=O)$), 1.85 (s, 6H, C(=N)Me), 1.78 (s, 6H, $C_6H_3Me_2$) 1. 77 (d, 6H, *J* = 7 Hz, (CH*(Me)*Ph). ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K): δ 178.2 (C=O), 159.0 (C=N), 148.3, 134.6, 127.9, 127.1, 126.1, 97.5 (*C*H(C=N)$_2$), 59.3 (*C*HMePh), 28.0 (*Me*C(=N)), 26.7 (CH*Me*Ph), 18.5 (*C*H_2C(=O)), 17.2 ($C_6H_3Me_2$)**.** Four peaks are elusive**.** Anal. Calcd for $C_{34}H_{37}N_4O_2Cu$: C, 68.38; H, 6.24; N, 19.38. Found: C, 68.12; H, 6.31; N, 9.05. IR (toluene): ν_{CN} = 2117 cm^{-1}.

General experimental procedure for NMR experiments

A vial was charged with *SS*-**1**H (10 mg, 33 μmol), CuO*t*Bu (4-5 mg, 33-40 μmol) or 2,4,6-mesityl copper (6 mg, 40 μmol) with catalytic amounts of CuO*t*Bu (3-4 μmol), and the respective Lewis base (33-159 μmol). C_6D_6 (0.6-0.7 mL) was added. After shaking thoroughly to obtain a homogeneous solution, the content was transferred to a J. Young tube. ^{1}H NMR (C_6D_6, 400 MHz) were taken immediately, after1 h, and - in some cases - after 1 day.

(*SS*-1)Cu(NCMe), 3c. δ 7.07-7.57 (m, 10H, CH(Me)*Ph*), 5.01 (q, 2H, *J* = 6 Hz C*H*(Me)Ph), 4.60 (s,1H, CH(C=N)$_2$), 2.02 (s, 6H, MeC(=N)), 1.78 (d, 6H, *J* = 6 Hz, CH(*Me*)Ph), 0.73 (s, 3H, NCMe). Only 60% conversion was observed before decomposition

(*SS*-1)CuPy, 3e. δ 6.51–7.40 (m , 15H, CH(Me)*Ph* & Py), 4.96 (q, 2H, *J* = 6 Hz C*H*(Me)Ph), 4.72 (s,1H, CH(C=N)$_2$), 2.09 (s, 6H, MeC(=N)), 1.40 (d, 6H, *J* = 6 Hz, CH(*Me*)Ph).

(*SS*-1)Cu(PMe$_3$), 3f. δ 7.10-7.53 (m, 10H, CH(Me)*Ph*), 4.94 (q, 2H, *J* = 6 Hz C*H*(Me)Ph), 4.72 (s, 1H, CH(C=N)$_2$), 2.04 (s, 6H, MeC(=N)), 1.57 (d, 6H, *J* = 6 Hz, CH(*Me*)Ph), 0.35 (bs, 9H, PMe$_3$).

(*SS*-2)CuPy, 4e. δ 6.60–8.52 (CH(Me)*Ph* & Py), 4.93 (q, 2H, *J* = 6 Hz C*H*(Me)Ph), 1.86 (s, 4H, C(=O)CH$_2$), 1.51-1.52 (MeC(=N)), 1.38 (d, 6H, *J* = 6 Hz CH(*Me*)Ph). Several peaks overlap with those of **2**H.

X-ray diffraction studies. Diffraction data were collected on a Bruker Smart Bruker Smart APEX II with graphite monochromated Mo Kα radiation (**3a & 3c**) and a Bruker SMART 6000, equipped with a rotating anode source and Mirror Montel 200-monochromated Cu Kα radiation. Cell refinement and data reduction were done using APEX2.[27] Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97.[28] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropic on calculated positions using a riding model. Further experimental details are listed in Table III-2 and given in the supporting information. Refinement of the Flack-x parameter in **1**H and **2**H resulted in unacceptable standard deviations and Friedel pairs have thus been merged prior to refinement for this structure.

Table III-3. Details of X-ray Diffraction Studies

	SS-**1**H	*RR*-**2**H	*SS*-**3c**	*SS*-**3b**	*SS*-**3a**	*SS*-**4d**	{(RNC)Cu(O^tBu)}$_4$
Formula	$C_{21}H_{26}N_2$	$C_{25}H_{29}N_3O_2$	$C_{23}H_{28}CuN_3$	$C_{28}H_{35}CuN_4$	$C_{39}H_{40}CuN_2P$	$C_{34}H_{37}CuN_4O_2$	$C_{52}H_{72}Cu_4N_4O_4$
Mw (g/mol); $d_{calcd.}$ (g/cm^3)	306.44; 1.093	403.51; 1.218	410.02; 1.310	491.14; 1.248	631.24; 1.303	597.22;	1071.30; 1.331
T (K); F(000)	150; 332	150; 864	150; 864	150; 2080	150; 1328	150; 1256	150; 2240
Crystal System	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	Aba2
Unit Cell: *a* (Å)	10.8574(5)	9.7805(3)	7.1000(3)	16.3922(8)	10.1345(6)	10.0461(9)	24.4180(8)
b (Å)	7.5650(3)	12.5052(4)	8.6253(4)	19.2373(9)	16.2516(9)	13.1703(11)	23.1746(9)
c (Å)	12.5158(6)	17.9988(6)	33.9399(17)	18.4203(12)	19.5435(11)	22.9287(19)	9.4477(3)
β (°)	115.054(2)			115.838(1)			
V ($Å^3$); Z	931.27(7); 2	2201.4(1); 4	2078.5(2); 4	5228.0(5); 8	3218.9(3); 4	3033.7(4); 4	5346.2(3); 4
θ range (°); completeness	3.9-71.1; 0.99	4.3-75.5; 1.00	1.2-31.4; 0.97	2.7-72.7; 0.99	1.6-31.4; 0.97	3.9-72.7; 1.00	3.6-72.6; 0.99
Refl.: collec./indep.; R_{int}	11088/1929; 8.8%	28674/2474; 3.2%	48406/6597; 2.6%	68189/19992; 4.0%	73790/10102; 3.5%	39607/5976; 4.8%	34639/5249; 4.0%
μ (mm^{-1}); Abs. Corr.	0.483; multi-scan	0.617; multi-scan	1.062; multi-scan	1.332; multi-scan	0.758; multi-scan	1.299; multi-scan	2.133; multi-scan
R1(F); $wR(F^2)$; $GoF(F^2)$ [a]	4.9%; 13.6%; 1.05	3.73%; 10.4%; 1.05	2.7%; 6.5%; 1.08	6.1%; 17.5%; 1.0	3.1%; 6.6%; 0.95	4.5%; 10.4%; 0.94	3.6%; 8.6%; 1.02
Flack x-parameter	-	-	0.019(8)	0.05(3)	0.015(6)	-0.05(3)	-
Residual electron density	0.15; –0.17	0.36; –0.41	0.46; –0.43	0.60; –0.39	0.30; –0.45	0.22; –0.68	0.39; –0.54

[a] R1(F) based on observed reflections with I>2s(I), $wR(F^2)$ and $GoF(F^2)$ based on all data.

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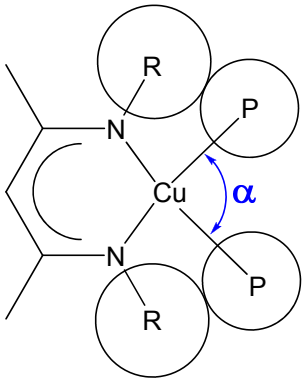
Supplementary material

To address the respective steric bulk of the chiral ligand **1**, we calculated the "in-plane accessible aperture" for several complexes. For this purpose, atomic coordinates (H excluded) of the diketiminate copper fragment in (*nacnac*)Cu(PPh_3) complexes were used. A phosphorous atom in an idealized distance of 2.2 Å from the Cu center was moved in the N_2Cu-plane. The accessible angle range before the distance of P to one of the ligand atoms went below the sum of the VdW-radii was considered the "in-plane accessible aperture", α.



R	α	X-ray data
-CH(Me)Ph	13°	this work
2,6-dimethylphenyl	40°	ref. 1
1,4,6-trimethylphenyl	41°	ref. 2
2,6-diisopropylphenyl	46°	ref. 3
vdW-radii: C_{Ar}, 1.7 Å, $C_{aliph.}$, 1.9 Å, P, 1.8 Å. Hydrogen atoms were ignored.		

Figure S3.1: Calculation of the lateral aperture angle in *nacnac*CuPPh_3 complexes

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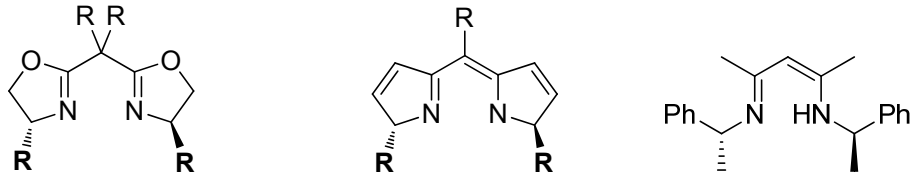
Chapter 4

Applications of N-Alkyl β-Diketiminato Copper Complexes in Organic Synthesis

4.1 Introduction

Copper compounds are involved in numerous organic transformations both catalytically and stoichiometrically,[1] and the use of chiral supporting ligands in the presence of prochiral substrates allows for asymmetric induction. β-Diketiminato copper complexes have not been much applied for this purpose. Warren applied *nacnac* copper complexes in cyclopropanation,[2] oxygen transfer to an organic substrate,[3] aziridination[4] and C-H amination,[5] while Sadigh and co-workers used fluorinated β-diketiminato copper complexes for intramolecular aerobic hydroxylation.[6] To the best of my knowledge, there are no other cases where copper β-diketiminate complexes have been employed in organic synthesis.

Chirality is easily introduced in *N*-alkyl substituted *nacnac* ligands. In chapter three, the synthesis of the chiral complexes *S*,*S*-*nacnac*$^{CH(Me)Ph}$CuL (L = PPh_3, PMe_3, $CNC_6H_3(Me)_2$, DMAP, lutidine, Py, MeCN) was reported. The ligand framework structurally resembles the BOX[7] and the semicorrin[8] ligands, which have been employed successfully in catalysis, especially in the cyclopropanation of olefins (Figure 4.1).[9] As a result, the complexes with PPh_3 and MeCN as supporting Lewis bases, were employed in the cyclopropanation of styrene and the conjugate addition of of $ZnEt_2$ to 2-cyclohexenone. For the sake of comparison, some achiral complexes were also employed.



A **B** **C**

Figure 4.1: BOX ligand (**A**), semicorrin (**B**) and *S*,*S*-nacnac$^{CH(Me)Ph}$H (**C**).

4.2 Results and Discussion

The preparation of the catalysts (Figure 4.2)[10] is described in other chapters. All copper complexes display a preferred conformation with the hydrogen atom of the CH(Me)Ph substituent oriented towards the ligand backbone in their crystal structures.

Chapter 1, section 1.1 might be consulted for more information on cyclopropanation and conjugate addition reactions.

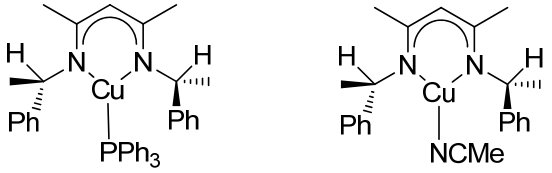


Figure 4.2: Chiral complexes used in cyclopropanation and conjugate addition reactions.

4.2.1 Cyclopropanation

Drop-wise addition of ethyldiazoacetate (EDA) to a solution of styrene with 2 mol% copper catalyst present gave the cyclopropanation products together with side products **4-1** and **4-2** resulting from EDA coupling (GC/MS analysis). Similar olefins resulting from the coupling of diazo compounds have been reported[2,11] and they account for the low yields observed in some cases. The results obtained in the cyclopropanation reaction are shown in table IV-1.

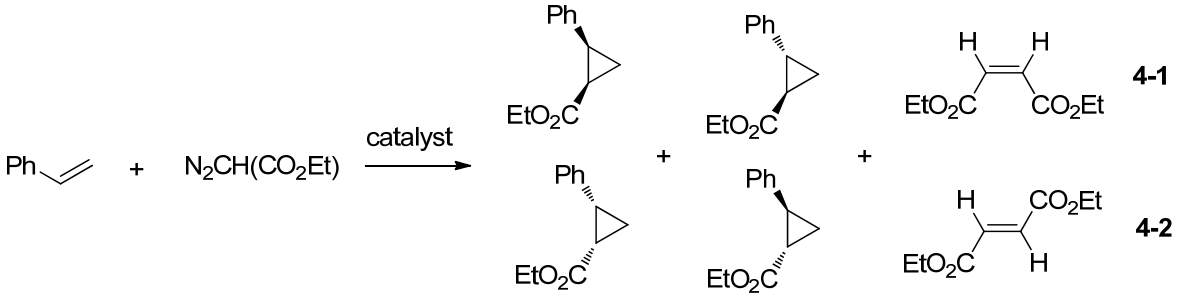


Figure 4.3: Cyclopropanation of styrene with EDA.

Table IV-1: Results of cyclopropanation of styrene with EDA

Entry	**Catalyst**	**Equiv styrene**	**T/°C**	**dr[b]**	**Time/h**	**Yield (%)**
1	no catalyst	2	25	34/66	2	20
2	*nacnac*$^{CH(Me)Ph}$CuPPh$_3$	2	0	34/66	2	12
3	*nacnac*$^{CH(Me)Ph}$CuNCMe	2	25	34/66	2	26
4	*nacnac*$^{CH(Me)Ph}$CuPPh$_3$	1	25	34/66	2	8
5	*nacnac*$^{CH(Me)Ph}$CuPPh$_3$	2	25	32/68	2	75
6	*nacnac*$^{CH(Me)Ph}$CuNCMe	5	25	34/66	2	44
7	*nacnac*$^{CH(Me)Ph}$CuNCMe	5	60	33/67	24	51[d]
8	*nacnac*$^{CH(Me)Ph}$CuPPh$_3$	5	60	32/68	24	81[c]
9	*nacnac*^{Bn}Cu(stilbene)	5	60	32/68	24	28
10	CuO*t*Bu + PPh$_3$	5	60	32/68	24	82
11	CuO*t*Bu + *nacnac*$^{CH(Me)Ph}$H	5	60	33/67	24	24
12	Cu(MeCN)$_4$PF$_6$	5	60	33/68	24	70
13	no catalyst	5	60	32/68	24	24

Typical errors in repeated experiments (not shown) for dr and yields are in the range $\pm$2% and $\pm$5% respectively. [a]Reaction conditions: 2 mol% catalyst, toluene solution. [b]Yields and *cis-trans* ratio were determined by GC. [c]ee = 0, determined by chiral HPLC. [d]ee results pending.

The *cis*-*trans* ratio is almost the same for all the entries. This was not surprising, as previous studies have shown that the diastereomeric ratio is mostly affected by steric interactions between EDA and the olefin.[12] Increasing the concentration of styrene increases the yields. With only one equiv of styrene, there is practically no reaction (entry **4**). Temperature also has a profound influence on the reaction and only 12% cyclopropanation product was obtained when the reaction was performed at 0 °C (entry **2**). At this temperature, more side products were formed. Under identical reaction condition but at 60 °C, the yields increased.

Comparing entries **1** and **13** with the other entries, it is obvious that there is some catalytic influence. From entries **3, 6, 7** and **9**, it could be seen that *nacnac*$^{CH(Me)Ph}$CuNCMe and *nacnac*^{Bn}Cu(stilbene) appear to be less active than *nacnac*$^{CH(Me)Ph}$CuPPh$_3$. This was unexpected, given the stronger binding of PPh$_3$ to the coordination site required for catalysis. In fact, we have shown by adding 1,10-phenanthroline to a C_6D_6 solution of the complexes that the PPh$_3$ adduct is more stable than the MeCN and stilbene adducts. While MeCN and stilbene are completely displaced to form *nacnac*$^{CH(Me)Ph}$Cu(phen) and *nacnac*^{Bn}Cu(phen) complexes, no such product was identified in the ^{1}H NMR spectrum of a solution of *nacnac*$^{CH(Me)Ph}$CuPPh$_3$ and 1,10-phenanthroline. Furthermore, a mixture of CuO*t*Bu and PPh$_3$ (entry **10**) or the cationic complex Cu(MeCN)$_4$PF$_6$ (entry **12**) gave activities comparable to *nacnac*$^{CH(Me)Ph}$CuPPh$_3$, while only low activities were observed with mixtures of CuO*t*Bu and *nacnac*$^{CH(Me)Ph}$H (Entry **11**). The stability of the copper PPh$_3$ complex, coupled with the high activity of the CuO*t*Bu/PPh$_3$ mixture suggest that the active species is $[Cu(PPh_3)_n]^+$ rather than *nacnac*Cu and that the *nacnac* ligand is displaced before the active species enters the catalytic cycle. Consequently, no chiral induction is observed in these reactions. Slightly lower activities of *nacnac*$^{CH(Me)Ph}$Cu(NCMe) compared to *nacnac*$^{CH(Me)Ph}$CuPPh$_3$ might be related to the fact that diketiminate dissociation is less pronounced in these cases.

4.2.2 Conjugate addition reaction

The addition of alkylating agents to enones may lead either to 1,2- or 1,4-products, the outcome depending on the nature of the nucleophile. While organolithium and organomagnesium reagents favour the 1,2-product, soft nucleophiles like cuprates and $ZnEt_2$ yield mostly the 1,4-addition product. $ZnEt_2$ can be used to efficiently ethylate 2-cyclohexenone in the presence of a chiral catalyst in order to obtain regio- and enantioselective reactions.

The reaction was performed on a large scale and purified by flash chromatography in order to obtain pure samples for the construction of a calibration curve using dodecane as internal standard. In further reactions, products were identified by GC/MS, subsequent analyses were done using GC/FID while ee was determined by SFC (Supercritical Fluid Chromatography). The results are depicted in table IV-2.

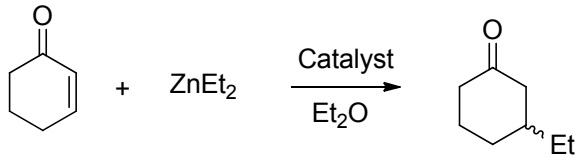


Figure 4.4 : Conjugate addition of $ZnEt_2$ to 2-cyclohexenone.

Table IV-2: Results obtained for the addition of $ZnEt_2$ to 2-cyclohexenone.

Entry	**Catalyst**	**%Catalyst**	**Yield**
1	no catalyst		8
2	LH	5	6
3	PPh_3	5	10
4	CuO*t*Bu	5	25
5	$Cu(MeCN)_4PF_6$	5	71
6	CuO*t*Bu + PPh_3	5	77
7	*nacnac*^{Bn}Cu(styrene)	5	48
8	*nacnac*$^{CH(Me)Ph}$Cu(NCMe)	5	61[b]
9	*nacnac*$^{CH(Me)Ph}$CuPPh$_3$	5	80[c]
10	*nacnac*^{Bn}CuPPh$_3$	5	75
11	*nacnac*$^{CH(Me)Ph}$CuPPh$_3$	10	100

Typical errors in repeated experiments (not shown) for yields are in the range $\pm$5%. [a]Yields were determined by GC. [b]ee result pending. [c]ee = 0 (SFC).

As can be seen for entries **1**-**3**, $ZnEt_2$ is not a good reagent for the reaction even in the presence of potential ligands such as *nacnac* or PPh_3. Copper salts alone do catalyze the reaction, though sluggishly (entry **4**) while high activities are observed in the presence of $[L_nCu]^+$, where L = PPh_3 or MeCN (entries **5** and **6**). Diketiminate complexes *nacnac*^{R}CuL proved to be active catalyst precursors. As observed before, higher activities were observed with the strongly coordinating PPh_3 as the ancilliary ligand. This, combined with complete absence of chiral induction and general lower activities of *nacnac*CuL compared to $[L_nCu]^+$, indicate that again, the diketiminate ligand was lost before the compound enters the catalytic cycle.

4.3 Summary

The chiral β-diketiminato copper(I) complexes do not show any chiral induction in the cyclopropanation of styrene with EDA or in conjugate addition of $ZnEt_2$ to 2-cyclohexenone. This is most likely due to the loss of the chiral ligand prior to the catalytic cycle.

4.4 Experimental

4.4.1 General procedure for the conjugate addition reaction

2-Cyclohexenone (300 mg, 3.0 mmol) and the catalyst, *nacnac*$^{CH(Me)Ph}$$CuPPh_3$ (190 mg, 0.3 mmol) were suspended in ether (5 mL). $ZnEt_2$ in ether (5 mL) was added drop-wise to the yellow suspension. The resulting brown suspension was stirred for 3h and then HCl (20 mL, 0.1 M) was added. Ether (15 mL) was added. The reaction mixture was stirred for 30 minutes. The etheral layer was collected, dried over $MgSO_4$ and passed through a pad of silica. Evaporation of the colourless solution gave brown oils.

4.4.2 General procedure for cyclopropanation of styrene

The catalyst (2 mol%) and styrene were dissolved in toluene (1-3 mL) to give a yellow solution. EDA in toluene (1-3 mL) was added drop-wise. After stirring for 2-24 h, the resulting brown suspension was passed through a pad of silica and analysed by GC and GC-MS.

4.5 References

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Chapter 5

Synthesis and Structures of Isopropyl-β-Diketiminato Copper(I) Complexes

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Paul O. Oguadinma and Frank Schaper

Département de chimie, Université de Montréal, Montréal, Québec, H3C 3J7, Canada.

Abstract

Reaction of *N,N'*-diisopropyl-2-amino-4-iminopent-2-ene (*nacnac*^{iPr}H, **1**) with CuO*t*Bu or mesityl copper and 10% CuO*t*Bu in the presence of PPh_3, $CN(C_6Me_2H_3)$ or MeCN afforded the Lewis base-coordinated complexes *nacnac*^{iPr}CuPPh$_3$·0.5 C_6H_{14}, **2**, *nacnac*^{iPr}CuCN($C_6Me_2H_3$), **3**, and *nacnac*^{iPr}Cu(NCMe), **4**. Compounds **2**, **3** and **4** were characterised by single crystal X-ray diffraction studies. Compound **4** afforded two species in deuterated benzene in a 2:1 ratio, which were assigned to {*nacnac*^{iPr}Cu}$_2$(μ-NCMe) and *nacnac*^{iPr}CuNCMe, **4**. Upon addition of 5 equiv. of MeCN the two sets collapsed into that of **4**. No copper complexes were formed in the presence of styrene, stilbene or diphenylacetylene.

La réaction du *N,N'*-diisopropyl-2-amino-4-iminopent-2-ene (*nacnac*^{iPr}H, **1**) avec le CuO*t*Bu ou le mesityle de cuivre et 10% de CuO*t*Bu en présence de PPh_3, de $CN(C_6Me_2H_3)$ ou de MeCN a donné les complexes *nacnac*^{iPr}CuPPh$_3$·0.5 C_6H_{14}, **2**, *nacnac*^{iPr}CuCN($C_6Me_2H_3$), **3**, et *nacnac*^{iPr}Cu(NCMe), **4**. Composés **2**, **3** et **4** ont été caractérisés par diffraction des rayons X sur monocristaux. Le spectre RMN de **4** dans C_6D_6 montre deux sets de signaux avec un ratio 2:1, assignés au {*nacnac*^{iPr}Cu}$_2$(μ-NCMe) et au *nacnac*^{iPr}CuNCMe, **4**. Après l'addition de 5 éq. de MeCN, seulement les signaux de **4** ont été observés. Aucun complexe de cuivre n'a été obtenu en présence de styrène, stilbène ou diphenylacétylène.

KEYWORDS: diketiminate, copper, coordination chemistry
MOTS CLÉS: dikétiminate, cuivre, chimie de coordination

Introduction

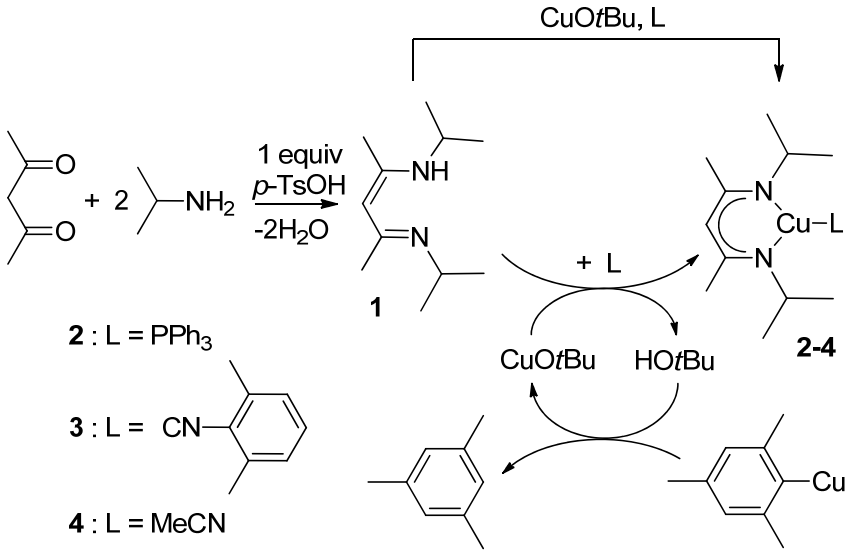
Brookhart's demonstration in the mid 90s that late transition metal α-diimine complexes of Pd and Ni were effective as catalysts in olefin polymerisation[1] paved the way for the synthesis of the corresponding anionic diketiminate versions of these ligand systems.[2] Since then, interest in diketiminates has continued unabatedly and β-diketiminates represent today one of the most extensively employed nitrogen-based,

bidentate ligands in coordination chemistry.[3] The acronym '*nacnac*' is often used to describe 2-amino-4-iminopent-2-ene, which is the *N*-analogue of the ubiquitous acetylacetonate (*acac*). *Nacnac* ligands are monoanionic spectator ligands which have assisted in the isolation of metal complexes in unusual oxidation states and/or coordination numbers.[4] For copper in particular, Tolman's group used diketiminate complexes to model the active site of metalloproteins.[5] Warren and coworkers isolated a *nacnac* copper carbene complex, which they employed in catalytic cyclopropanation, and used copper diketiminates for amination reactions.[6-8] While most applications of diketiminate ligands revolve around *N*-aryl substituents, their *N*-alkyl derivatives have not been well exploited. For copper(I), they are limited to applications in atomic layer deposition,[9] or analyses of copper ligand bonding.[10] In continuation of previous work on diketiminate copper complexes with *N*-alkyl substituents,[11, 12] we report here the syntheses and characterisation of *N,N'*-diisopropyl *nacnac* Cu^{I} complexes. Just prior to submission of this manuscript, Arii *et al*. reported *nacnac*$^{i\text{Pr}}$Cu germylene complexes, using the same ligand.[13]

Results and Discussion

Ligand and complex synthesis. Ligand **1** has been obtained previously by a multi-step protocol, which is generally used to prepare *N*-alkyl diketiminates, either by employing Meerwein salt (32-60% yield)[14] or dimethylsulfate (74% yield, from the aminoketone)[15] as *O*-alkylating agents. We employed a one-step procedure for condensation of acetylacetone with isopropylamine in the presence of equimolar amounts of *p*-toluenesulfonic acid,[16] which afforded **1** directly, albeit in a relatively low yield of 23% after 5 days of reflux (Scheme 5.1). The analogous ligands *nacnac*$^{\text{Bn}}$H and *nacnac*$^{\text{iBu}}$H, bearing primary alkyl groups, have been obtained in 1-2 days using the same procedure,[12, 17] while *nacnac*$^{\text{CH(Me)Ph}}$H required 5 days.[11] Longer reaction times thus seem to be necessary for secondary amines. Complexes **2**-**4** were obtained as yellow air- and moisture-sensitive powders or crystals in 26-84% yield by reaction of **1** in the presence of PPh_3, xylyl isocyanide or acetonitrile either with Cu*O*t*Bu*, a procedure employed by Dai and Warren for preparing *N*-aryl *nacnac*Cu^{I} complexes,[6] or with mesityl copper and catalytic amounts

of CuO*t*Bu (Scheme 5.1). Mesityl copper in the absence of CuO*t*Bu has been shown to be unreactive.[11] Though no major differences in terms of yields were observed between the use of CuO*t*Bu or MesCu/CuO*t*Bu, the complexes crystallize easier when MesCu/CuO*t*Bu was used, probably due to the smaller amounts of *tert*-butanol present.



Scheme 5.1

Compound **1** did not react with CuO*t*Bu in the presence of styrene, stilbene or diphenylacetylene. Identical observations were made with copper complexes carrying the chiral *nacnac*$^{CH(Me)Ph}$ ligand.[11] On the other hand, Cu styrene complexes are readily obtained with *nacnac*^{Mes} (Mes = 2,4,6-$Me_3C_6H_3$)[18] or *nacnac*^{dipp} (dipp = 2,6-*i*$Pr_2C_6H_3$, see Exp. Section), one of the most sterically encumbered *N*-aryl diketiminates, as well as with *nacnac*^{Bn} or *nacnac*^{iBu}.[12, 17] In-plane coordination of the two carbon atoms of an olefin is thus possible for diketiminate ligands with aryl or primary alkyl substituents, but not if secondary alkyls are present on nitrogen atoms. The implied increased steric demand of *nacnac*^{iPr} compared to *nacnac*^{dipp} has to be set into contrast to observations for other systems. When compared to *nacnac*^{dipp}, diketiminate ligands with secondary alkyl substituents on nitrogen allow additional intramolecular π-coordination in Ti complexes[19]

or coordination of a second *nacnac* to Zr.[20] When considering steric congestion imposed by diketiminate ligands, it is thus important to differentiate between the first coordination sphere around the metal centre, where *nacnac*$^{i\text{Pr}}$ imposes a congested environment, and general steric demand in the (outer) coordination sphere, where it does not.

Crystal structure studies. All three compounds are monomeric and crystallize in the $P2_1/c$ space group with copper in a distorted trigonal planar geometry. Complex **2 (**Figure 5.1) co-crystallizes with half a molecule of hexane. The methine hydrogen atoms of the *i*Pr substituent point towards the methyl groups in the ligand backbone, even in the sterically encumbered **2**. C-N and C-C bond lengths of the diketiminate ligand are in agreement with complete delocalisation of the double bonds (Table V-1). Cu-N bond distances in **3** and **4** are close to the average generally observed in *nacnac*Cu complexes (1.94±0.06 Å)[21] and the copper centre is found in the mean plane of the ligand. With the bulkier phosphine ligand in **2**, longer Cu-N distances and a displacement of C3 and the copper atom by 0.1 and 0.4 Å, respectively, out of the ligand mean plane are observed (plane defined by N1, N2, C2 and C4). While Cu-P and Cu-N bond distances (2.191(1) Å and 1.978(1) & 1.983(1) Å) are comparable to those in *nacnac*$^{\text{CH(Me)Ph}}$$CuPPh_3$ (2.195(1) Å and 1.972(1) & 1.983(1) Å),[11] they are longer than in *nacnac*$^{\text{Ar}}$$Cu(PPh_3)$ complexes (2.16-2.18 Å and 1.94-1.97 Å)[7, 22-24] in agreement with increased steric bulk introduced by a secondary alkyl substituent on the nitrogen atoms.

Table V-1: Selected bond distances [Å] and bond angles [deg] for **2**, **3** and **4**.

	2	**3**	**4**
Cu1-N1	1.978(1)	1.939(2)	1.940(1)
Cu1-N2	1.987(1)	1.935(2)	1.961(2)
Cu1-X [a]	2.191(1)	1.822(2)	1.893(2)
N1-C2	1.323(2)	1.332(2)	1.326(3)
N2-C4	1.321(2)	1.331(2)	1.314(3)
C2-C3	1.408(2)	1.407(3)	1.413(3)
C3-C4	1.411(2)	1.407(3)	1.416(2)
X-Y [b]	1.839(2)	1.161(2)	1.148(3)
N1-Cu1-N2	97.7(1)	100.2(1)	100.6(1)
N1-Cu1-X [c]	132.6(1)	130.9(1)	134.7(1)
N2-Cu1-X [c]	129.4(1)	128.9(1)	124.8(1)

[a] Cu1-P1 (**2**), Cu1-C20 (**3**), Cu1-N3 (**4**). [b] average of P1-C12, P1-C18 and P1-C24 (**2**), N3-C20 (**3**), N3-C12 (**4**). [c] N1,2-Cu1-P1 (**2**), N1,2-Cu1-C20 (**3**), N1,2-Cu1-N3 (**4**).

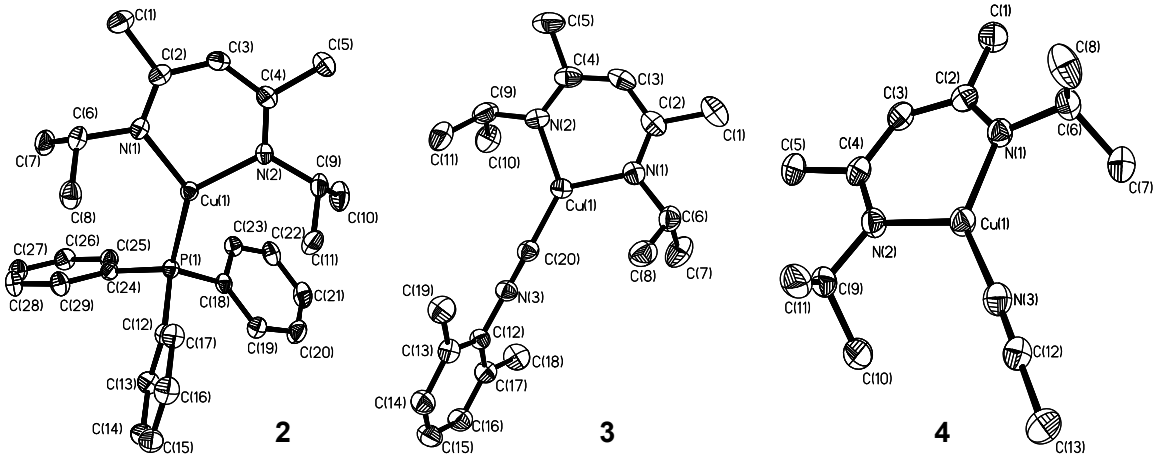
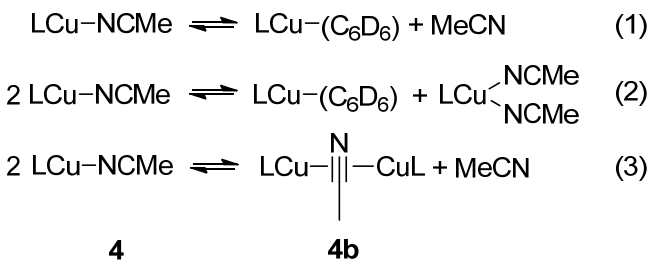


Figure 5.1: Crystal structure of **2**-**4**. Hydrogen atoms and solvent are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Spectroscopic properties. The PPh_3 resonance in the ^{31}P NMR spectrum of compound **2** in C_6D_6 was observed at δ 4.0. This value is intermediate between those of *nacnac*^{Ar}CuPPh$_3$ complexes (Ar = $Me_3C_6H_2$: 5.2 ppm,[7] Ar = $Me_2C_6H_3$: 5.4 ppm,[23] Ar = *i*$Pr_2C_6H_3$: 3.6 ppm[22]) and *nacnac*^{R}CuPPh$_3$ complexes (R = Bn: 3.5 ppm,[12] CH(Me)C_6H_5: 3.9 ppm[11]). While *N*-aryl substituted diketiminate ligands tend to show ^{31}P resonances at lower field, differences are too small to be correlated to ligand properties. Similar to the behaviour observed for *nacnac*$^{CH(Me)Ph}$Cu(NCMe),[11] which also carries a secondary alkyl substituent on N, pure crystals of **4** dissolved in C_6D_6 gave two sets of *nacnac* resonances in a ratio of 2:1 in its ^1H NMR spectrum; the resonances of the major species being slightly broadened. Only one resonance was observed for MeCN. Fast exchange of coordinated and free Lewis base was observed previously in *nacnac*CuL complexes,[11, 12, 25] and the amount of coordinated MeCN in the two species thus cannot be derived from NMR. Only one peak for ν_{CN} was observed at 2259 cm^{-1} in the IR spectrum of **4** in toluene solution, 5 cm^{-1} higher than that of free MeCN.[26] Addition of excess MeCN (5 equiv) caused the peaks to collapse to one set of resonances in its ^1H and ^{13}C spectrum, belonging to the previously minor component. Changes in the overall concentration, on the other hand, did not affect the observed ratio, which rules out equilibrium (1) in scheme 5.2. Complete MeCN redistribution (eq. (2), Scheme 5.2) also seems unlikely, since bis(acetonitrile) complexes have not been reported for diketiminate copper complexes and *nacnac*^{iPr}Cu complexes could not be obtained in the absence of ancillary ligands. We thus assign the species favoured at higher acetonitrile concentrations to the MeCN complex *nacnac*^{iPr}CuNCMe, **4**, observed in the crystal structure, and the broadened peaks of the major species to the bridged complex {*nacnac*^{iPr}Cu}$_2$(μ-NCMe), **4b** (eq. (3), Scheme 5.2). While bridging coordination of acetonitrile is rare, it is not unknown.[27] Monomer-dimer equilibria similar to eq. (3) have been observed for *nacnac*^{Bn}Cu, which forms a diphenylacetylene bridged dimer in the solid state and a monomeric complex in solution when excess diphenylacetylene is present,[12] and for *nacnac*^{Ar}Cu complexes, which display an equilibrium between a monomeric and a dimeric benzene-coordinated complex in solution.[7, 25] While single crystal diffraction studies confirmed the formation of **4**, we were not able to obtain satisfactory elemental analyses, even from crystalline material. Synthesis of **4** was reported at the time of

submission of this article by Arii *et al*. from the reaction of $[Cu(NCMe)_4][CF_3SO_3]$ with *nacnac*^{iPr}Li.[13] Although not discussed therein, they also observed a variable ratio of two products in NMR spectra of **4**.[28]



Scheme 5.2

The stretching frequency ν_{CN} = 2105 cm^{-1} of the isocyanide ligand in **3** is the lowest frequency observed in 2,6-xylyl isocyanide copper complexes with either *N*-alkyl substituted (ν_{CN} = 2111-2117 cm^{-1})[11, 12, 17] or *N*-aryl substituted diketiminate ligands (ν_{CN} = 2121-2126 cm^{-1}),[7, 25, 29] indicating an increased, but still weak π back-donation (free isocyanide: ν_{CN} = 2119 cm^{-1}).

In the course of preparing compound **3**, a minor side product, **5**, was obtained. ^{1}H and ^{13}C NMR spectra of **5** showed resonances of the diketiminate ligand and isocyanide in a ratio of 1:2, which would suggest the formation of *nacnac*^{iPr}Cu$(CNC_6Me_2H_3)_2$. Satisfactory elemental analysis of **5**, however, could not be obtained and, more importantly, addition of one equiv xylyl isocyanide did not transform **3** into **5**. Complex **5** showed the same stretching frequency in its IR spectrum as **3**. Taking also the low solubility of **5** in toluene into account, assignment as a bisisocyanide adduct seems improbable and the structure of **5** remains unclear.

Conclusions

Copper complexes of *nacnac*^{iPr} were readily prepared if additional Lewis base was present to stabilize the complex. In agreement with observations made for *nacnac*$^{CH(Me)Ph}$,[11] diketiminate ligands with secondary alkyl substituents are slightly more Lewis-basic, but

sterically more demanding in the first coordination sphere than diketiminates with aryl or primary alkyl substituents.

Experimental Section

All reactions, except ligand synthesis, were carried out under nitrogen atmosphere using Schlenk or glove box techniques. Solvents were dried by passage through activated aluminum oxide (MBraun SPS) and de-oxygenated by repeated extraction with nitrogen. C_6D_6 was distilled from Na and de-oxygenated by three freeze-pump-thaw cycles. Cu*O*t*Bu[30] and mesitylcopper[31] were synthesized as reported. All other chemicals were obtained from commercial suppliers and used as received. Elemental analyses were performed at the Laboratoire d'Analyse Elémentaire (Université de Montréal). NMR spectra were recorded on a Bruker ARX 400 MHz spectrometer and referenced to residual solvent (C_6D_5H: δ 7.15, C_6D_6: δ 128.02) or external reference (^{31}P, 75% H_3PO_4).

***Nacnac*^{iPr}H, 1.**[14, 15] Acetylacetone (4.0 mL, 38 mmol), *p*-toluenesulfonic acid monohydrate (7.2 g, 38 mmol) and isopropylamine (6.1 mL, 76 mmol) were added to toluene (200 mL) and refluxed with the help of a Dean-Stark apparatus for 5 days, during which the yellow suspension turned brown. After cooling to room temperature, the brown precipitate formed was filtered. The precipitate was washed with toluene (100 mL) and transferred to a K_2CO_3 solution (5 g in 100 mL of water). After stirring for 30 min, the aqueous phase was extracted with toluene (3x100 mL). The combined organic phases were dried over $MgSO_4$ and then filtered. The filtrate was evaporated to obtain brown oil (1.6 g, 23%), which was employed without further purification in subsequent synthesis.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.44 (bs, 1H, NH), 4.38 (s, 1H, *H*C(C=N)$_2$), 3.64 (sp, *J* = 6 Hz, 2H, C*H*(CH$_3$)$_2$), 1.89 (s, 6H, Me(C=N)$_2$), 1.16 (d, *J* = 6 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 158.5 (C=N), 93.5 (H*C*(C=N)$_2$), 46.7 (*C*H(CH$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 18.7 (*Me*(C=N)$_2$). ^{1}H NMR (C_6D_6, 400 MHz): δ 11.63 (bs, 1H, NH), 4.46 (s, 1H, *H*C(C=N)$_2$), 3.46 (sp, *J* = 6 Hz, 2H, C*H*(CH$_3$)$_2$), 1.71 (s, 6H, Me(C=N)$_2$), 1.11 (d, *J* = 6 Hz,

12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 101 MHz): δ 158.0 (C=N), 94.6 (H*C*(C=N)$_2$), 47.0 (*C*H(CH$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 18.8 (*Me*(C=N)$_2$).

***Nacnac*^{iPr}CuPPh$_3$·0.5 C$_6$H$_{14}$, 2**. *Nacnac*^{iPr}H (300 mg, 1.65 mmol), mesitylcopper (301 mg, 1.65 mmol), CuO^{t}Bu (22 mg, 0.165 mmol) and PPh$_3$ (437 mg, 1.65 mmol) were dissolved in toluene (12 mL) to give a yellow-brown solution. After stirring for 1 h, the solution was filtered, concentrated to 1/5 of its volume and layered with hexane (5 mL). It was then kept at -35 ºC. Yellow crystals together with powder formed after 3 day (700 mg, 84%).

^{1}H NMR (C_6D_6, 400 MHz): ^{1}H NMR (C_6D_6, 400 MHz): δ 7.66-7.02 (m, 15H, PPh$_3$), 4.67 (s, 1H, *H*C(C=N)$_2$), 3.86 (sp, *J* = 6 Hz, 2H C*H*(CH$_3$)$_2$), 2.10 (s, 6H, Me(C=N)$_2$), 0.98 (d, *J* = 6 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 101 MHz): δ 161.3 (C=N), 135.1 (d, *J* =30 Hz, *ipso* PPh$_3$), 134.7 (d, *J* =14 Hz, *ortho* PPh$_3$), 129.7 (*para* PPh$_3$), 128.6 (d, *J* = 9 Hz, *ortho* PPh$_3$), 95.4 (H*C*(C=N)$_2$), 51.4 (*C*H(CH$_3$)$_2$), 26.7 (CH(*C*H$_3$)$_2$), 23.1 (*Me*(C=N)$_2$). ^{31}P NMR (C_6D_6, 75 MHz): δ 4.0. Anal. Calcd. for $C_{29}H_{36}N_2PCu$: C, 68.68; H, 7.15; N, 5.52. Found: C, 67.85; H, 7.48; N, 4.97.

***Nacnac*^{iPr}CuCN(C$_6$Me$_2$H$_3$), 3**. *Nacnac*^{iPr}H (200 mg, 1.10 mmol), mesitylcopper (201 mg, 1.10 mmol), CuO*t*Bu (15 mg, 0.11 mmol) and xylyl isocyanide (151 mg, 1.15 mmol) were dissolved in toluene (4 mL). The yellow-brown solution was stirred for 1 h and then concentrated to half its volume to afford a yellow-brown suspension. The suspension was filtered, the filtrate was layered with 4 mL of hexanes and kept at -35 °C. Yellow crystals of **3** formed after 1 day (190 mg, 46%).

^{1}H NMR (C_6D_6, 400 MHz): δ 6.75 (t, *J* = 8 Hz, 2H, *p*-CN(C$_6$Me$_2$*H*$_3$)), 6.59 (d, *J* = 8 Hz, *m*-CN(C$_6$Me$_2$*H*$_3$), 2H) 4.60 (s, 1H, *H*C(C=N)$_2$), 4.01 (septet, *J* = 6 Hz, C*H*(CH$_3$)$_2$, 2H), 2.11 (s, 6H, Me(C=N)$_2$), 2.08 (s, 6H, CN(C$_6$*Me*$_2$H$_3$), 1.42 (d, 12H, *J* = 6 Hz CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 101 MHz): δ. 160.7 (C=N), 134.8, 94.8 (H*C*(C=N)$_2$), 50.9 (*C*H(CH$_3$)$_2$). 27.5 (CH(*C*H$_3$)$_2$), 22.3 (*Me*(C=N)$_2$), 18.8 (CN(C$_6$*Me*$_2$H$_3$)). (*C*N(C$_6$Me$_2$H$_3$) and three aromatic resonances were not detected). Anal. Calcd. for $C_{20}H_{30}N_3Cu$: C, 63.88; H, 8.04; N, 11.17. Found: C, 63.83; H, 8.11; N, 11.12. IR (toluene): ν_{CN} = 2114 cm^{-1}.

The solid obtained after filtration, **5,** gave**:** ^{1}H NMR (C_6D_6, 400 MHz): δ 6.69 (t, *J* = 8 Hz, *p*-CN($C_6Me_2H_3$), 2H), 6.52 (d, *J* = 8 Hz, *m*-CN($C_6Me_2H_3$), 4H), 4.61 (s, 1H, *H*C(C=N)$_2$) , 4.02 (septet, *J* = 6 Hz, C*H*(CH_3)$_2$, 2H), 2.14 (s, 12H, CN($C_6Me_2H_3$), 2.08 (s, 6H, Me(C=N)$_2$), 1.43 (d, 12H, *J* = 6 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 101 MHz): δ 160.7 (C=N), 135.4, 128.6, 128.1, 127.8, 94.8 (H*C*(C=N)$_2$), 50.8 (*C*H(CH_3)$_2$), 27.5 (CH(*C*H$_3$)$_2$), 22.4 (*Me*(C=N)$_2$), 18.8. (CN($C_6Me_2H_3$)). (*C*N($C_6Me_2H_3$) elusive). IR (toluene): ν_{CN} = 2114 cm^{-1}.

***Nacnac*^{iPr}CuNCMe, 4**. *Nacnac*^{iPr}H (75 mg, 0.41 mmol) and MeCN (41 mg, 0.82 mmol) were mixed and transferred to a vial containing a yellow solution of CuO*t*Bu (69 mg, 0.41 mmol) in toluene (2 mL). The resulting yellow-brown solution was kept at –30 ºC. Colourless crystals formed after 1 h together with a brown precipitate (mirror) indicative of decomposition. Decantation of the brown suspension gave after drying 31 mg (26%) of yellow crystals, **4**.

Two species were observed in C_6D_6 solutions of **4** (see text). **4**: ^{1}H NMR (C_6D_6, 400 MHz): δ 4.52 (s, 1H, *H*C(C=N)$_2$), 4.03 (septet, *J* = 6 Hz, C*H*(CH_3)$_2$, 2H), 2.11 (s, 6H, Me(C=N)$_2$), 1.38-1.52 (m, 12H, CH(C*H*$_3$)$_2$), 0.57 (NCMe). ^{13}C NMR (C_6D_6, 101 MHz): δ 160.6 (C=N), 116.5 (N*C*Me), 65.9 (H*C*(C=N)$_2$), 50.7 (*C*H(CH_3)$_2$), 26.9 (CH(*C*H$_3$)$_2$), 22.3 (*Me*(C=N)$_2$) and 0.3 (NC*Me*). **4b**: ^{1}H NMR (C_6D_6, 400 MHz): δ 5.29 (bs, 1H, *H*C(C=N)$_2$), 3.92-3.99 (featureless septet, C*H*(CH_3)$_2$, 2H), 2.56 (bs, 6H, Me(C=N)$_2$), 2.08 (s, 6H, CN($C_6Me_2H_3$) and 1.38-1.52 (m, 12H, CH(C*H*$_3$)$_2$) overlapping with that of **4.** Elemental analysis was unsatisfactory with varying results (ΔC = 2-3%), which might be related to acetonitrile dissociation and complex decomposition. IR (toluene): ν_{NC} = 2259 cm^{-1}.

NMR scale preparation of *nacnac*^{dipp}Cu(styrene). A vial was charged with *nacnac*^{dipp}H (dipp = 2,6-*i*Pr$_2$C$_6$H$_3$) (10 mg, 24 μmol), CuO*t*Bu (4 mg, 30 μmol) and styrene (3 μL, 25 μmol). C_6D_6 (0.6-0.7 mL) was added. After shaking thoroughly to obtain a homogeneous solution, the content was transferred to a J. Young tube and heated at 60 ºC for 24 h.

^{1}H NMR (C_6D_6, 400 MHz) δ 6.35-7.21 (m, 11H, 2,6-*i*$Pr_2C_6H_3$ & styrene), 5.08 (dd, *J* = 9 Hz and 14 Hz, 1H, Ph*H*C=), 4.97 (s, 1H, $HC(C{=}N)_2$), 3.48-3.56 (m, 3H, C*H*$(CH_3)_2$ & *cis* H_2C=), 3.34 (d, *J* = 9 Hz, 1H, *trans* H_2C=), 3.07 (sp, *J* = 7 Hz, 2H, C*H*$(CH_3)_2$, 1.75 (s, 6H, Me(C=N)), 1.33 (d, *J* = 7 Hz, 6H, CH(*CH*$_3)_2$), 1.15 (d, *J* = 7 Hz, 12H, CH(*CH*$_3)_2$), 1.09 (d, *J* = 7 Hz, 6H, CH(*CH*$_3)_2$).

X-ray diffraction studies. Compounds were crystallized by layering a toluene solution with hexane at –30 °C, except for compound **4** which crystallised directly from the toluene solution of the reaction at –30 °C. Data sets for **2** and **3** were recorded on a Bruker SMART 6000 with Montel 200 monochromator, while that of compound **4** was collected on a Bruker Microstar-Proteum with Helios optics, both equipped with a rotating anode source for Cu Kα radiation (λ = 1.54178 Å). Cell refinement and data reduction were performed using APEX2.[32] Absorption corrections were applied using SADABS.[33] Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97.[34] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on calculated positions using a riding model.

Table V-2. Details of X-ray diffraction studies

		2	3	4
Formula		$C_{29}H_{36}CuN_2P\cdot(C_6H_{14})_{0.5}$	$C_{20}H_{30}CuN_3$	$C_{13}H_{24}CuN_3$
Mw(g/mol); $d_{calcd.}$(g/cm^3)		550.19; 1.247	376.01; 1.239	285.89; 1.277
T (K); F(000)		150 ; 1172	150; 800	150; 608
Crystal System		Monoclinic	Monoclinic	Monoclinic
Space Group		$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit Cell:	*a* (Å)	13.9417(4)	8.9807(3)	6.8103(1)
	b (Å)	12.4813(4)	13.3632(4)	11.4563(3)
	c (Å)	17.8496(6)	16.9799(5)	19.1252(3)
	β (°)	109.348(1)	98.320(1)	94.780(1)
V (Å^3); Z		2930.60(16); 4	2016.33(11); 4	1486.97(5); 4
θ range (°); completeness		3.36-73.61; 0.99	4.23-71.45; 0.99	4.50-67.82; 0.93
Refl.: collec./indep.; R_{int}		41989/5843; 0.037	24118/3879; 0.038	23408/2512; 0.034
μ (mm^{-1}); abs. corr		1.72; SADABS	1.55; SADABS	1.93; SADABS
R1(F); wR(F^2); GoF(F^2) [a]		0.0348; 0.0959; 1.052	0.0413; 0.1128; 1.00	0.0308; 0.0906; 1.067
Residual electron density		0.68; -0.38	0.32; -0.36	0.32; -0.51

[a] R1(F) based on observed reflections with I>2σ(I), wR(F^2) and GoF(F^2) based on all data.

Supplementary data

Supplementary data (CIF) for this article are available on the journal Web site (http://canjchem.nrc.ca), or, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Chapter 6

π Back-Bonding in Dibenzyl-β-diketiminato Copper Olefin Complexes

Paul O. Oguadinma and Frank Schaper

Département de chimie, Université de Montréal, Montréal, Québec, H3C 3J7, Canada.

Abstract

N,N'-dibenzyl-4-amino-2-imino-pent-3-ene, *nacnac*^{Bn}H, was obtained in a one-step synthesis starting from benzylamine and acetylacetone. Reaction of *nacnac*^{Bn}H with CuO*t*Bu in the presence of various Lewis bases gave the corresponding copper complexes (*nacnac*^{Bn})CuL (L: **2**, styrene; **3**, η^2-acrylonitrile; **4**, allylphenylether; **5**, stilbene, **7**, xylylisonitrile; **8**, triphenylphosphine). With diphenylacetylene (DPA) the dimeric complex {(*nacnac*^{Bn})Cu}$_2$(μ-DPA), **6**, was obtained. In the presence of excess DPA, **6** coordinates additional acetylene to form the monomeric complex (*nacnac*^{Bn})Cu(DPA), **6b**. All complexes, with exception of **4** and **6b,** were characterized by X-ray diffraction studies. Structural and spectroscopic data indicate that π back-bonding in **2**-**8** is still weak when compared to other transition metals, but stronger than in most Cu(I) complexes. Olefin exchange experiments indicate preferred binding of electron-deficient olefins. Reaction of **3** with morpholine did not yield any hydroamination products, in agreement with significant π back-bonding towards the olefin.

Introduction

Copper(I) η^2-olefin complexes are involved as intermediates or resting states in a number of catalytic reactions, in industrial applications, and have been investigated as bio-mimetic model complexes for the ethylene receptor site in plants.[1, 2] In the Dewar-Chatt-Duncanson model, olefin binding consists of σ donation from the olefin into the Cu s-orbital, with accompanying π back-bonding from the metal into the olefin π^*-orbital.[3] While some theoretical studies suggest that binding of olefins to copper cations is purely electrostatic in nature with only marginal covalent contributions,[4] others claim significant covalent contributions in which π back-bonding is dominant.[5] Most of the recent studies, however, describe the bonding as mainly electrostatic, but with covalent contributions up to 45%. Population analyses suggest π back-bonding in cationic Cu(I) olefin complexes to be of minor importance compared to σ donation and to account for 1/6 to 1/3 of the covalent bonding (Table VI-1).[6] Experimental evidence on the importance of π back-bonding for the Cu(I) olefin bond is ambiguous.[7, 8] Kamau and Jordan found that the formation constants of Cu(I) olefin complexes in aqueous solutions correlate with the inductive constants (F) of

the olefins.[9] Reduced binding of electron-poor olefins was interpreted as a sign that olefin binding is dominated by σ donation, in agreement with the theoretical studies. Pampaloni *et al.* also reported reduced binding of olefins with electron-withdrawing substituents to $(F_3CCO_2)Cu$ complexes.[10] For Cu(I) phenanthroline complexes, on the other hand, divergent trends were observed when olefin binding constants were correlated with the Hammett parameters of the olefin substituent(s).[11] Thompson, Bradley *et al*. reported that the amount of π backbonding in Cu(I) acetylene complexes can be significantly increased in the presence of a more basic ancillary ligand.[12] We have recently started to investigate the chemistry of β-diketiminate ligands with aliphatic substituents on nitrogen,[13] which for copper was only sparingly reported, mostly for ALD/CVD applications.[12, 14] We report here the synthesis of *N,N′*-dibenzyl-diketiminato copper complexes, which show increased π backbonding and a clear preference to coordinate electron-deficient olefins.

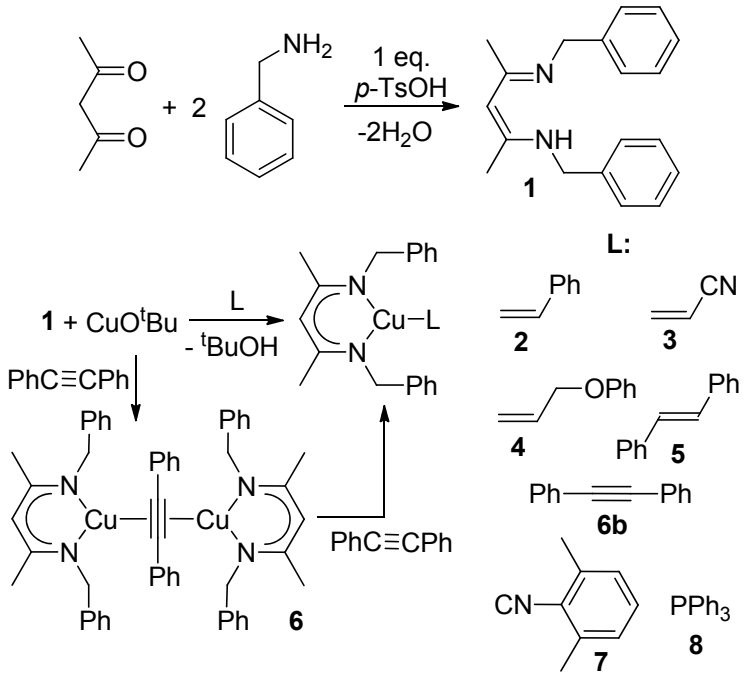
Table VI-1: Bond dissociation energy of Cu-olefin bonding according to calculation.

Electrostatic	55-60%
σ-Donation	24-38%
π-Back donation	7-16%

Results and Discussion

Ligand and Complex Synthesis. *N,N′*-Dibenzyl-β-diketimine, **1**, or other diketimine ligands with aliphatic *N*-substituents have previously been prepared employing *O*-alkylation of the monocondensation product[15] or the ethylene glycol monoketal of acetylacetone.[16] We obtained **1** in high yield of 80% by direct condensation of benzylamine and acetylacetone in the presence of one equiv. of acid.[17] Copper complexes **2-8** were obtained, following the procedure proposed by Dai and Warren,[18] in 30-60% yield after crystallization by reaction of Cu*O*t*Bu* with **1** in the presence of the respective olefin/Lewis base in toluene or ether (Scheme 6.1). The use of copper mesityl as an alternative copper source in the presence of catalytic amounts of Cu*O*t*Bu* or *t*BuOH[13] did not significantly change the obtained complex yields. Reaction of the lithium salt of **1** with

$[Cu(NCMe)_4][PF_6]$ in the presence of Lewis bases yielded identical complexes, albeit in lower yields. Complex **2** was also obtained from reaction of the lithium salt of **1** with CuI and excess styrene in acetonitrile (60% yield before recrystallisation). Complexes **2-8** are colorless to yellow solids, which are sensitive to air, but thermally stable under inert atmosphere. Solutions of complexes **2**, **5** and **8** in C_6D_6 did not decompose when heated to 60 °C under exclusion of light over a period of 2-3 days. No reaction was observed between CuO*t*Bu and **1** in the absence of Lewis bases or in the presence of acetone, 1-hexene, or benzonitrile. Reaction in presence of acetonitrile led to decomposition products. We have previously shown that for the related di(methylbenzyl)diketimine ligand a lack of reactivity towards CuO*t*Bu correlates with a reduced stability of the respective copper complex. If a salt metathesis pathway was used in these cases, only decomposition products were obtained.[13]



Scheme 6.1

Crystal Structure Studies. The crystal structures of complexes **2**, **3** & **5-8** display the copper center in a planar environment. As typically observed in copper(I) olefin complexes with bidentate supporting ligands, the multiple bond of the π ligand in **2**, **3**, **5** and **6** lies in the coordination plane of the complex. The benzyl ligands have a *syn* conformation in **6** &

8 and an *anti* conformation in **2**, **3**, **5** & **7**. Both, the C_S- and the C_2-symmetric rotamer of the ligand thus seem to be of comparable energy and the ligand is free to adopt the most favorable conformation in each case. Extensive π interactions are observed in all complexes (*vide infra*). Strong steric interactions between the benzyl substituents and the coordinated Lewis base seem to be absent: (i) The coordination around the copper atom is very similar in all complexes and Cu-N bond lengths (1.90(1)-1.955(1) Å, Table VI-2) as well as N1-Cu1-N2 angles (97.9(3)-100.4(1)°) are close to the average values of reported diketiminato copper complexes (Cu-N: 1.94±0.06 Å, N-Cu-N: 99±3°).[19, 20] (ii) The metal is coordinated symmetrically and a significant difference in Cu-N bond lengths was observed only for the phosphine complex **8**, which is, however, still smaller than the average Δd(Cu-N) of 0.03 Å in reported complexes.[19, 20] (iii) The Cu-L fragment is coordinated in the plane of the diketiminate ligand and the small values of the complex bending angle (Table VI-2) do not correlate with the steric demand of the coordinated Lewis base.

Table VI-2: Selected bond distances [Å] and bond angles [deg] for **2**, **3** and **5**-**8**.

	2	**3**	**5**	**6**	**7**	**8**
Cu1-N1	1.917(2)	1.912(3)	1.921(1)	1.903(7) -	1.941(1)	1.955(1)
Cu1-N2	1.919(2)	1.908(3)	1.922(1)	1.926(6)	1.941(1)	1.933(1)
Cu1-X/CH_2(CHR)[a,b]	1.972(2)	1.960(3)		1.948(7) - 1.987(7)	1.816(2)	2.159(1)
Cu1-C(H)R(CH_2) [c]	2.022(2)	1.989(3)	2.014(2) & 2.019(1)			
X - Y [a]	1.385(4)	1.388(4)	1.391(2)	1.291(10) & 1.308(10)	1.159(2)	1.825(1)-1.835(1)
N1-Cu1-N2	100.0(1)	100.2(1)	100.2(1)	97.9(3) - 99.2(3)	98.4(1)	100.4(1)
Cu1-C=C-C_R [d]	106	103	100	129 - 141		
complex bending [e]	10	7	4	11-17	8	3

[a] C26-C27 (**2**); C20-C21 (**3**); C32-C33 (**5**); C28-N3 (**7**); P1-C20/C26/C32 (**8**). [b] Cu1-C26 (**2**); Cu1-C20 (**3**). [c] Cu1-C27 (**2**); Cu1-C21 (**3**); Cu1-C32, Cu1-C33 (**5**). [d] torsion angle: Cu1-C26-C27-C20 (**2**); Cu1-C20-C21-C22 (**3**); Cu-C33-C32-C20, Cu1-C32-C33-C26 (**5**). [e] angle between the least-square planes defined by C2-C4,N1,N2,Cu1 and N1,N2,Cu1,X.

The olefinic bond of coordinated styrene in **2** (1.385(4) Å, Figure 6.1, Table VI-2) is significantly elongated compared to that of the free olefin (1.318(2) & 1.325(2)).[21] Compared to other transition metal styrene complexes the bond length is at the lower end of the range observed (1.35-1.48 Å),[8, 20, 22-26] but is one of the longest observed in Cu(I) styrene complexes (1.35-1.39 Å).[8, 24-26] The bending of the phenyl ligand out of the plane of the olefinic double bond can be taken as a measure to indicate the degree of π back-bonding and can be described by means of the Cu-C=C-C_{Ph} torsion angle.[27] The value of 106° in **2** is higher than those observed in other copper styrene complexes (93-105°).[8, 24-26] As usually observed in monosubstituted olefin complexes, styrene is bound asymmetrically with the unsubstituted carbon forming a slightly shorter metal-carbon bond. Cu-C bond lengths of 1.972(2) and 2.022(2) Å, respectively, are again at the extreme of the ranges observed in other Cu(I) styrene complexes (1.97-2.05 Å and 2.00-2.11 Å, respectively).[8, 24-26] While π back-bonding will be discussed in detail below, the geometric data indicate that styrene is more strongly bound in **2** than in most other copper complexes. Coordination of

styrene to the copper center is aided by a π stacking interaction of one benzyl substituent (C6-C11) with the phenyl substituent on styrene. The two phenyl rings are in a coplanar (6°), displaced orientation with shortest contacts of 3.5 Å between the overlapping carbon atoms and the mean plane of the π-stacked phenyl ring.

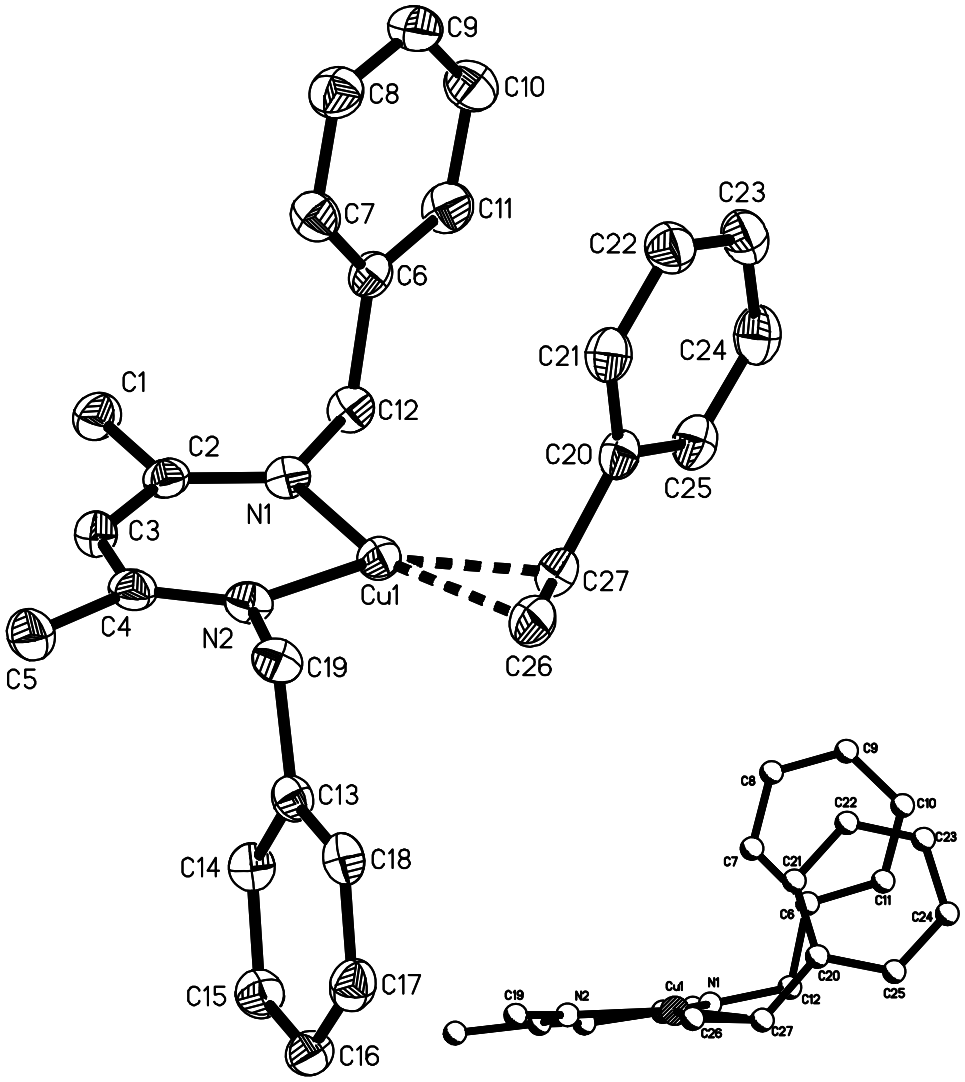


Figure 6.1: Crystal structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. The inset shows the π stacking interaction between styrene and one benzyl ligand.

Only a limited number of η^2-acrylonitrile complexes have been structurally characterized and, with the notable exception of its $(CuCl)_2$ adduct, in which acrylonitrile is found in a bridging η^1-N,η^2-coordination,[28] they contain good π back-bonding metal centers, i. e. Ni(0),[29, 30] Fe(0),[31] Mo(0),[32] and Ru(II).[33] Coordination of acrylonitrile in **3** (Figure 6.2, Table VI-1) is very comparable to the styrene coordination in **2**. Cu-C bond lengths are shorter by 0.01-0.03 Å in **3**, which might indicate a slightly stronger coordination. As observed for the styrene complex **2**, the olefin is asymmetrically bound (Δd(Cu-C) = 0.03 Å). Its C=C double bond (1.388(4) Å) is longer than that of the free olefin (1.339(1) Å),[34] comparable to the one observed in the $(CuCl)_2$ adduct (1.38(2) & 1.39 Å),[28] but shorter than those observed in complexes of better back-bonding metals (1.40-1.46 Å).[29-33] Although π interactions between the benzyl substituent and the electron-poor nitrile substituent on the olefin would be possible, they are not observed in the solid state. In fact, the benzyl substituent is bent away from the nitrile, with an angle between olefin and phenyl least square planes of 20° and without any superposition of nitrile and phenyl substituents. The reason for this apparent repulsion is the formation of a 1D-chain of antiparallel nitrile substituents, parallel to the monoclinic axis and with intermolecular C22-N3 distances of 3.2 Å. The nitrile nitrogen is in relatively close contact (2.9 Å) to the copper center of an adjacent molecule, where it occupies an axial position (N3A-Cu1-X: 82-107°). When compared to *N*-coordinated acrylonitrile complexes,[35] including the $(CuCl)_2$ adduct with acrylonitrile in a bridging coordination,[28] the long Cu-N distance (**3**: 2.9 Å, *N*-coordinated AN: 1.9-2.1 Å), the angled coordination of acrylonitrile (Cu1-N3A-C22A, **3**: 136°; *N*-coordinated AN: 153-180°), and the small deviation of the trigonal complex from planarity (bending angle in Table VI-2: 7°) indicate that the interaction is probably mostly electrostatic in character and of minor importance.

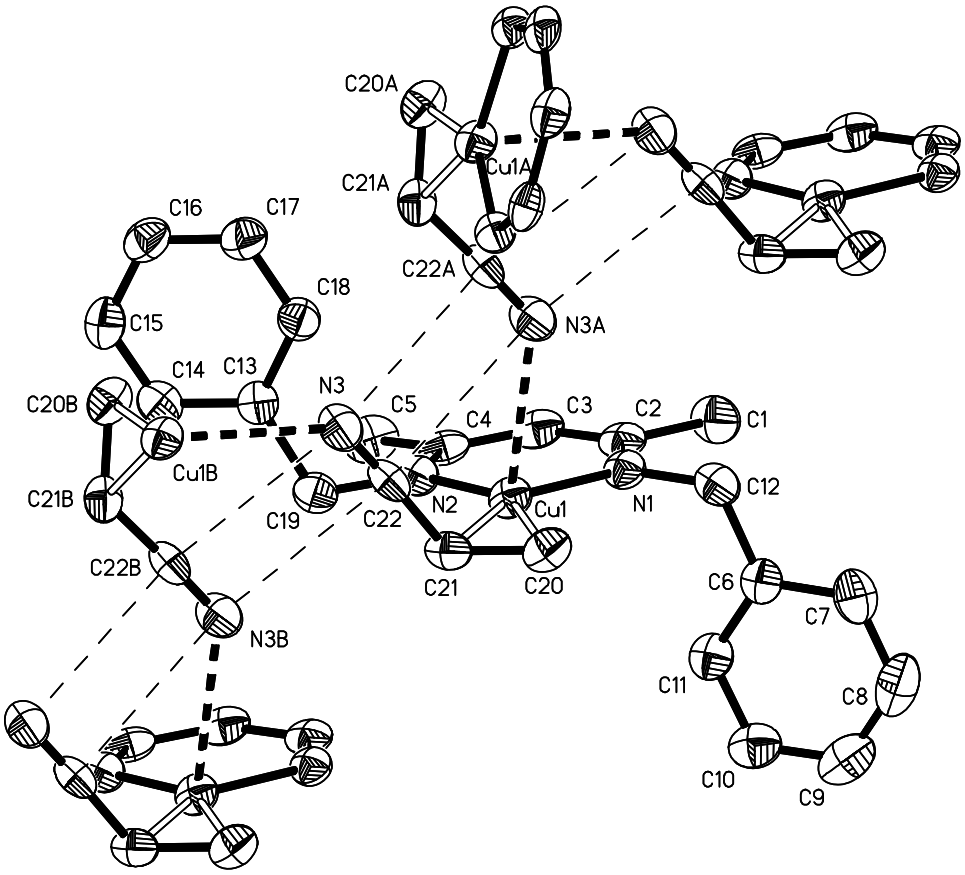


Figure 6.2: Crystal structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Additional fragments were generated using the symmetry operations 1-*x*, *y*-0.5, 0.5-*z* (A) and 1-*x*, 0.5+*y*, 0.5-*z* (B).

The coordination of *trans*-stilbene in **5** (Figure 6.3, Table VI-2) closely resembles that of styrene in **2**. The olefinic bond (1.391(2) Å) is again longer than in the free olefin (1.32±0.02 Å),[20, 36] but at the shorter end of the range observed in other transition metal stilbene complexes (1.41(1)-1.47(2) Å).[20, 36] The main differences are the now symmetrical Cu-C_{olefin} bonds, the lack of π stacking between the benzyl substituent and the phenyl substituent of the olefin and a 20° tilt of the olefin out of the mean diketiminate-copper plane. The latter two observations are caused by the formation of intermolecular, instead of intramolecular π interactions between stilbene and the benzyl substituent. The phenyl ring C6-C11 is coplanar (3°) with the stilbene of an adjacent molecule (C26A-C27A+C33A) with a 3.6-3.7 Å distance between the planes. The co-crystallized toluene molecule is

sandwiched between two benzyl substituents not involved in π stacking interactions with stilbene in an edge-on CH-π interaction.

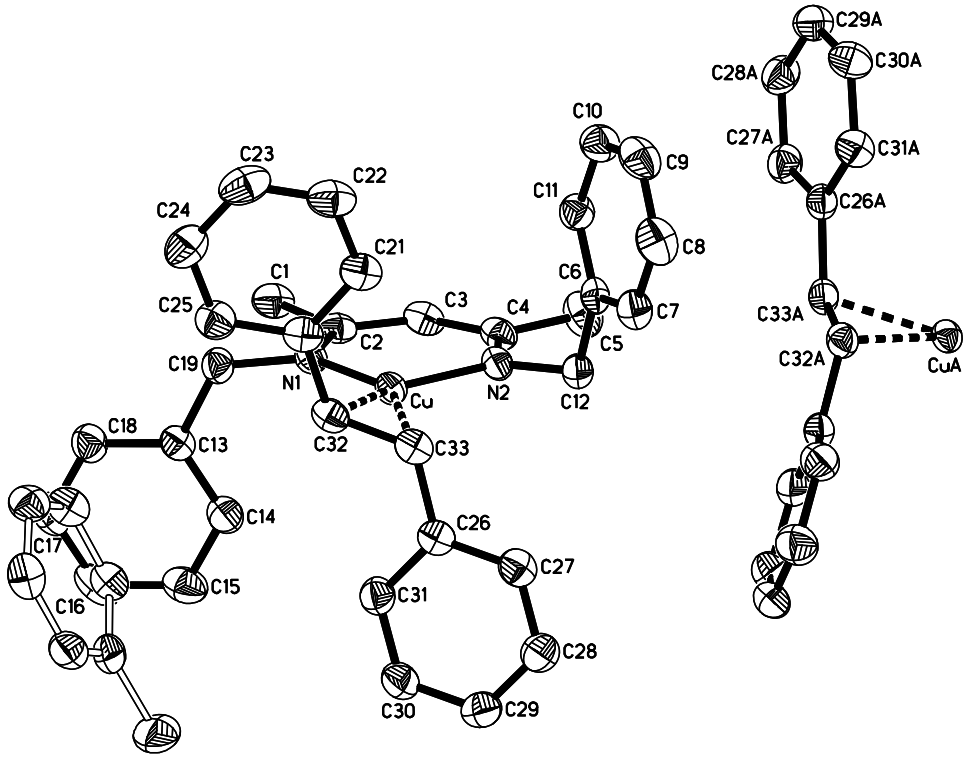


Figure 6.3: Crystal structure of **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% level. The co-crystallized toluene molecule is disordered around an inversion center. The π-stacked fragment was generated by 0.5-*x*, 0.5+*y*, 0.5-*z*.

The crystal structure of **6** (Figure 6.4, Table VI-2) contains two independent molecules in the unit cell. All benzyl ligands show evidence of slight rotational disorder, which lowers the overall quality of the structural data. In agreement with relative NMR intensities, the crystal structure showed **6** as the acetylene bridged dimer. While many transition metal complexes coordinate acetylene in a bridging fashion, copper usually prefers to form unbridged acetylene complexes and **6** is one of the few reported examples in which close copper-copper distances were not enforced by other bridging ligands.[37] The C-C distances of the bridging acetylenes (1.29(1) & 1.31(1) Å) and the Cu-C distances (1.95(1)-1.99(1) Å) are comparable to those in other μ-acetylene copper complexes, while Cu-Cu distances (2.621(2) & 2.635(2) Å) are slightly shorter (c. f. C-C: 1.29±0.03 Å, Cu-

C: 1.96±0.04 Å, Cu-Cu: 2.8±0.1 Å).[38] However, **6** is the only complex in this group which does not contain additional ligands bridging the copper centers and the Cu-Cu distances in **6** are still well in the usual range observed for dicopper complexes in general. A possible explanation for the formation of **6** and why the mononuclear acetylene complex **6b** is formed only in the presence of excess acetylene (*vide infra*) might be found in steric strain introduced between the carbon substituent on nitrogen atom and the *ipso*-carbon atom of diphenylacetylene when the latter is located in the mean ligand plane (Scheme 6.3). A complex comparable to **6b**, (*N,N'*-di(^{t}Bu)diketiminato)Cu($Me_3SiCCSiMe_3$), showed a strongly increased bending between the mean diketiminate-copper and acetylene-copper planes of 22°, which is absent in the corresponding acetylacetonate complex.[12]

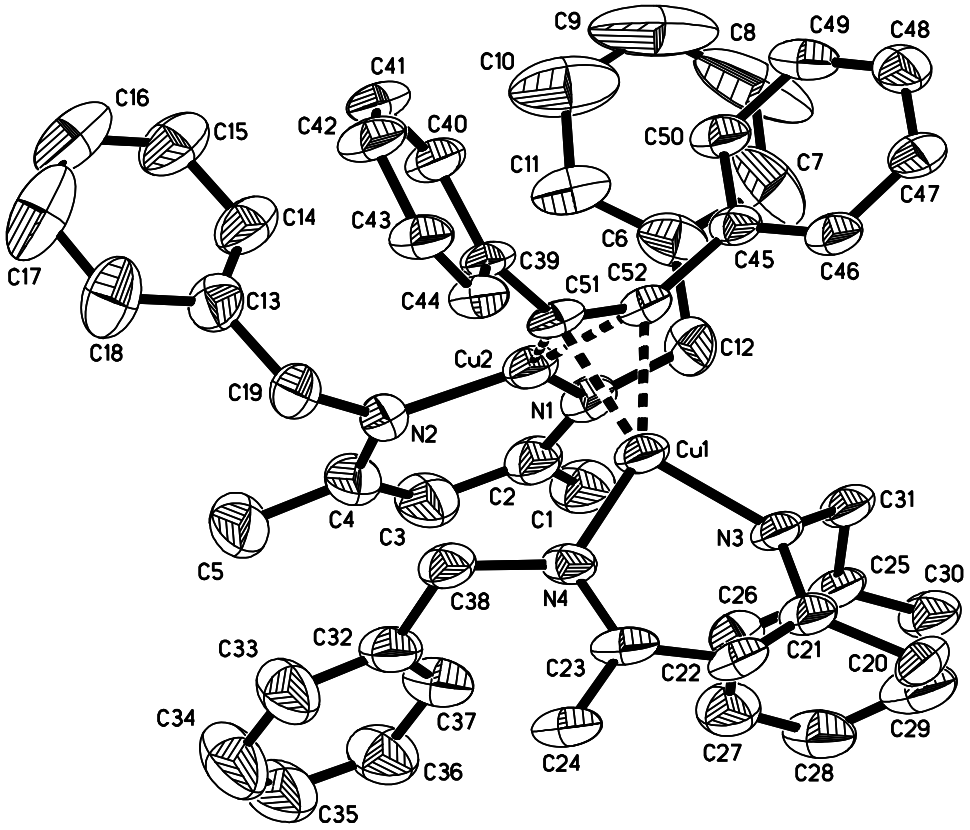
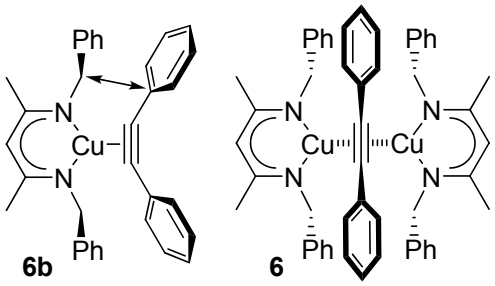


Figure 6.4: Crystal Structure of **6**. Only one of two independent molecules in the unit cell is shown. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.



Scheme 6.2

Structures **7** and **8** (Figure 6.5 & 6.6, Table VI-2) resemble closely those of other diketiminate copper complexes with a coordinated triphenylphosphine[13, 39-41] or 2,6-xylylisonitrile ligand, respectively.[13, 39, 42] The isonitrile ligand in **7** is bent towards the benzyl groups, indicating that the *syn*-orientation of the benzyl substituents observed in **7** is caused by an attractive CH_3-π interaction and not by steric repulsion. Complex **8**, carrying the bulky triphenylphosphine group, does not show any indication of steric strain in the complex. The analogous complex with a chiral methylbenzyl-substituent on nitrogen displays a pronounced complex bending of 25° and average Cu-N and Cu-P distances (1.98 Å and 2.20 Å, respectively)[13] which are longer than those in corresponding *N*-aryl substituted diketiminate copper PPh_3 complexes (Cu-N: 1.94-1.97 Å, Cu-P: 2.16-2.18 Å, complex bending: 4-17°).[39-41] The average Cu-N distance (1.94±0.02 Å) and the Cu-P distance (2.159(1) Å) in **8**, on the other hand, are at the short extremes of these ranges, and the complex bending of 8° is comparable to that observed in **2**-**7** and does not indicate pronounced steric strain. While the steric environment in diketiminate complexes generated by aliphatic and aromatic substituents on N is fundamentally different, diketimine ligands derived from secondary amines can be considered sterically more demanding than *N*-aryl substituted diketimines,[13] while those derived from primary amines, such as **1**, impose the least steric strain.

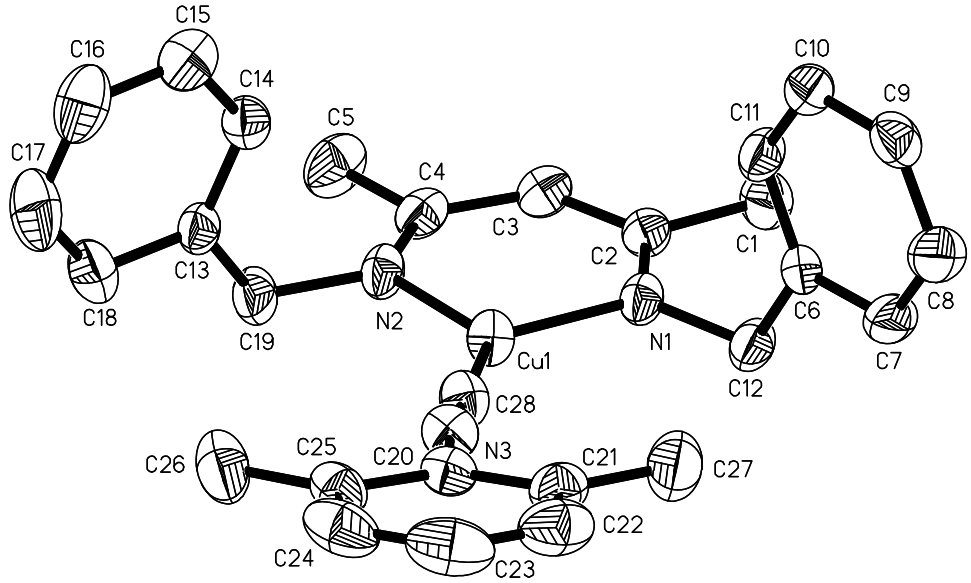


Figure 6.5: Crystal Structure of **7**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

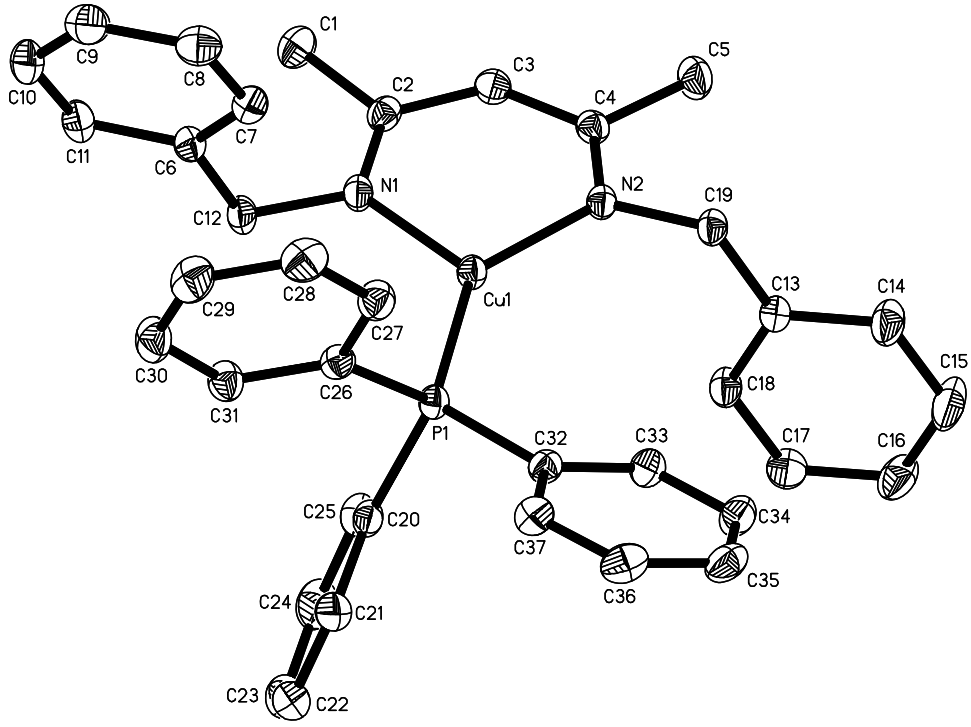


Figure 6.6: Crystal Structure of **8**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

NMR spectroscopy. While the coordinated phosphine and isonitrile ligand in **7** and **8** exchange fast on the NMR time scale with free Lewis base present in solution, separate signal sets for coordinated and free olefins were observed for **2**-**5**. EXSY spectra of **2** in the presence of free styrene show crosspeaks between free and coordinated styrene, indicating that olefin exchange – while slow on the NMR time scale – is still occurring. Reactions of **2** or **3** with 1 equiv. of xylyl isonitrile led to complete olefin displacement and formation of the xylyl isonitrile adduct **8**. The fast exchange observed with stronger binding Lewis bases is in agreement with the associative exchange mechanism proposed for these systems.[13] ^{1}H NMR spectra of the acetylene bridged dimer **6** in the presence of excess diphenylacetylene displayed, next to free acetylene, a new set of signals, which were assigned to the acetylene coordinated monomeric complex **6b** from their relative intensities (Schemes 6.2 & 6.3). On titration with diphenylacetylene the ratio of **6b**/**6** increased with increasing acetylene concentration and at acetylene/Cu ratios > 10 only signals of **6b** and free acetylene remained. The coordinated olefin has only a slight influence on the chemical displacements of the diketiminate ligand. For example, the displacement of the central CH-carbon atom of the ligand in ^{13}C NMR spectra of **2**-**5**, which corresponds to the *para*-position of the "metallapyrimidine" cycle, remains virtually unaffected (δ = 96.6-96.9 ppm) by the exchange of the coordinated olefin.

NMR spectra of the olefin complexes **2**-**4** indicate an apparent symmetry of the complex at room temperature, i.e. only one signal is observed for the diketiminate methyl group in ^{1}H and ^{13}C spectra. Rotation around the Cu-olefin bond is thus fast on the NMR time scale for all complexes. Variable temperature NMR experiments in toluene-d_8 showed that olefin rotation in **2** is sufficiently slow to observe a non-symmetric complex featuring two methyl resonances and 4 doublets for the benzylic CH_2 group below –40 °C. Rate constants could be extracted by simulation of the spectra and Eyring plots of the exchange rate constants yielded $\Delta H^{\ddagger}$ = 62.3(7) kJ/mol, $\Delta S^{\ddagger}$ = 49(3) J/(mol·K) (see supp. info.). While styrene rotation in **2** is fast at room temperature on the NMR time scale (as generally observed for Cu(I) styrene complexes), its barrier is the highest reported so far for Cu(I) styrene complexes (Table VI-3). A slightly faster rotation is observed in the comparable *nacnac*^{Xyl}Cu(styrene) complex of Dai and Warren (Xyl = 2,6-$Me_2C_6H_3$),[25] while olefin rotation is fast, even at 180 K, with the less Lewis-basic bipyridine ligand.[26] The likewise

low rotation barrier in tBu$_2$P{(Me$_3$Si)N}$_2$Cu(styrene)[43] is not readily explained with electronic reasons and might be either related to decreased π back-bonding in this system[44] or to the sterically undemanding 4-membered metallacycle.

Table VI-3: Olefin rotation barriers in LCu^{I}(styrene) complexes with bidentate ligands L.

LCu	Styrene rotation	$k/k(2)$ [a]	Reference
nacnac^{Xyl}Cu	$\Delta G^{\ddagger}_{215K}$ = 45(3) kJ/mol	50	25
tBu$_2$P{(Me$_3$Si)N}$_2$Cu	$\Delta G^{\ddagger}_{180K}$ = 37.0 kJ/mol	$6 \cdot 10^4$	43
(bipyridine)Cu$^+$	fast at 180K	$> 10^5$	26

[a] relative rate of styrene rotation in LCu(styrene) and **2** at the given temperature.

One of the methyl resonances of **2** started to broaden at –60 °C, indicating another dynamic process such as *N*-Bn rotation (supplementary information, figure 6.S1), which was not further investigated. When heated above room temperature the two broad doublets of the benzylic CH_2 groups start to coalesce. At the same time signals of coordinated and free styrene (present in 1-5% due to decomposition) started to broaden (supplementary information, figure 6.S3). Both observations can be traced to the olefin exchange process observed in EXSY spectra of **2** + free styrene at room temperature, without the need to invoke an enantiotopic side flip mechanism.

While acrylonitrile prefers to bond via the nitrogen atom to harder Lewis acids[45] and displays a somewhat bridging coordination in the solid state structure of **3** (Figure 6.2), complex **3** shows in solution the typical features of π-coordinated acrylonitrile:[30, 45, 46] the ν_{CN} frequency of 2225 cm^{-1} is marginally lower than the one observed in the free olefin (2230 cm^{-1}), while *N*-coordination should lead to significantly increased ν_{CN} frequencies. As well, ^{13}C NMR resonances of the coordinated olefin (δ = 70.6 and 54.0 ppm) are shifted strongly upfield compared to free acrylonitrile (δ = 136.5 and 107.4 ppm), while no changes or slight upfield shifts would be expected for *N*-coordinated acrylonitrile. Complexes **2**, **4** & **5** also display in their ^{13}C NMR spectra the upfield shift of the olefinic

resonances expected upon η^2-coordination of the olefin. The acrylonitrile complex **3** displays a dynamic process comparable to that observed for **2**, and splitting of the methyl group was observed at low temperatures. Due to the small $\Delta\delta$ of 2-5 Hz, rate constants could not be determined for this exchange. The benzyl CH_2 groups appear at low temperature as two coupled doublets for one CH_2 group and as one broad multiplet of double intensity for the other, indicating a C_1-symmetric complex with accidentally identical chemical displacements for two protons. The appearance of the benzyl groups remains unchanged up to 0 °C in toluene-d_8. Above 0 °C all three peaks start to broaden and coalesce into one broad peak above 30 °C (in benzene-d_6 and at lower field strength, one broad peak is observed for all CH_2 protons already at room temperature and the ^{13}C spectra is in the fast exchange region). Since olefin exchange with traces of free olefin was already observed at this temperature for **2** and would be expected to be even faster for **3**, we cannot distinguish olefin exchange from olefin rotation. From the available data, however, we can estimate an upper barrier of $k < 500\ s^{-1}$ for the acrylonitrile rotation at 30 °C. Styrene rotation at this temperature is thus at least 80 times faster than acrylonitrile rotation. While aryl-aryl π stacking in **2** might thus stabilize the complex, the slower olefin rotation in **3** and comparable rotation barriers for styrene rotation in *nacnac*^{Xyl}Cu(styrene)[25] argue that π stacking contributions to olefin binding are subtle at best.

Evidence of π back-bonding. Copper(I) is generally considered a poor back-bonding metal center, which is in agreement with the obtained spectroscopic data. The average P-C carbon bond distance in **8** (1.83±0.05 Å), proposed as a measure of back-bonding into the phosphine ligand,[47] is within the margin of experimental error identical to average P-C bond lengths in free PPh_3 (1.826-1.835 Å).[48] Elongation of P-C bonds in PPh_3 is, however, a relatively small effect and barely statistically significant even for good back-bonding metal centers (e. g. average P-C bond lengths in Ni^0PPh_3: 1.85 Å, in Cr^0PPh_3: 1.84 Å).[20, 49] The ν_{CN} stretching frequency of the coordinated xylyl isonitrile ligand in **7** is observed at 2114 cm^{-1}, only 5 cm^{-1} below that of free xylyl isonitrile (2119 cm^{-1}), and indicates rather weak back-bonding. Nevertheless, it is the lowest stretching frequency observed so far in Cu(I) xylyl isonitrile complexes (ν_{CN} = 2115-2164 cm^{-1}).[39, 42, 50] Elongation of the C=C

double bond of the olefin is normally considered a rather poor signifier of π back-bonding, since σ donation as well as π back-bonding weakens the olefinic bond. Nevertheless, we find a clear, if noisy, correlation of the olefinic bond length and the bending of the phenyl substituent out of the olefinic plane (a further indicator of the amount of metallacyclopropane character in olefin complexes and expressed in form of the M-C=C-C_{Ph} torsion angle) for structurally characterized styrene complexes (Figure 6.7).[8, 23-26, 51] With free styrene[21] and unsubstituted[52] or substituted phenylcyclopropanes[53] at the extremes, C=C bond lengths and the back-bending of the phenyl substituent increase qualitatively with the back-bonding ability of the metal center in the order Cu(I) < Pd(II) < Pt(II) < Re(II), Os(II), Mo(II) < Ta(III). Judging from Figure 6.7, back-bonding in **2** is still rather weak, but more important than in other reported Cu(I) styrene complexes.

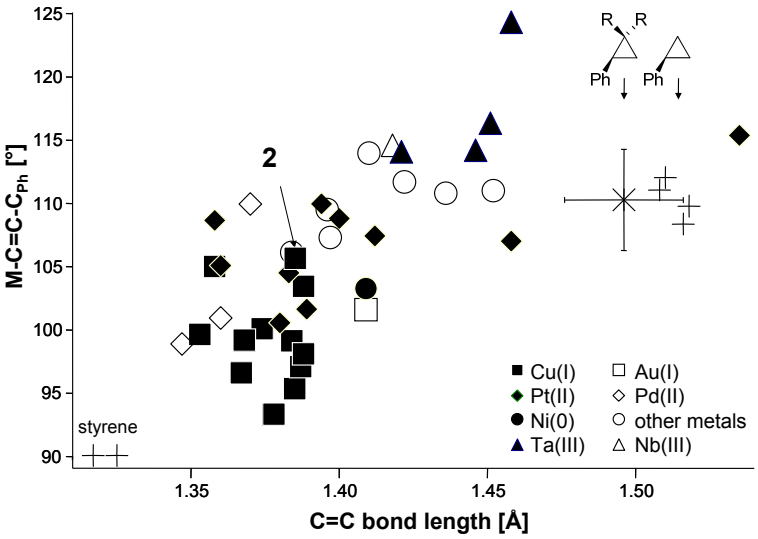


Figure 6.7: Correlation between the length of the coordinated double bond and the bending of the phenyl substituent out of the olefinic plane in structurally characterized transition metal styrene complexes. Only high quality structures with R1 values lower than 5% were considered. Outliers with double bonds shorter than that of the free olefin are not shown. The torsion angle was set to 90° for styrene. For the determination of the torsion angle in substituted cyclopropanes, the CR_2 group took the position of the metal center. In unsubstituted cyclopropane, both CH_2 groups were used alternately.

In ^{13}C NMR spectra of **2**, resonances of the olefinic carbon atoms are displaced by 47-48 ppm towards higher field when compared to those of the free olefin. The amount of this displacement is a measure of the amount of charge delocalization towards the olefin, i. e. π back-donation.[1, 8, 54, 55] In agreement with the conclusions drawn from the structural studies, **2** shows significant π back-bonding when compared to other copper complexes, but falls in the lower range of transition metal styrene complexes in general (Figure 6.8). The olefinic carbon atoms of the coordinated styrene in **2** show $^{1}J_{CH}$-coupling constants of 172 and 161 Hz, significantly higher than those in free styrene (*C*H(Ph): 155 Hz; CH_2: 154 and 160 Hz)[56] and close to the values expected for phenylcyclopropane or phenyloxirane (160-180 Hz). The fast rotation around the Cu-olefin bond and the rather small upfield shift (Figure 6.8) indicate, however, that **2** has relatively little metallacyclopropane character.

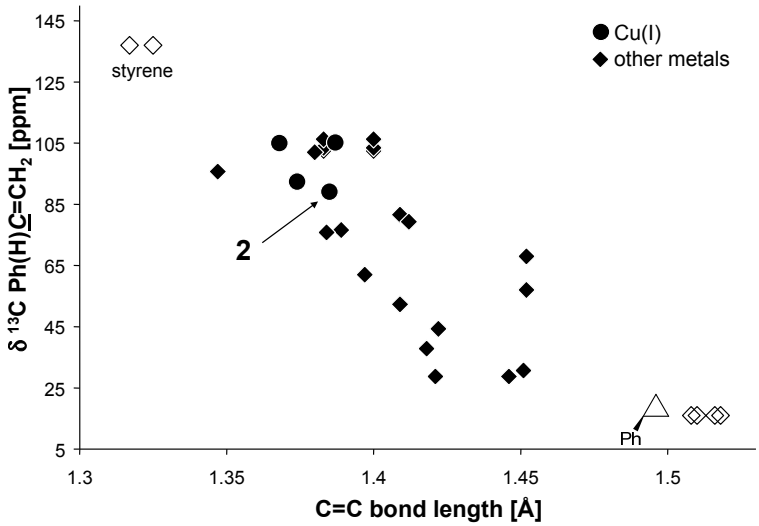


Figure 6.8: Correlation between crystallographically determined lengths of the olefinic bond and the displacement of the benzylic carbon atom in ^{13}C NMR spectra of transition metal styrene complexes.

A comparison of the chemical displacements of the olefinic carbon atoms in ^{13}C spectra of **2-5** in benzene-d_6 is shown in table VI-4. The smallest displacement is observed for the stilbene complex **5**, followed by allylphenylether and styrene, which show similar values, while the highest displacement from the values of the free olefin is observed for the acrylonitrile complex **3**. Since higher upfield shifts are considered evidence for increased π

back-bonding[1, 8, 54, 55] and have been found to correlate with the temperature of olefin dissociation in Cu(I) complexes,[8] the NMR data in table VI-4 indicates that olefin binding is strongest for the electron-poor acrylonitrile. This is in contradiction to computational studies on Cu(I) olefin complexes, which predict that olefin binding can be described as approximately 50% electrostatic, 35% σ donation and 15% π back-bonding.[6] In this bonding picture, one would expect a decreased binding of electron-deficient olefins, a situation which was experimentally confirmed by Kamau and Jordan's results of olefin binding to Cu^+ in aqueous solution[9] and partly in other studies.[10, 11, 57] As a quantitative measure of the relative strength of olefin binding, we investigated olefin exchange equilibria between **2** and various olefins in benzene-d_6 via ^{1}H NMR. Acrylonitrile was indeed found to coordinate strongest to copper, while styrene and allylphenylether yielded comparable binding constants.[58] No free styrene was observed even in the presence of a large excess of ethylvinylether, and we can only estimate the exchange constant to be lower than 0.01. The observed binding constants correlate well with the upfield shift of the olefinic carbons in their ^{13}C NMR spectra (Table VI-4)[59] and indicate a preferential binding of electron-poor olefins to the diketiminate copper complex investigated here. While acrylonitrile only binds moderately more strongly than styrene, rotation around the copper olefin bond was found to be significantly slower. Leaving aside possible steric explanations, this is in agreement with reduced σ-donor and increased π-acceptor properties of acrylonitrile when compared to styrene. While only the increased π back-bonding in **3** influences the olefin rotation barrier, both affect the olefin binding strength.

The reduced coordination constant for *trans*-stilbene indicates that – as is usually observed in copper olefin complexes – steric interactions are more important than electronic differences. In agreement with the importance of steric effects, diketiminate copper olefin complexes with ligands carrying secondary alkyl substituents on the nitrogen did not coordinate olefins, but do coordinate PPh_3 or isonitriles.[13, 60] Since acetylenes are generally considered to be slightly weaker σ donors, but better π acceptors than olefins, the weak coordination of diphenylacetylene when compared to styrene and stilbene was somewhat surprising. Acetylene coordination might be hindered by steric strain in the monomeric **6b** (*vide supra*). Alternatively or additionally, stabilizing π-π interactions between the benzyl group and the olefin substituent might be present in solution for

complexes **2-5**, which are geometrically impossible in **6b** (and due to the absence of a π ligand also absent for ethylvinylether). While intramolecular π-π interactions were only observed in the crystal structure of **2**, we believe them to be effective for all complexes, when the intermolecular interactions observed in the solid state for **3** and **5** are no longer possible. However, in view of the low binding constant of stilbene and the relative olefin rotation barriers in **2** and **3**, it is improbable that π-π interactions have a dominant influence on the olefin binding strength.

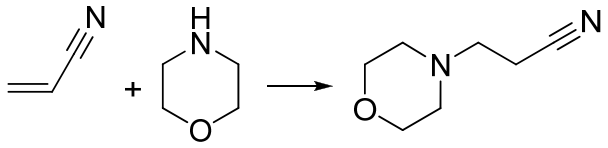
Table VI-4: Chemical displacement of coordinated olefins in ^{13}C NMR spectra and equilibrium constants of olefin exchange reactions (benzene-d_6, room temperature).

complex	coordinated olefin	δ *C*H$_2$	δ *C*H(R)	Δ δ [a]	$K = \frac{[Cu-olefin]\cdot[styrene]}{[Cu-styrene]\cdot[olefin]}$
		ppm			
3	acrylonitrile	70.6	54.0	53-66	6.2 ± 20% [b]
2	styrene	67.1	89.1	47-48	1
4	H_2C=C(H)CH_2OPh	71.7	84.8	45-49	0.9 ± 20% [b]
	H_2C=C(H)OEt				< 0.01
5	*trans*-stilbene		85.0	20	0.1 ± 15% [b]
6b	diphenylacetylene [c]				0.02 ± 20% [b]

[a] Upfield shift relative to the free olefin in benzene-d_6. δ (^{13}C, C_6D_6, ppm): Styrene, 113.7 (CH_2), 137.3 (*C*HPh); acrylonitrile, 136.5 (CH_2), 107.4 (*C*HCN); H_2C=C(H)CH_2OPh, 116.9 (CH_2), 133.8 (*C*(H)CH_2OPh); stilbene, 105.4. [b] Errors cover the observed range of values in repeated experiments. [c] Under excess acetylene to ensure the absence of **6**.

To confirm the charge transfer from the metal onto coordinated olefin indicated by the spectroscopic data, we investigated the reactivity of the acrylonitrile complex **3** towards nucleophiles. Uncatalyzed reaction of acrylonitrile and morpholine in benzene-d_6 for 24 h at 60 °C led to 30-50% hydroamination of acrylonitrile (Scheme 6.3). In the presence of 5 mol-% of (insoluble) $[Cu(NCMe)_4][PF_6]$, complete hydroamination was observed after 24 h even at room temperature. Tetrakis(acetonitrile)copper thus catalyses the nucleophilic attack on acrylonitrile, most likely by *N*-coordination of acrylonitrile to copper. On the

other hand, reaction of the acrylonitrile complex **3** with one equiv. of morpholine in benzene-d_6 at 60 °C for 24 h yielded only unreacted **3** and morpholine. The presence of the diketiminate ligand thus not only favors η^2-coordination over *N*-coordination of acrylonitrile to an extent that the complex no longer serves as a catalyst, but π back-donation from the copper metal center into the LUMO of coordinated acrylonitrile is sufficient to prevent the nucleophilic attack on the coordinated double bond, which is feasible in the uncoordinated olefin.



Scheme 6.3

The ability of β-diketiminate ligands to favor metal-ligand back-donation has been previously noted by others. Holland and coworkers showed that the orbital geometry in three-coordinated *nacnac*Fe complexes is ideally suited for metal-ligand π interactions[61, 62] and observed significant π back-bonding in *nacnac*Fe(alkyne) and (*nacnac*Fe)$_2$(μ-N_2) complexes.[62, 63] For diketiminate copper complexes in particular, Thompson *et al*. observed significant spectroscopic differences between copper(BTMS) complexes (BTMS = bistrimethylacetylene) carrying either a diketonate or a diketiminate ligand, which they attributed to increased π back-bonding in the presence of the diketiminate ligand.[12] This has been confirmed by a recent theoretical study of Srebro and Mitoraj: π back-donation is increased in diketiminate copper(BTMS) complexes, even if the diketonate complexes bind BTMS more strongly due to the lack of steric congestion.[44] The latter is in line with our observations that steric differences affect olefin binding constants more strongly than electronic ones. Badiei and Warren calculated significant Cu-C π back-bonding for the mono- and dinuclear copper carbene complexes with the *nacnac*^{Mes} ligand (Mes = 2,4,6-$Me_3C_6H_2$) they prepared.[39] Tolman and coworkers found that *nacnac*Cu(O_2) complexes have substantial Cu(III)-peroxo character,[64, 65] while complexes such as TpCu(O_2) are best described as Cu(II)-superoxo.[65, 66] Electron donation from the *nacnac*Cu fragment into

coordinated O_2 is also considered to be responsible for the preferred side-on coordination of oxygen[67] and the low oxidation power of these complexes,[40] which is in line with the preferred π- over σ-coordination of acrylonitrile in **3** and its deactivation towards nucleophilic attack. In summary, the observed high degree of π back donation in *nacnac*^{Bn}Cu complexes can be ascribed to a combination of different factors: (i) the trigonal (counting only σ bonds) coordination geometry of copper, (ii) the general ability of diketiminate ligands to increase electron density at the metal center in general and (iii) the increased Lewis basicity of *N*-alkyl substituted diketiminates in particular.

Conclusions

Copper(I) is a borderline case with regard to the importance of π back-donation. Theoretical studies of Cu(I) olefin bonding, mostly undertaken on cationic Cu(I) or CuX complexes, predict a net charge transfer from the olefin towards the metal. The amount of π back-bonding in copper complexes is however strongly influenced by the ancillary ligand,[10, 12, 54, 68] and a bonding picture dominated by σ-donation cannot be sustained for neutral copper complexes with a Lewis basic ligand. Copper complexes **2**-**5** still have relatively little metallacyclopropane character and are best described as Cu(I) olefin complexes (as evidenced, e. g., by the free rotation around the Cu-olefin bond on the NMR time scale for most complexes). Nevertheless, compared to other Cu(I) complexes, the low ν_{CN} frequency in **8**, the strong upfield shift of the ^{13}C resonances of coordinated olefins, the crystallographic data, the (relatively) high barriers for olefin rotation and the preferred binding of electron-deficient olefins indicate that π back-bonding is strongly increased in the presence of the anionic dibenzyldiketiminate ligand **1**. In particular for coordinated acrylonitrile, the deactivation towards nucleophilic attack and the slow olefin rotation justify to describe **3** at least partly as a Cu(III) metallacyclopropane. Further investigations into the role of attractive π interactions, as well as into potential applications of the preferential coordination of electron-deficient olefins are in progress.

Experimental Section

All reactions, except ligand synthesis, were carried out under nitrogen atmosphere using Schlenk or glove box techniques. Solvents were dried by passage through activated aluminum oxide (MBraun SPS) and de-oxygenated by repeated extraction with nitrogen. C_6D_6 was distilled from Na and de-oxygenated by three freeze-pump-thaw cycles. Cu*O*t*Bu was synthesized as reported.[69] All other chemicals were obtained from commercial suppliers and used as received. Elemental analyses were performed by the Laboratoire d'Analyse Elémentaire (Université de Montréal). NMR spectra were recorded on a Bruker ARX 400 MHz spectrometer and referenced to residual solvent (C_6D_5H: δ 7.15, C_6D_6: δ 128.02) or external reference (^{31}P, 75% H_3PO_4). ^{13}C and ^{1}H assignments of coordinated olefins were confirmed by HMQC spectra. In the following "*trans* CH_2" denotes the olefinic proton *trans* to the substituent on the coordinated olefins. Exchange rates were obtained by comparison of experimental and simulated spectra with the WINDNMR program.[70]

***N,N'*-dibenzyl-4-amino-2-imino-pent-3-ene, *nacnac*^{Bn}H, 1**. Acetylacetone (2.00 mL, 19.4 mmol), *para*-toluenesulfonic acid-semihydrate (3.7 g, 19.4 mmol) and benzylamine (2.25 mL, 19.4 mmol) were suspended in toluene (40 mL) and refluxed for 1 h to afford a yellow solution. A second equivalent of benzylamine (2.25 mL, 19.4 mmol) was added after cooling to room temperature and the mixture was refluxed for 24 h with the help of a Dean-Stark apparatus. From the obtained brown solution a brown precipitate formed upon cooling, which was isolated by filtration and dissolved in aqueous K_2CO_3 (30 g in 150 mL H_2O). The aqueous phase was extracted with 3 x 100 mL of toluene. The combined organic phases were dried over Na_2SO_4, filtered and evaporated to give a beige solid, which was recrystallized from hot EtOH (4.4 g colourless needles, 82 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 11.47 (bs, 1H, NH), 7.21 (m, 10H, Bn), 4.63 (s, 1H, $HC(C=N)_2$), 4.45 (s, 4H, Bn CH_2), 1.94 (s, 6H, $Me(C=N)_2$). $^{13}CNMR$ ($CDCl_3$, 101 MHz): δ 161.1 (C=N), 140.8 (*ipso* Bn), 128.3 (*ortho* or *meta* Bn), 127.2 (*ortho* or *meta* Bn), 126.4 (*para* Bn), 95.1 ($HC(C=N)_2$), 50.7. (Bn CH_2), 19.6 ($Me(C=N)_2$). Anal. Calcd. for $C_{19}H_{22}N_2$: C, 81.97; H, 7.96; N, 10.06. Found C, 81.55; H, 8.12; N, 10.10.

(*Nacnac*^{Bn})Cu(styrene), 2. To a mixture of **1** (250 mg, 0.90 mmol), CuO*t*Bu (120 mg, 0.88 mmol) and styrene (200 mg, 1.80 mmol) was added toluene (5 mL) to afford a yellow solution. After stirring for 1 h, the solution was reduced to 1/8th of its volume and layered with 2 mL of hexane. A colourless powder formed after 1 day (250 mg, 63 %). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 6.93-7.19 (m, 15H, Bn & styrene), 4.75-4.52 (m, 6H, C*H*$_2$Ph, HC(C=N)$_2$ & Ph*H*C=), 3.45 (d, *J* = 14 Hz, 1H, *cis* H_2C=), 3.19 (d, *J* = 9 Hz, 1H, *trans* H_2C=), 1.64 (s, 6H, Me(C=N)). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 165.1 (C=N), 143.3 (*ipso* Bn), 140.1 (*ipso* styrene) 128.7 (*ortho* styrene), 128.6 (*meta* or *ortho* Bn), 126.6 (*para* styrene), 126.5 (*meta or ortho* Bn), 126.3 (*meta* styrene), 125.6 (*para* Bn), 96.6 (H*C*(C=N)$_2$), 89.1 ($^{1}J_{CH}$ = 172 Hz, Ph*H*C=), 67.1 ($^{1}J_{CH}$ = 161 Hz, H_2C=), 57.3 (Bn CH_2), 21.8 (*Me*(C=N)). Anal. Calcd. for $C_{27}H_{29}N_2Cu$: C, 72.86; H, 6.57; N, 6.29. Found: C, 72.84; H, 6.60; N, 6.39. Crystals suitable for x-ray were obtained from toluene solution in the presence of excess styrene at –35 °C.

(*Nacnac*^{Bn})Cu(H_2C=CHCN), 3. CuO*t*Bu (137 mg, 1.0 mmol), **1** (300 mg, 1.1 mmol) and acrylonitrile (1.0 g, 19 mmol) were dissolved in toluene (5 mL) to give a yellow solution. After stirring for 15 min, the solution was evaporated to give yellow-brown oil. Hexane (6 mL) was added and the resulting suspension was kept at -35 °C for 1 day. The supernatant was decanted and residual solvent removed on the vacuum line to afford a yellow powder (115 mg, 29%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.01-7.11 (m, 10H, Bn), 4.72 (s, 1H, HC(C=N)$_2$), 4.61 (bs, 4H, Bn), 2.72-2.86 (m, 2H, =CHCN & *cis* H_2C=), 2.39 (d, *J* = 9 Hz, 1H, *trans* H_2C=), 1.79 (s, 6H, Me(C=N)$_2$). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 165.1 (C=N), 142.5 (*ipso* Bn), 128.8 (*ortho* or *meta* Bn), 126.7, 126.4, 105.4 (=CH*C*N), 96.9 (H*C*(C=N)$_2$), 70.6 (H_2C=), 58.0 (=*C*HCN), 54.0 (Bn *C*H_2), 21.7 (*Me*(C=N)$_2$). IR (toluene): ν_{CN} = 2225 cm^{-1}. Anal. Calcd. for $C_{22}H_{24}N_3Cu$: C, 67.07; H, 6.14; N, 10.66. Found: C, 66.25; H, 6.09; N, 10.14. Crystals obtained by layering a concentrated toluene solution with hexane at -35 °C were too small for X-ray diffraction studies. Good quality crystals were obtained, if 2 drops of DMSO were added to the toluene solution before layering with hexane at -35 °C for 24 h.

(*Nacnac*^{Bn})Cu(H_2C=$CHCH_2OPh$), 4. Cu*O*t*Bu* (137 mg, 1.0 mmol), **1** (300 mg, 1.1 mmol) and allylphenylether (86 mg, 1.0 mmol) were dissolved in toluene (5 mL) to give a yellow solution. After stirring for 15 min, hexane (5 mL) was added. The resulting suspension was kept at -35 °C for 1 day. The supernatant was decanted and residual solvent removed on the vacuum line to afford a yellow powder (300 mg 59%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 6.54-7.17 (m, 15H, Bn & OPh), 4.68-4.79 (m, 5H, Bn CH_2 & HC(C=N)$_2$), 4.00 (m, 1H, PhOCH$_2$(*H*)C=), 3.79 (dd, *J* = 3 Hz, 11 Hz, 1H, PhOC*H*$_2$-), 3.49 (dd, *J* = 3 Hz, 11 Hz, 1H, PhOC*H*$_2$-), 3.29 (d, *J* = 14 Hz, 1H, *cis* H_2C=), 3.16 (d, *J* = 9 Hz, 1H, *trans* H_2C=), 1.87 (s, 6H, Me(C=N)$_2$). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 165.3 (C=N), 159.1 (ipso OPh) 143.0 (*ipso* Bn), 129.5 (*ortho* or *meta* OPh) 128.7 (*ortho*, or *meta* Bn), 126.4 (*meta or ortho* Bn), 120.8 (*para*, OPh), 114.9 (*para* Bn), 96.7 (H*C*(C=N)$_2$), 84.8 (-OCH$_2$*C*H=), 71.7 (H_2C=), 68.2 (-O*C*H$_2$CH=), 58.2 (Bn CH_2), 21.8 (*Me*(C=N)$_2$). One peak (*ortho* or *meta* OPh) missing. Anal. Calcd. for $C_{28}H_{31}N_2OCu$: C, 70.78; H, 6.58; N, 5.90. Found: C, 70.36; H, 6.72; N, 5.92.

(*Nacnac*^{Bn})Cu(*trans*-stilbene), 5. To a mixture **1** (200 mg, 0.72 mmol), Cu*O*t*Bu* (100 mg, 0.73 mmol) and *trans*-stilbene (130 mg, 0.72 mmol) toluene (4 mL) was added to afford a yellow solution. After stirring for 15 min, the solution was layered with hexane (4 mL) and kept at -35 °C. Yellow crystals formed after 6 h (189 mg, 50 %). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.00-7.28 (m, 20H, Bn & C(H)*Ph*), 4.92 (s, 2H, Ph(*H*)C=), 4.65 (s, 1H, HC(C=N)$_2$), 4.59 (bs, 4H, Bn C*H*$_2$), 1.70 (s, 6H, Me(C=N)$_2$). ^{13}C NMR (C_6D_6, 101 MHz) δ 165.0 (C=N), 143.5 (*ipso* Bn), 139.4 (*ipso* C(H)*Ph*), 128.8, 128.7, 126.6, 126.4, 125.7, 96.6 (H*C*(C=N)$_2$), 85.0 (*C*(H)Ph) 56.2 (Bn *C*H$_2$), 21.7 (*Me*(C=N)$_2$). Anal. Calcd. for $C_{33}H_{33}N_2Cu$: C, 76.05; H, 6.30; N, 5.37. Found: C, 75.90; H, 6.45; N, 5.32.

{(*Nacnac*^{Bn})Cu}$_2$(μ-PhCCPh), 6. Diphenylacetylene (DPA) (64 mg, 0.36 mmol) and **1** (100 mg, 0.36 mmol) were dissolved in ether (2 mL). Cu*O*t*Bu* (49 mg, 0.36 mmol) was dissolved in ether (4 mL) to give a yellow solution and added. After stirring for 15 min, a yellow precipitate formed. The mixture was filtered and the residue washed with hexane (2 ml). Residual solvent was removed on the vacuum line to afford a yellow powder (65 mg, 42%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.21-6.70 (m, 30H, CPh & Bn), 4.67 (s, 2H,

HC(C=N)$_2$), 4.66 (bs, 8H, Bn C*H$_2$*), 1.62 (s, 12H, Me(C=N)$_2$). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 165.9 (C=N), 144.1 (*ipso* Bn), 131.2, 128.9, 128.4 (*ortho* or *meta* Bn), 127.9, 127.2 126.7, 126.1, 101.3 (Ph*CC*Ph), 98.9 (H*C*(C=N)$_2$), 58.8 (Bn CH_2), 21.7 (*Me*(C=N)$_2$). Anal. Calcd. for $C_{52}H_{52}N_4Cu_2$: C, 72.62; H, 6.09; N, 6.51. Found: C, 71.70; H, 6.30; N, 6.45. Crystals suitable for X-ray diffraction studies were obtained from a 1:1 toluene/hexane solution upon cooling to -35 °C.

(*Nacnac*^{Bn})Cu(PhCCPh), 6b. In the presence of excess (> 10 equiv.) diphenylacetylene in C_6D_6 at room temperature, **6** converts completely into the monometallic complex **6b**. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.26-6.80 (m, 20H, CPh & Bn), 4.83 (s, 1H, HC(C=N)$_2$), 4.54 (bs, 4H, Bn C*H$_2$*), 1.85 (s, 6H, Me(C=N)$_2$). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 165.3 (C=N), 142.7 (*ipso* Bn), 129.0 (*ortho* or *meta* Bn), 128.6, 126.9, 126.6 (*ortho* or *meta* Bn), 126.2, 125.8, 103.9 (Ph*CC*Ph), 96.7 (H*C*(C=N)$_2$), 56.7 (Bn *C*H$_2$), 21.8 (*Me*(C=N)$_2$). One resonance missing.

(*Nacnac*^{Bn})CuPPh$_3$, 7. CuO*t*Bu (244 mg, 1.80 mmol), **1** (500 mg, 1.80 mmol) and PPh_3 (477 mg, 1.82 mmol) were dissolved in toluene (5 mL) to give a yellow solution which became brown within 5 min. After stirring for 1 h, the solvent was evaporated to yield a viscous, gummy residue. Washing twice with 30 mL hexanes yielded a white solid (760 mg, 70 %). After 1 day, additional colourless crystals were obtained from the hexane wash. ^{1}H NMR (C_6D_6 400 MHz): δ 7.22-6.86 (m, 25H, PPh_3 & Bn), 4.97 (s, 1H, HC(C=N)$_2$), 4.93 (s, 4H, Bn CH_2), 2.01 (s, 6H, Me(C=N)$_2$). ^{13}C NMR (C_6D_6 101 MHz): δ 165.4 (C=N), 144.0 (*ipso* Bn), 134.6 (d, *J* = 6 Hz, *ipso* PPh_3), 133.8 (d, *J* = 4 Hz, *ortho* or *meta* PPh_3), 129.5, 128.7 (d, *J* = 4 Hz *ortho* or *meta* PPh_3), 126.8, 125.9, 96.7 (H*C*(C=N)$_2$), 58.9 (Bn CH_2), 21.9 (*Me*(C=N)$_2$) (one peak lacking). ^{31}P NMR (C_6D_6, 101 MHz): δ 3.5. $C_{37}H_{36}N_2PCu$: Anal. calcd. C 73.67, H 6.02, N 4.69; found: C 73.82, H 6.52, N 4.91.

(*Nacnac*^{Bn})CuCN($C_6Me_2H_3$), 8. A yellow solution of CuO*t*Bu (80 mg, 0.60 mmol) in toluene (2 mL) was added to a flask containing **1** (155 mg, 0.55 mmol) and xylyl isocyanide (72 mg, 0.55 mmol). The resulting yellow solution was layered with hexane (4 mL) and kept at -35°C. Yellow crystals formed after 1 day (145 mg, 53 %). ^{1}H NMR

(C_6D_6, 400 MHz): δ 7.40 (d, *J* = 8 Hz, 4H, *ortho* Bn), 7.12 (m, 4H, *meta* Bn), 6.97 (t, *J* = 8 Hz, 2H, *para* Bn), 6.69 (t, *J* = 8 Hz, 1H, CN*Ar*Me_2), 6.52 (d, *J* = 8 Hz, 2H, CN*Ar*Me_2), 5.00(s, 4H, Bn CH_2), 4.82 (s, 1H, *H*C(C=N)$_2$), 2.02 (s, 6H, Me(C=N)$_2$), 1.75 (s, 6H, CNAr*Me*$_2$). ^{13}C NMR (C_6D_6 101 MHz): δ 164.6 (C=N), 144.4 (ipso Bn), 134.3, 128.3, 127.9, 127.8, 127.6, 126.2, 96.0 (H*C*(C=N)$_2$), 59.2, 21.9 (*Me*(C=N)$_2$), 18.5 (CNAr*Me*$_2$). Anal. calcd. for $C_{30}H_{30}N_3Cu$: C 71.23, H 6.40, N 8.90; Found: C 70.96, H 6.04, N 8.90. IR (toluene): ν_{CN} = 2114 cm^{-1}.

General experimental procedure for the exchange experiments. Complex **2** (10 mg, 11 μmol) was dissolved in C_6D_6 (700 μL) and the olefin (0.5 equiv) was added. The solution was transferred to a J. Young tube for ^{1}H NMR analysis. The procedure was repeated with 1 and 2 equiv of olefin. For stilbene and diphenylacetylene peak overlap prevented the determination of the free olefin concentration directly form the NMR spectra. The olefin was thus combined with free styrene and their ratio determined by NMR (olefin/styrene = 5-12), before complex **2** was added. The olefins were used in >5-fold excess of styrene to **2** to assure an unchanged olefin/styrene ratio. Diphenylacetylene : [Cu] ratios were > 10, to avoid the presence of **6** instead of **6b**.

(N*acnac*^{Bn})Cu(CH$_2$=C(H)C$_6$H$_5$F). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.23-6.37 (m, 14H, -C$_6$*H*$_4$F & Bn), 4.43-4.75 (m, 6H, Bn CH_2, =C(*H*)C$_6$H$_4$F & HC(C=N)$_2$), 3.32 (d, *J* = 14 Hz, 1H, *cis* H_2C=), 3.12 (d, *J* = 9 Hz, 1H, *trans* H_2C=) 1.82 (s, 6H, Me(C=N)$_2$).

(*Nacnac*^{Bn})Cu(CH$_2$=C(H)C$_6$H$_5$OMe). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.23-6.53 (m, 14H, Bn & -C$_6$*H*$_4$OMe), 4.51-4.77 (m, 6H, Bn CH_2, =C(*H*)C$_6$H$_4$OMe & HC(C=N)$_2$), 3.43 (d, *J* = 14 Hz, 1H, *cis* H_2C=), 3.38 (s, 3H, OMe), 3.15 (d, *J* = 9 Hz, 1H, *trans* H_2C=) 1.96 (s, 6H, Me(C=N)$_2$).

X-ray diffraction studies. Diffraction data were collected on a Bruker Smart APEX II with graphite monochromated Mo Kα radiation (**8**), a Bruker SMART 6000 with Montel 200 monochromator (**3** & **5**-**7**) and a Bruker Microstar-Proteum with Helios optics (**2**), both equipped with a rotating anode source for Cu Kα radiation. Cell refinement and data

reduction were done using APEX2.[71] Absorption corrections were applied using SADABS.[71] Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97.[72] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropic on calculated positions using a riding model. Further experimental details are listed in Table VI-5.

Table VI-5. Details of X-ray Diffraction Studies

		2	**3**	**5**	**6**	**7**	**8**
Formula		$C_{27}H_{29}N_2Cu$	$C_{22}H_{24}N_3Cu$	$C_{33}H_{33}N_2Cu \cdot 0.5\ C_7H_8$	$C_{52}H_{52}N_4Cu_2$	$C_{28}H_{30}N_3Cu$	$C_{37}H_{36}N_2PCu$
Mw (g/mol); $d_{calcd.}$ (g/cm^3)		445.07; 1.364	393.98; 1.361	567.23; 1.300	430.03; 1.308	470.09; 1.285	6.03.19; 1.325
T (K); F(000)		150; 936	150; 824	150; 1196	150; 1800	150; 1984	150; 632
Crystal System		Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space Group		$P2_1/c$	$P2_1/c$	$P2_1/n$	P-1	C2/c	P-1
Unit Cell:	*a* (Å)	24.5143(5)	14.3009(7)	11.353(4)	11.317(2)	17.3118(6)	11.1477(11)
	b (Å)	5.64490(10)	6.0688(3)	11.6674(4)	11.331(2)	17.0767(6)	11.2906(11)
	c (Å)	15.9542(3)	22.73.08(11)	21.9442(7)	36.015(7)	15.9761(5)	12.9378(13)
	α (°)				93.520(6)		101.041(3)
	β (°)	101.0520(10)	102.916(2)	94.6670(10)	98.623(6)	93.694(2)	107.854(2)
	γ (°)				105.864(5)		92.613(3)
V ($Å^3$); Z		2166.87(7); 4	1922.88(16); 4	2897.12(17); 4	4366.7(15); 8	4878.8(3); 8	1511.8(3); 2
θ range (°); completeness		1.84-67.65; 0.949	3.17-63.66; 0.989	4.04-71.21; 0.988	1.25-68.64; 0.963	3.58-72.88; 0.992	1.69-31.34; 0.936
Refl.: collec./indep.; R_{int}		21600/3224; 0.035	25535/2102; 0.07	34599/4951; 0.047	52719/5520; 0.113	36753/4212; 0.038	35181/7909; 0.023
μ (mm^{-1})		1.525	1.661	1.259	1.497	1.398	0.804
R1(F); $wR(F^2)$; $GoF(F^2)$ [a]		0.0347; 0.1010; 1.045	0.0425; 0.1058; 0.951	0.0376; 0.1051; 1.073	0.1084; 0.3258; 0.952	0.0362; 0.1056; 1.075	0.0304; 0.0858; 1.099
Residual electron density		0.369	0.234	0.295	0.617	0.328	0.634

[a] R1(F) based on observed reflections with I>2s(I), $wR(F^2)$ and $GoF(F^2)$ based on all data.

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(51) Correlations were found between five indicators of metallacyclopropane character (and thus π back-donation) in styrene copper(I) complexes: i) lengthening of the olefinic bond, ii) increased bending of the phenyl substituent out of the olefinic plane (see Figure 7), iii) upfield shift Δδ of olefinic carbon atoms in ^{13}C spectra (see Figure 8), iv) decreasing asymmetry of Cu-C distances and v) decreasing differences between $\delta(CH_2)$ and $\delta(CHPh)$ in ^{13}C spectra. Relative errors in the latter two were two big for meaningful analysis. In the cases considered here, lengthening of the olefinic bond thus seems to be a valid indicator for the amount of π back-bonding.

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Supplementary material

π Back-Bonding in Dibenzyl-β-diketiminato Copper Olefin Complexes

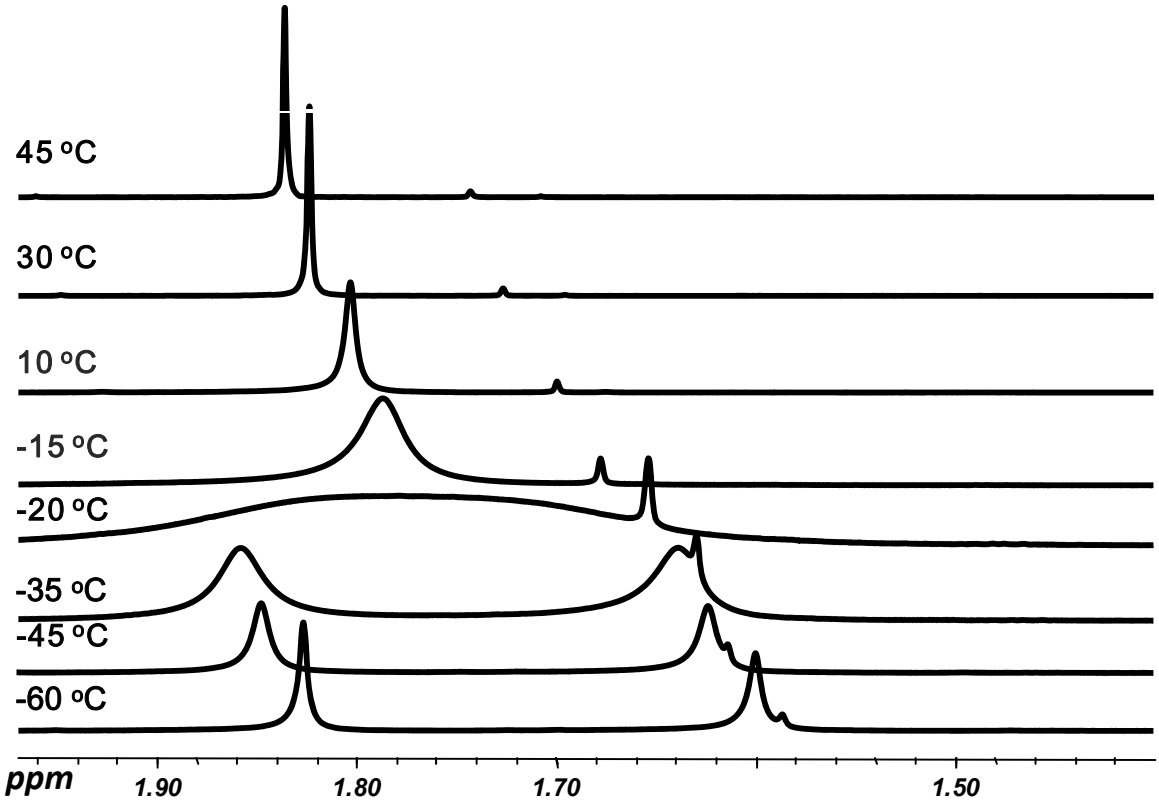

Figure 6.S1: VT NMR spectra for 2 in toluene-d_8 Exchange of nacnac CH_3 groups

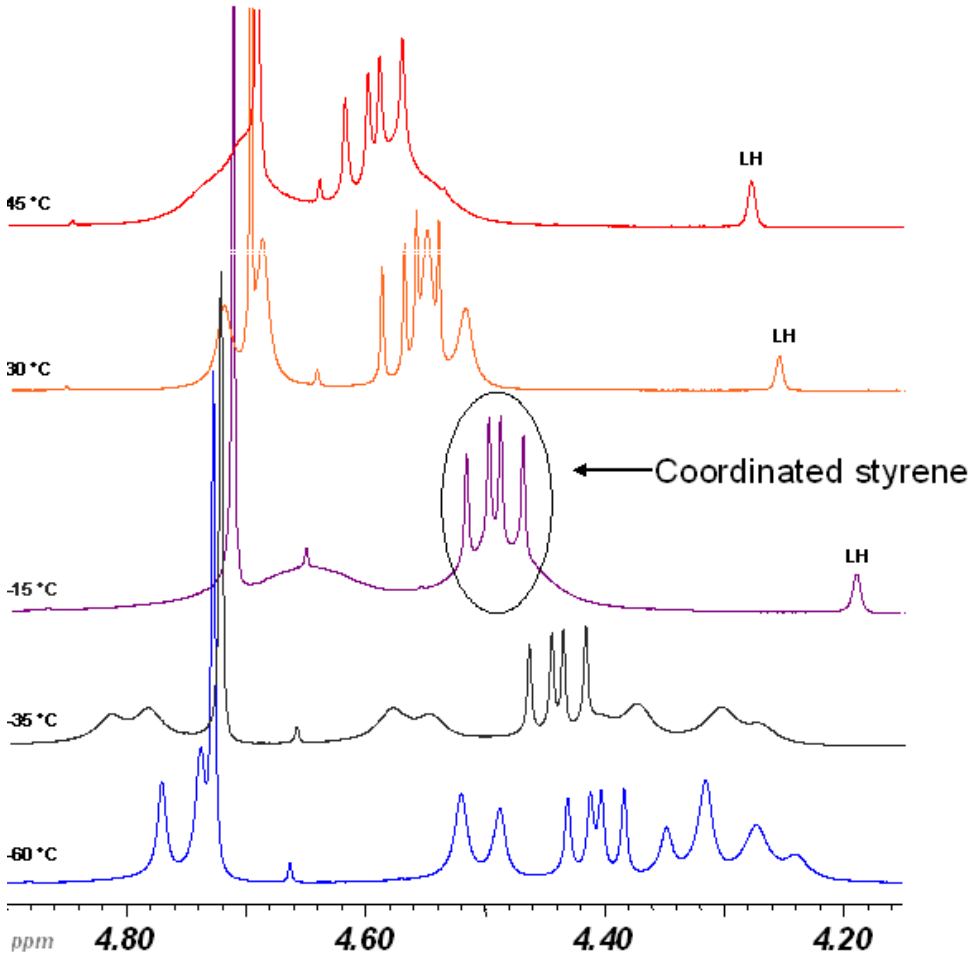

Figure 6.S2: VT NMR spectra for 2 in toluene-*d*8 Exchange of *nacnac* Bn CH_2 groups.

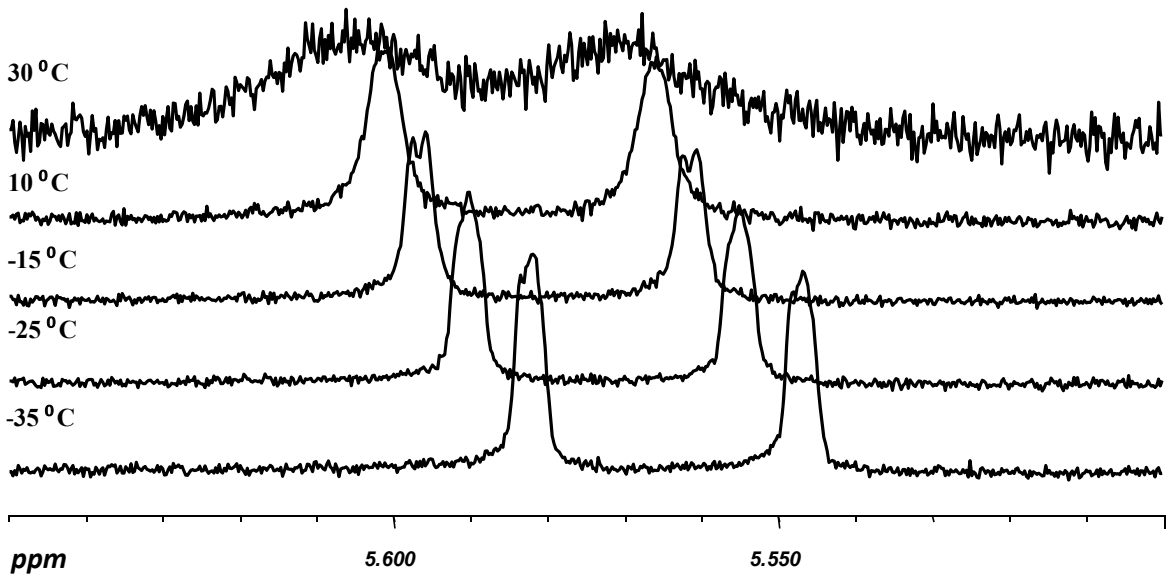

Figure 6.S3: VT NMR spectra for 2 in toluene-*d*8. Exchange of free/coordinated styrene. Peaks of coordinated styrene broaden slightly. For free styrene, which is present in smaller amounts the effect is more pronounced.

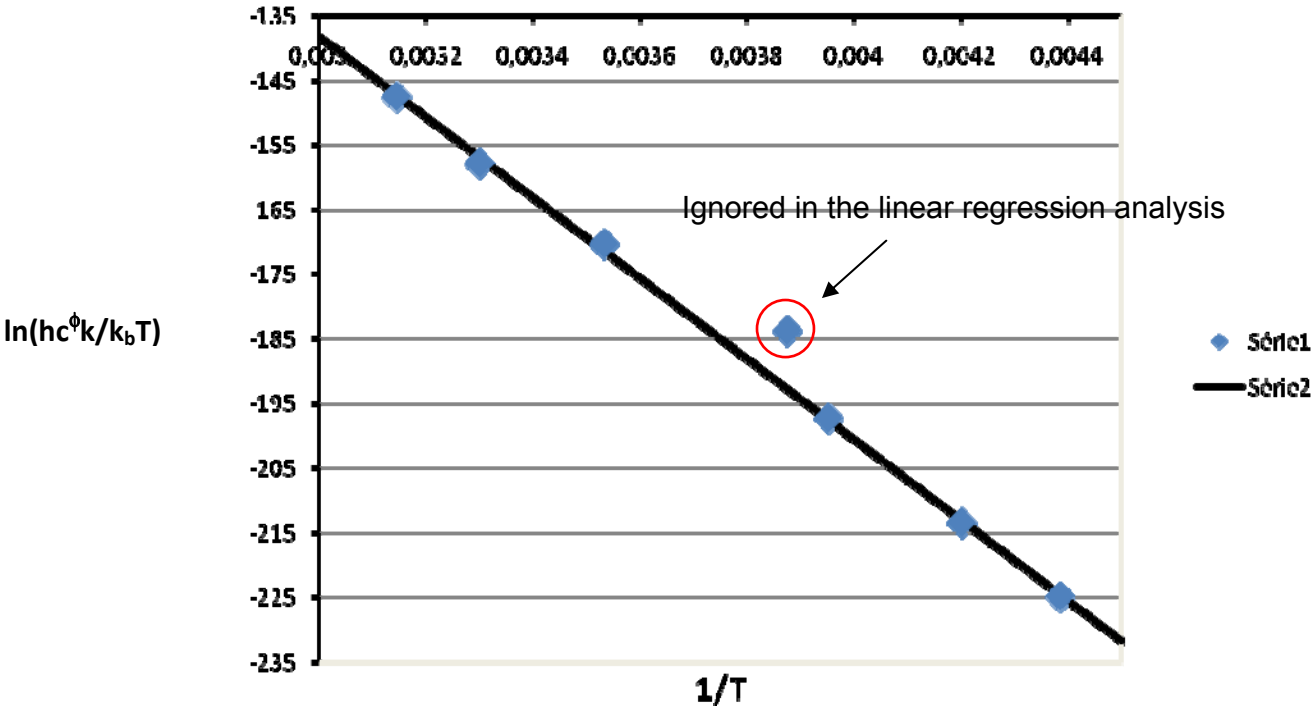

Figure 6.S4: Eyring plot of the styrene rotation

Chapter 7

Intramolecular π-Stacking in Copper(I) Diketiminate Phenanthroline complexes

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Paul O. Oguadinma, Alexandre Rodrigue-Witchel, Christian Reber, Frank Schaper

Département de chimie, Université de Montréal, Montréal, Québec, H3C 3J7, Canada.

Abstract

Diketimines *N,N'*-dibenzyl-2-amino-4-imino-pent-2-ene (**1**), *S,S-N,N'*-di(phenylethyl)-2-amino-4-imino-pent-2-ene (**2**), *N,N'*-bis(3,4,5-trimethoxyphenylmethyl)-2-amino-4-imino-pent-2-ene (**3**), *N,N'*-bis(pentafluorophenylmethyl)-2-amino-4-imino-pent-2-ene (**4**) and *N,N'*-diisobutyl-2-amino-4-imino-pent-2-ene (**5**) react with CuO*t*Bu in the presence of 2,9-R_2-1,10-phenanthroline to give the respective neutral, tetracoordinated diketiminate copper(I) phenanthroline complexes **1a & 2a** (R = H), **1b**, **3b-5b** (R = Me) and **1c** & **3c** (R = Ph). Crystal structures were obtained for all complexes except **5b** and intramolecular π stacking between the phenanthroline ligand and one or two *N*-benzyl substituents were observed in **1a**, **2a**, **1b** and **1c**, or **3b** and **4b**, respectively. UV/vis absorption spectra show two transitions in the visible region, a diketiminate-based transition at 373 – 386 nm and a transition at 600 – 666 nm, tentatively assigned to an MLCT to phenanthroline. All complexes were weakly luminescent in the solid state at room temperature with lifetimes of less than 60 ns. Weak luminescence was also observed in solution at room temperature with λ_{max} = 720 – 830 nm for **1b**, **1c**, **3b**, **4b** and **5b** and short luminescence lifetimes. Intramolecular π stacking interactions, which prevent flattening distortions in the solid state, appear to have advantageous effects on luminescence intensities.

Introduction

Luminescent metal complexes find application in solar light harvesting and conversion, and complexes of second and third row metals, in particular Ru(II) polypyridines, have been among the most prominent examples. Their widespread use is, however, limited by a notable toxicity and, in particular, high costs. There is, thus, interest in cheaper and more environmentally benign metal sources as alternatives [1]. Complexes with a d^{10} electron configuration, in particular Cu(I), have been considered as potential candidates, since their closed shell structure prevents the non-radiative deactivation through low-lying MC transitions, which are prevalent with other first-row transition metals [2]. Copper(I) phenanthroline complexes are among the most studied copper complexes in this regard [2-6], following the pioneering work of McMillin and coworkers [7, 8]. However, these complexes do deactivate non-radiatively after irradiation by means

other than thermal equilibration of the MC and the MLCT levels. Bisphenanthroline copper(I) complexes, for example, undergo a flattening distortion in the excited state rendering them prone to nucleophilic attack by solvent molecule or counter ion to form a penta-coordinated exciplex, which deactivates *via* non-radiative relaxation (Chart 7.1). Substitution at the 2,9-positions of the phenanthroline ligand, avoiding coordinating solvents and excited state equilibration with organic auxiliaries have been used as strategies to avoid the excited state quenching [2-6].

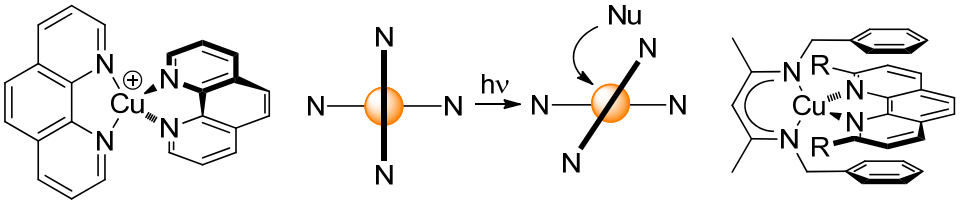


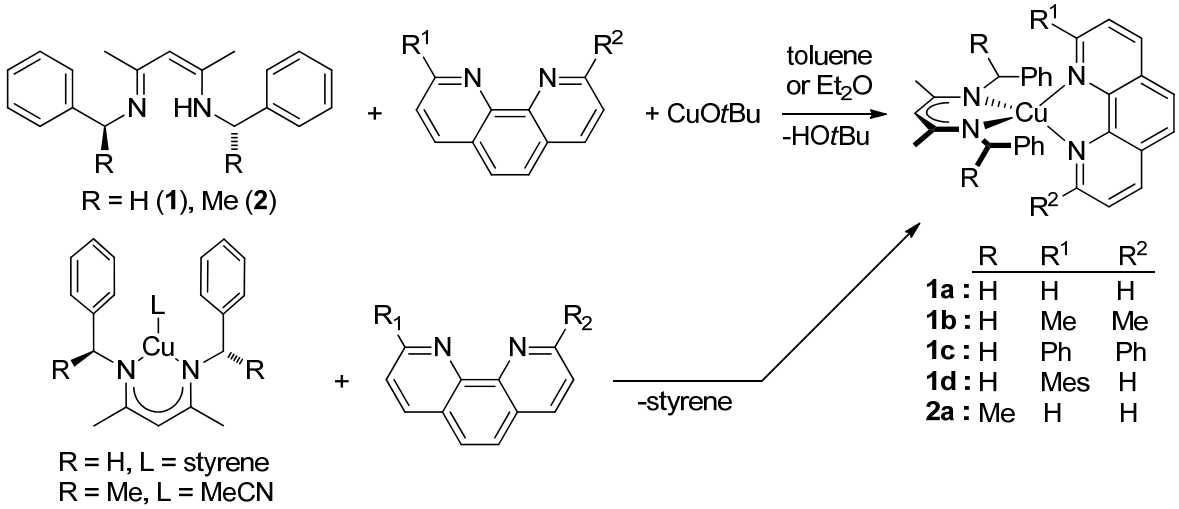
Chart 7.1

We have previously reported the syntheses of copper(I) complexes with *N*-alkyl substituted diketiminate ligands (*nacnac*^{R}) [9-11], in particular *nacnac*^{Bn} [10], in which π stacking interactions are present in most of its complexes. We envisaged that this ligand would allow a "sandwiched" π stacking arrangement of the phenanthroline ligand between the *N*-benzyl substituents, thus minimising excited state distortion (Chart 7.1). Due to the neutral nature of diketiminate copper complexes, exciplex quenching by the counter ion might be prevented as well. Not counting Cu(I) halogen compounds [12] and polynuclear complexes [13], we are aware of only one report on neutral copper phenanthroline complexes [14], although luminescent neutral copper complexes have been reported with other ligands [15-18].

Results and Discussion

***Nacnac*^{Bn} and *nacnac*$^{CH(Me)Ph}$ complexes.** Reaction of diketimines **1** and **2** with CuO*t*Bu [19] in the presence of the appropriate phenanthroline afforded the four-coordinated copper(I) complexes **1a-1d** and **2a** (Scheme 7.1). Complexes **1a-1d** could also be obtained by displacement of styrene from *nacnac*^{Bn}Cu(styrene) with phenanthroline if liberated styrene was removed under vacuum. Analogously, phenanthroline replaced acetonitrile in *nacnac*$^{CH(Me)Ph}$CuNCMe to yield **2a**. Only decomposition products were observed with

either method when sterically bulky 2,9-di(tert-butyl)phenanthroline or 2,9-dimesitylphenanthroline was employed. This mirrors common reactivity patterns of phenanthroline copper complexes: $[Cu(tbp)_2]^+$ (tbp = 2,9-di(tert-butyl)-1,10-phenanthroline) was only synthesized indirectly by oxidation of elemental copper in the presence of tbp [20] after conventional methods had failed [21], while copper complexes of 2,9-dimesitylphenanthroline have not been reported. The corresponding monosubstituted 2-mesitylphenanthroline, on the other hand, cleanly yielded the respective copper complex **1d**. All complexes are dark-blue in colour and sensitive to air and moisture. The complexes are soluble in dichloromethane, toluene and THF and moderately soluble in ether [22].The ^{1}H NMR spectra of **1a-1c** display a singlet for the benzylic protons, indicating a C_{2v}-symmetric structure or fast rotation around the N-C_{Bn} bond. In **1d**, the benzylic protons split into two doublets due to the non-symmetric mesitylphenanthroline ligand.



Scheme 7.1

Solid-state structures of **1a-1d** and **2a** are displayed in Figure 7.1. Cu-N bond distances and N-Cu-N bond angles for the diketiminate ligand (1.959(2) – 1.981(2) Å, 98.3(2) – 100.8(1)°, table VII-1) and for the phenanthroline ligand (1.998(2) – 2.194(1) Å, 79.3(1) – 83.4(4)°) are in the usual range expected for these ligands (*nacnac* : 1.94(2) Å, 99(1)°; phenanthroline: 2.05(4) Å, 82(1)° [23]). All structures show a common motif, with one phenyl ring of the benzyl (or phenylethyl) substituent in a parallel π-stacking arrangement with phenanthroline (angles and distances between least-square planes: 5 – 15°, 3.0 – 3.8 Å), while the other is rotated out of a parallel arrangement. The symmetric

NMR spectra obtained for all complexes indicate that π-stacked and non-π-stacked rings interchange easily or that in solution a C_{2v}-symmetric arrangement of both substituents is preferred. There are no evident structural reasons which would prevent the π stacking of the second *N*-substituent in solution. In **1a** and **1d**, slight intermolecular π stacking between two phenanthroline ligands is observed, but it seems to be a minor structural motif and is absent in the other structures. With the exception of **1c**, N-CH_2-C_{Ph} angles of 114 – 116° (Table VII-1) for the non-π-stacked substituent (e. g. N1-C12-C6 in **1a**) are comparable to those observed in other *nacnac*^{Bn} metal complexes (Cu: 114 – 116° [10], Zr: 115° [24], Zn: 112 – 113° [25]). Corresponding angles for the π-stacked substituent (e. g. N2-C19-C13 in **1a**) are 3 – 5° smaller, indicating a bending of the phenyl substituent towards the phenanthroline ligand. Analogously, the phenanthroline ligand is either placed on the bisector of the diketiminate ligand (**1d** and **2a**, Figure 7.2) or angled slightly towards the π-stacked *N*-substituent in **1a-1c** (Figure 7.2). π Stacking between the benzyl and the phenanthroline substituent seems, thus, to require a slight deformation of the N-C-C_{Ph} angle from its equilibrium position, but appears to be a stabilizing interaction.

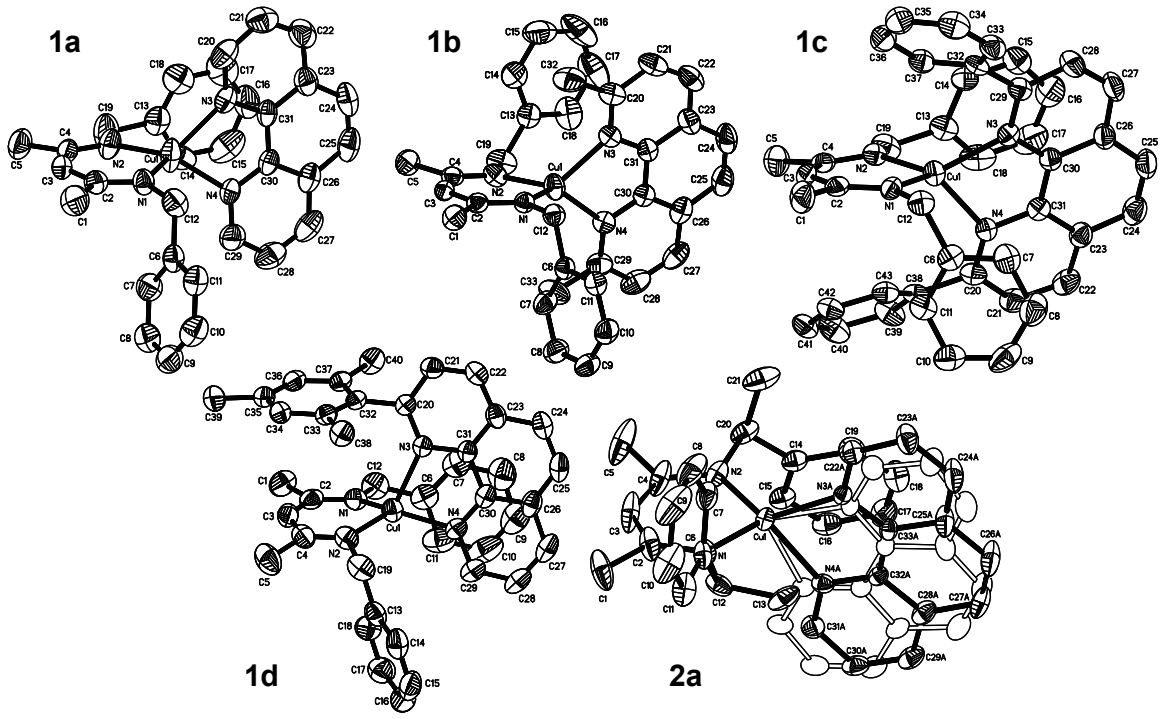


Figure 7.1: X-ray structures of **1a-d** and **2a**. Thermal ellipsoids are drawn at the 50% probability level (30% for **2a**). Hydrogen atoms were omitted for clarity.

Table VII-1: Selected bond distances [Å] and angles [°] for **1a-1d** and **2a**.

	1a	**1b**	**1c**	**1d**	**2a**
Cu-N1/2	1.959(2)/1.981(2)	1.963(4)/1.975(4)	1.961(2)/1.964(2)	1.958(2)/1.965(2)	1.962(2)/1.963(2)
Cu-N3/4	2.148(2)/2.071(2)	2.085(4)/2.092(4)	2.058(2)/2.110(2)	2.194(1)/1.998(2)	2.006(6) – 2.204(6)
N1-Cu-N2	99.3(1)	98.3(2)	100.7(1)	101.4(1)	100.8(1)
N3-Cu-N4	78.7(1)	79.8(2)	81.3(1)	82.5(1)	83.4(4)[d]
N-CH_2-$C_{\pi\text{-Ph}}$ [a]	111.0(3)	111.7(4)	113.3(2)	111.0(2)	110.0(2)
N-CH_2-C_{Ph}	115.6(2)	115.1(4)	110.9(2)	113.8(2)	114.8(3)
∠ Ph – phen [b]	5	14	7	10	15
d Ph – phen [c]	3.2 – 3.5	3.3 – 3.9	3.1 – 3.5	3.1 – 3.6	3.0 – 3.8

[a] N-C-C angle of the π-stacked Bn substituent. [b] Angle between least-square planes of the π-stacked phenyl henanthroline ligand. [c] Distances of the carbon atoms of the π-stacked phenyl ring to the least-square plane throline ligand.

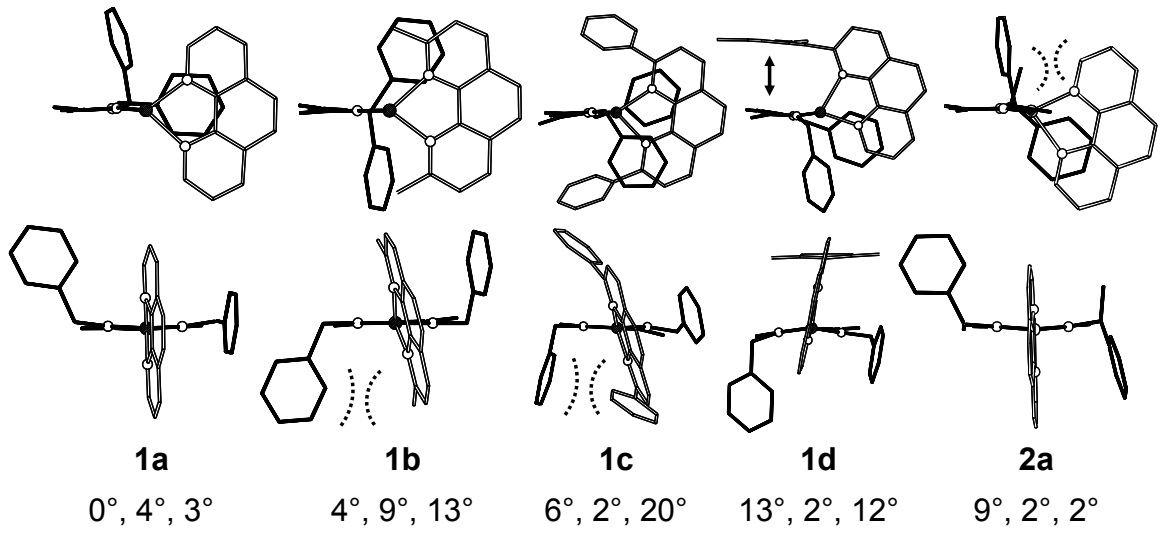
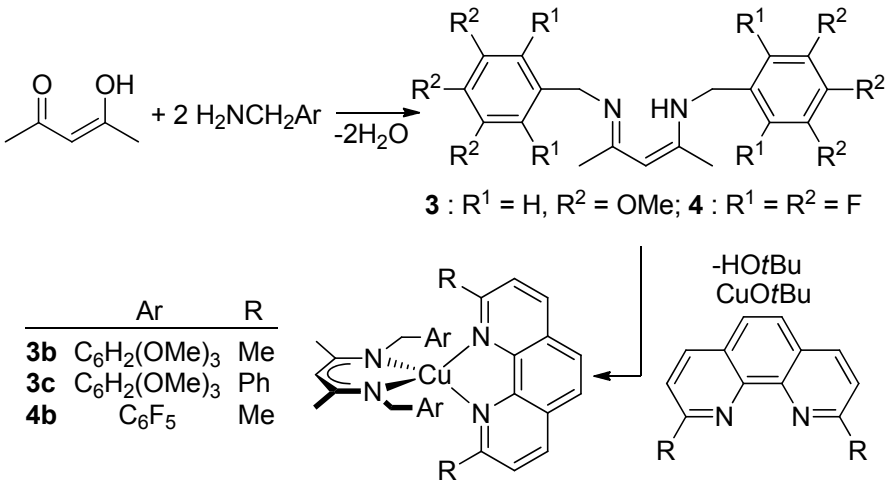


Figure 7.2: Rocking (top) and flattening (bottom) distortions in **1a-d** and **2a**. Numbers indicate $\Delta\theta_x$, $\Delta\theta_y$, and $\Delta\theta_z$. Dotted lines indicate steric interactions.

Distortions from an ideal geometry can be described using the θ_x, θ_y, and θ_z angles, introduced by White and coworkers [26]. Perfect C_{2v} symmetry yields $\theta_x = \theta_y = \theta_z = 90°$. A

rocking distortion of the phenanthroline ligand causes a deviation in θ_x and can be expressed in the form of $\Delta\theta_x = |90° - \theta_x|$ (Figure 7.2). Analogously, a flattening of the complex can be expressed by θ_z and $\Delta\theta_z = |90° - \theta_z|$, where θ_z is roughly equivalent to the angle between the mean planes of the ligands. Of the investigated complexes, sterically least encumbered **1a** displays the most symmetrical coordination. Introduction of an additional methyl group in **2a** does not seem to influence the phenyl-phenanthroline π stacking interaction, but steric crowding of the phenanthroline by methyl group C21 and phenyl group C6-C11 (Figure 7.1) introduces a rocking distortion of $\Delta\theta_x = 9°$. Symmetrical substitution of the phenanthroline ligand in **1b** and **1c** resulted in small rocking distortions, but significant complex flattening of 13° and 20°, respectively. Space-filling plots of both complexes indicate that vdW-contacts between the non-π-stacked phenyl ring and the phenanthroline substituent are responsible for this distortion. Complex **1d** with the unsymmetrically substituted mesityl-phenanthroline ligand shows the highest rocking deformation (13°), probably due to attractive π stacking between the mesityl substituent and the diketiminate ligand. Despite the high flexibility of the benzyl substituents and the unsymmetrical conformation with one π-stacked phenyl ring, the complexes do not deviate significantly from ideal geometry. The dmp-coordinated complex **1b**, for example, shows deviations of $\Delta\theta_{x,y,z} = 4°$, 9° and 13°, while values of $\Delta\theta_{x,y,z} = 0\text{-}12°$, 1-16°, and 2-18° were found for the symmetric $[Cu(dmp)_2]^+$ cation with different anions [26, 27].

Copper dmp complexes with different diketiminate ligands. In an attempt to stabilize the planar, π-stacked arrangement of the phenanthroline ligand with both *N*-benzyl substituents depicted in figure 7.1, we prepared diketimines **3** and **4** with trimethoxybenzyl or pentafluorobenzyl *N*-substituents, following the protocol established elsewhere (Scheme 7.2) [10, 28]. Ligand **3** could be further characterized by an X-ray diffraction study (Figure 7-S1, supp. information). Ligand **4** was obtained only in purities of 85-90%, which were however sufficient for subsequent reactions.



Scheme 7.2

Reaction of **3** or **4** with CuO*t*Bu in the presence of the corresponding phenanthroline yielded the respective copper complexes **3b**, **3c** and **4b** (Scheme 7.2). Their crystal structures showed indeed more symmetrical conformations (Figures 7.3, 7.4, and Table VII-2). In **3b**, the second phenyl ring is now found in a more planar arrangement with the dmp ligand (Ph – dmp angle: **3b**: 20°, **1b**: 79°). In **3c**, on the other hand, π stacking between benzyl substituents and the dpp ligand is lost and both substituents show phenyl – dpp angles (40°) and variations in the distances of C_{Ph} to the dpp mean plane (1.6 Å), which are comparable to the non-π-stacked substituent in **1c** (33°, 1.4 Å). Complex **4b**, carrying perfluorinated benzyl substituents, shows the targeted sandwich-like π stacking of both phenyl rings, characterized by small angles between the phenyl and phenanthroline planes (4° and 5°) and small distance variations (0.3 Å). Both N-C-C_{Ph} angles are now reduced to 109.9(2)° and 110.6(2)°, respectively, a deformation apparently required for a planar arrangement. The somewhat more planar conformation of the second phenyl ring in **3b** compared to **1b** is mirrored by a decrease of $\Delta\theta_z$ (13° in **1b**, 9° in **3b**) and the close planar arrangement of all aromatic rings in **4b** resulted in a very small $\Delta\theta_z$ of 3°. Increased π stacking thus seems to reduce the flattening distortion in the ground state, while slightly increasing rocking distortions (Figure 7.4). Complex **3c**, which is the only compound not showing any intramolecular π stacking interactions in the solid state, displayed the highest flattening distortion observed for all complexes (25°). Since **3c** crystallized on a

crystallographic C_2 axis, rocking and wagging distortions are consequently absent (Figure 7.4).

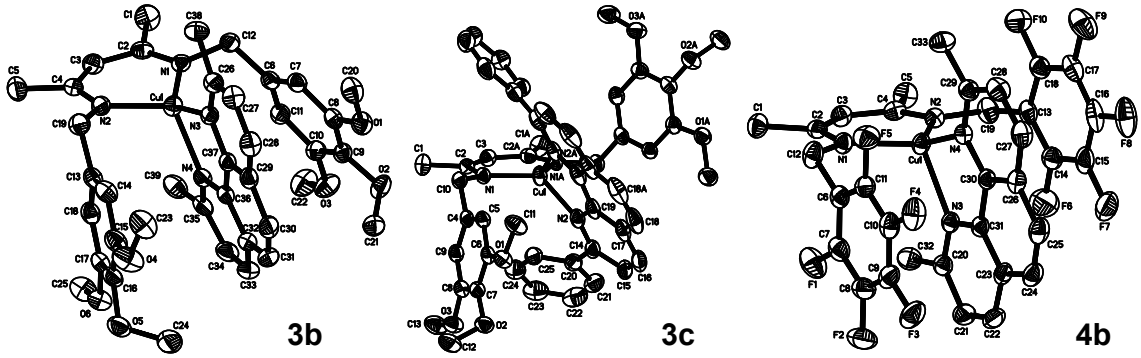


Figure 7.3 Crystal structures of **3b**, **3c** and **4b**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

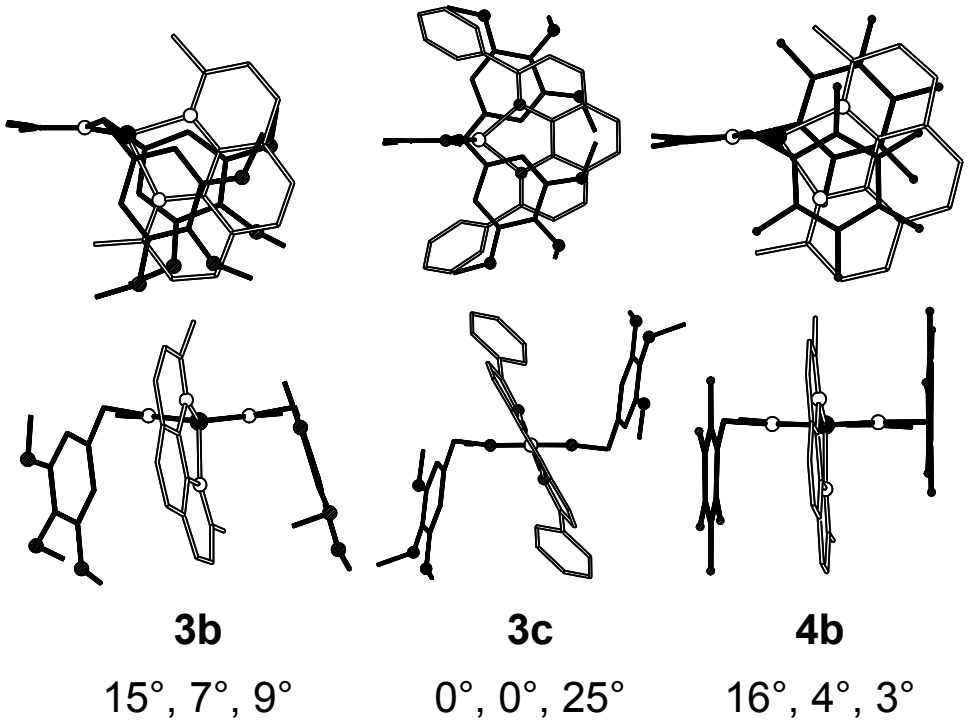


Figure 7.4: Rocking (top) and flattening (bottom) distortions in **3b**, **3c** and **4b**. Numbers indicate $\Delta\theta_x$, $\Delta\theta_y$, and $\Delta\theta_z$.

Table VII-2: Selected bond distances [Å] and angles [°] for **3b**, **3c** and **4b**.

	3b	**3c**	**4b**
Cu-N1/2	1.948(1)	1.959(1)	1.984(2)
	1.961(1)	1.959(1)	1.982(2)
Cu-N3/4	1.985(1)	2.060(1)	2.148(2)
	2.136(1)	2.060(1)	2.052(2)
N1-Cu-N2	100.3(1)	101.4(1)	99.3(1)
N3-Cu-N4	111.2(1)	82.5(1)	79.6(1)
N-CH_2-C_{Ph}	111.6(1)	112.5(1)	110.6(2)
	113.0(1)[a]		109.9(2)[a]
∠ Ph – phen [b]	13°, 20 °	40°	5°, 4°
d (Ph – phen) [c]	3.4 – 4.0 Å,	3.4 – 5.0 Å	3.0 – 3.3 Å,
	3.0 – 3.8 Å		3.0 – 3.3 Å

[a] N-C-C angles of the π-stacked Bn substituents. [b] Angle between least-square planes of π-stacked phenyl rings and the phenanthroline ligand. [c] Distances of the carbon atoms of π-stacked phenyl rings to the least-square plane of the phenanthroline ligand.

UV/vis spectroscopy. For the sake of comparison, we prepared *nacnac*$^{i\text{Bu}}$Cu(dmp), **5b**, where the benzyl substituents were replaced by sterically comparable isobutyl group, which, however, can not undergo π stacking interactions. UV/vis absorption and emission spectra were recorded in toluene and, for selected complexes, in diethyl ether at room temperature (Table VII-3). UV/vis absorption spectra of all compounds show two distinct peaks above 350 nm with ε = 1200 – 12000 $M^{-1}cm^{-1}$ (Figure 7.5). One transition is located at λ_{max} = 373 – 386 nm and appears as a shoulder on more intense π-π* transitions for several complexes (Table VII-3). A second transition of lower intensity, showing a distinctively asymmetric peak profile, is found at λ_{max} = 600 – 667 nm. Both transitions are weaker than π-π* transitions located below 350 nm in these compounds and might be associated with charge-transfer transitions. The higher-energy transition is found at lower wavelengths than the MLCT in $[CuL_2]^+$ complexes (L = phen [29, 30], dmp [30-33], dpp [29-31, 34, 35]: $\lambda_{max}(CH_2Cl_2)$ = 440 – 460 nm, with occasional shoulders at higher wavelength around 540 – 580 nm). Replacing an electron-poor phenanthroline ligand with

an anionic, electron-rich diketiminate would not be expected to result in a hypsochromic shift of the metal-phenanthroline CT. *N*-substituent effects also argue against an assignment of the transition around 380 nm as a charge transfer transition towards phenanthroline: in the series **1b** – **5b**, isobutyl-substituted **5b** displays the highest-energy transition (373 and 370 nm in toluene and Et_2O, respectively), while **4b**, carrying pentafluorobenzyl substituents, is found at the low-energy end of the observed range (386 and 384 nm). Thus, we assign transitions around 380 nm to diketiminate-based transition, not involving a phenanthroline acceptor orbital. In agreement with this, *nacnac*^{Bn}Cu(styrene) and (*nacnac*^{Bn})$_2$Zn show comparable transitions at 349 nm (ε = $2.2\cdot10^4$ $M^{-1}cm^{-1}$) and 362 nm (ε = $2.1\cdot10^4$ $M^{-1}cm^{-1}$). Intense transitions in copper diketiminate complexes around 350 nm have been previously assigned to diketiminate π-π* transitions [36, 37], but relatively low molar absorption coefficients (2800 – 15000 $M^{-1}cm^{-1}$), line widths of ≈80 nm at half maximum, and the effect on the *N*-substituent on λ_{max} for **2b** – **5b** would also be in agreement with a metal to diketiminate CT, normally hidden below π-π* transitions in this region.

Table VII-3 Longest wavelength absorption and luminescence maxima for *nacnac*^{R}Cu(L).

					toluene, λ_{max}/nm (ε·M·cm)		diethylether, λ_{max}/nm (ε·M·cm)	
	R	L	$\Delta\theta_z$	π-stacking	Absorption	Emission	Absorption	Emission
1a	Bn	phen	3°	moderate	382 (4448), 666 (2070)	none		
2a	CH(Me)Ph	phen	2°	moderate	377sh, 665 (1870)	none		
1b	Bn	dmp	13°	moderate	375sh, 662 (2460)	820	386 (6247), 646 (3017)	785
3b	$CH_2C_6H_2(OMe)_3$	dmp	9°	strong	376sh, 656 (1720)	801	385 (7721), 645 (3652)	825
4b	$CH_2C_6F_5$	dmp	3°	very strong	386 (9560), 605 (5270)	735	384 (13469), 600 (7458)	722
5b	*i*Bu	dmp	n.d.	none	373 (7163), 667 (1830)	822	370 (2836), 661 (1407)	814
1c	Bn	dpp	20°	moderate	376 (3786), 646 (1429)	805		
3c	$CH_2C_6H_2(OMe)_3$	dpp	25°	none	377sh, 661 (1670)	none		
1d	Bn	phen^{Mes}	12°	moderate	378sh, 661 (1340)	none		

Emission wavelengths are given for excitation at λ_{max} of the longest wavelength transition.

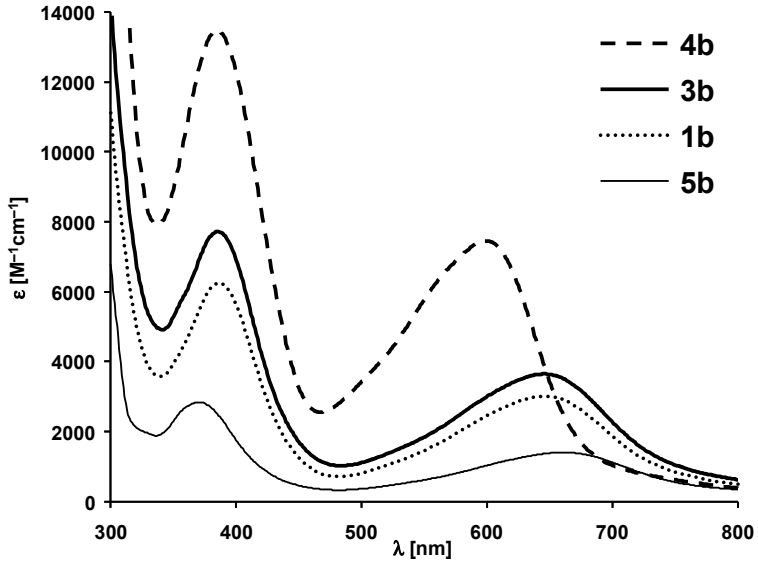


Figure 7.5: UV/vis absorption spectra of **1b** and **3b**-**5b** in diethyl ether at room temperature.

Room temperature luminescence in the solid state (λ_{exc} = 514.5 nm) was observed for all complexes, with emission wavelengths of 715 – 740 nm. Luminescence was weak and short-lived (τ < 60 ns). Overlapping emission peaks from decomposition of the air-sensitive compounds on the surface caused high errors in the determination of λ_{max}. For this reason, λ_{max} values for solid state emission were not reported.

Luminescence in solution was generally very weak (an exception seems to be **4b**) and again short-lived (τ < 60 ns). While other reasons cannot be excluded, a contributing factor to the low luminescence intensities is certainly the low energy of the emission, which makes non-radiative deactivation pathways more probable. Complexes **1a**, **2a**, **1c** and **1d** were not luminescent in solution. Qualitative luminescence intensity did not seem to correlate with the observed distortions in the solid state: undistorted complexes **1a** and **2a**, carrying an unsubstituted phenanthroline ligand, did not show any luminescence in solution. Analogous to $[Cu(phen^R)_2]^+$, lack of luminescence in **1a** and **2a** might be related to distortions in the excited state rather than to ground-state distortions [2-6, 38]: despite their symmetrical structures, both, **1a** and **2a**, show evidence for easy thermal motions following a rocking distortion mode in their crystal structures.

Luminescence spectra in toluene or diethyl ether solution showed the same general features for all luminescent complexes, which will be discussed in detail for **3b** in diethyl ether. Excitation of the longest-wavelength transition in **3b** yielded weak emission peaks, the position of which depended on the excitation wavelength: excitation at λ_{max} (646 nm) and above afforded an emission peak **E1** at 825 nm (Figure 7.6), while excitations below 630 nm led to an additional peak at 720 – 770 nm (**E2/3**). The maximum of the latter peak shifted to lower wavelengths in dependence of λ_{exc} (supp. inform.). Inspection of the excitation spectra revealed that the asymmetric absorption peak at λ_{max} = 646 nm consists of several transitions at appr. 660, 620 and 590 nm (Figure 7.7). Emission **E1** (825 nm) is associated with excitations at 660 nm and 590 nm. Excitation at 590 nm also affords an emission peak at ≈720 nm (**E3**), which overlaps with emission at ≈770 nm (**E2**) obtained upon excitation at 620 nm. The varying proportions of overlapping **E2** and **E3** are most likely responsible for the apparent shift in peak position when the excitation wavelength is varied between 590 – 640 nm. Excitation of the higher-energy transition at 385 nm did not lead to any observable luminescence (Figure 7.8), in agreement with its assignment as a diketiminate-based transition, not involving a phenanthroline acceptor orbital.

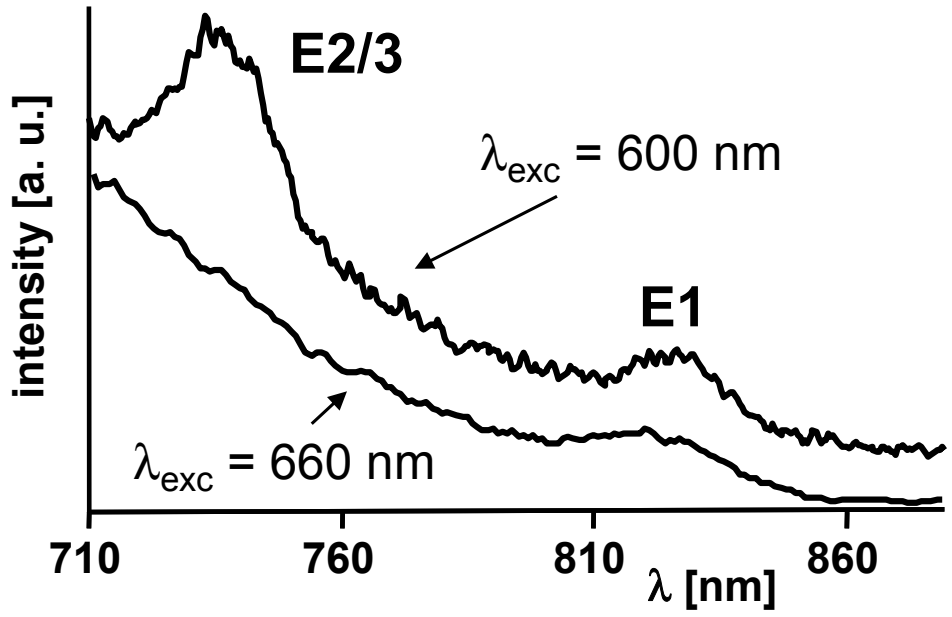


Figure 7.6: Emission spectra of **3b** with λ_{exc} = 600 nm (above) and 660 nm (below).

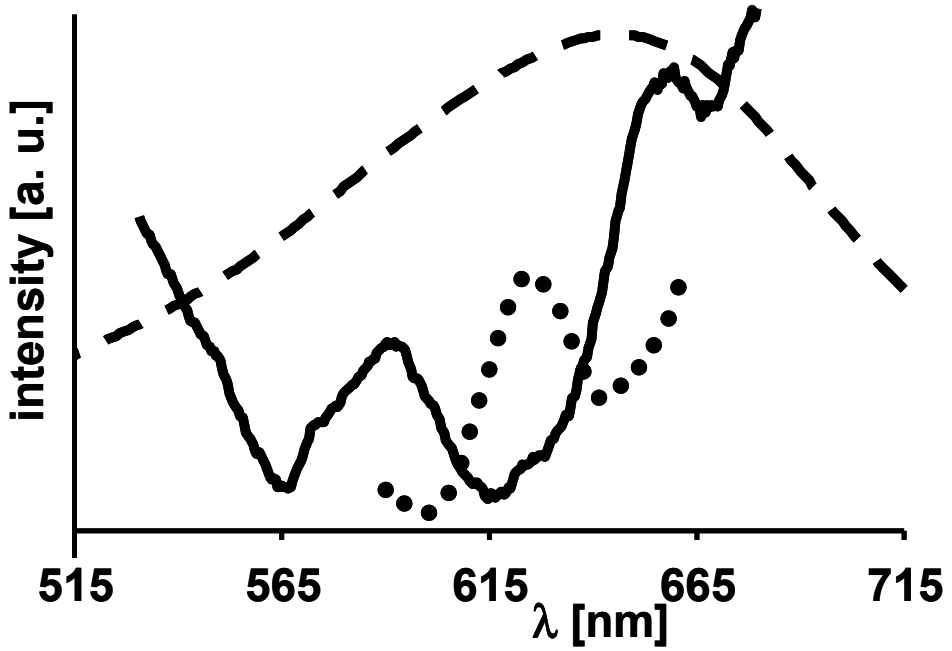


Figure 7.7: Absorption (dashed line) and excitation spectra (λ_{em} = 825 nm, solid line; λ_{em} = 770 nm, dotted line) of **3b** in diethyl ether.

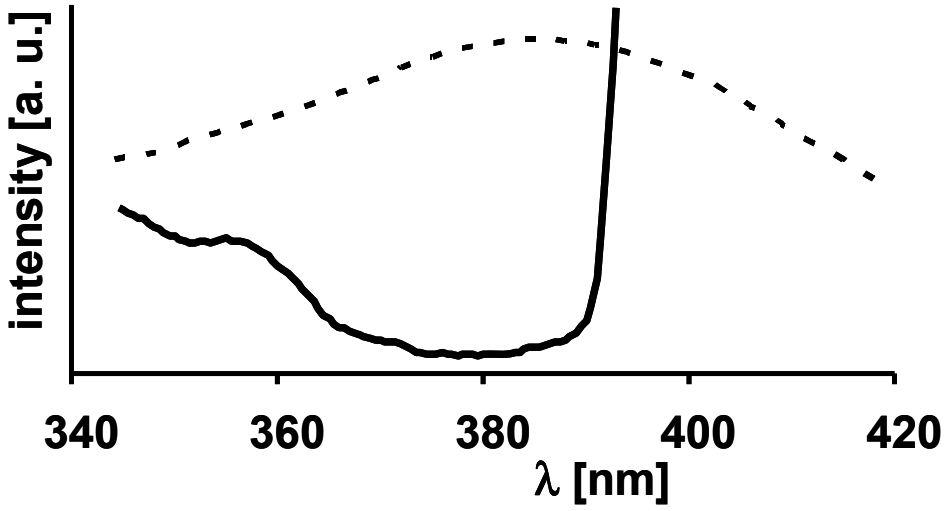


Figure 7.8: Absorption spectrum (dashed line) and excitation spectrum (λ_{em} = 825 nm, solid line) of **3b** in Et_2O. The increase of intensity in the excitation spectrum around 390 nm is due to stray light from the 2λ fraction in the excitation beam.

Based on the results above, the lower-energy transition in the obtained absorption spectra is most likely an MLCT transition to the phenanthroline ligand or a mixture of LLCT and MLCT transitions. Stokes shifts of 129 – 159 nm in toluene and 122 – 166 nm in diethyl ether solution are intermediate between those of $[CuL_2]^+$ (250 – 260 nm in CH_2Cl_2, L = dmp, dpp [29-35]) and those observed in neutral amidophosphine copper complexes (65 – 110 nm in C_6H_6), for which LLCT transitions have been proposed [16]. Substitution of a phenanthroline in cationic diphenanthroline copper complexes $[CuL_2]^+$ (L = phen, dmp, dpp [20]), which show maxima of the longest wavelength absorption at λ_{max} = 440 – 460 nm (in CH_2Cl_2) [29-35], with a diketiminate ligand thus led to a significant bathochromic shift of appr. 200 nm. Although reduction of complex symmetry from D_{2d} to D_2 is considered to be responsible for the formation of shoulders around 540 – 580 nm for bisphenanthroline copper complexes [39-41], reduction to C_{2v} symmetry does not seem to be the cause for the displacement of the MLCT here. Related C_{2v}-symmetric complexes (acac)Cu(dmp) (acac = acetylacetonate or derivatives), for example, display longest wavelength absorption maxima around 460 nm [42], very comparable to those of cationic bisphenanthroline complexes. Copper dmp complexes with neutral or anionic diphosphinesulfide ligands also display absorption maxima between 420 – 460 nm, which were again accompanied by shoulders at longer wavelengths (500 – 550 nm) [14]. The bathochromic shift of the longest wavelength transition is thus most likely due to the electron-donating nature of the *N*-alkyl substituted diketiminate ligand. The high electron-donor characteristics of β-diketiminate ligands have been described previously [19, 43-50]. In particular for copper complexes, π back-bonding to ancillary ligands is significantly increased in the presence of *N*-alkyl substituted diketiminate ligands [10, 51, 52]. A hypsochromic shift in λ_{max} of 60 nm when the isobutyl substituent in **5b** is replaced with pentafluorobenzyl (**4b**) further supports a strong influence of the diketiminate ligand on the position of the absorption maximum.

Complexes **1a-1d** and **2a** do not display any correlation of flattening or rocking distortions with λ_{max} in their absorption spectra. The difference in π-stacking interactions observed in the crystal structures of **1b/c**, **3b/c**, and **4b** and its correlation with $\Delta\theta_z$ make it interesting to compare the presence of these interactions with photophysical properties. Some qualitative indications argue that π stacking of the *N*-benzyl substituent and the

phenanthroline ligand might indeed increase luminescence intensity. Thus, no luminescence in solution is observed for the dpp complex **3c**, where π stacking was lost in the crystal structure, while complexes **1c** or **3b**, which show moderate π stacking interactions, are both luminescent in solution. Complex **4b**, which displays the targeted sandwich-like arrangement of all aryl rings, shows the highest luminescence intensity. However, even for **4b** luminescence is weak and short-lived, and the increased intensity might simply be a result of its high absorption coefficient.

While π stacking was only shown in the solid state, observed changes in λ_{max} values of absorption spectra of **1b** and **3b**, when the solvent was changed from toluene to ether, are in agreement with an increase of intramolecular π stacking in the non-aromatic solvent: the MLCT/LLCT is displaced slightly hypsochromically, the diketiminate-based transition around 380 nm slightly bathochromic, and π-π* transitions of the benzyl substituent, which were present above 350 nm in toluene, are now found below 350 nm. On the other hand, complexes **4b** and **5b** with very strong or no possible π stacking interactions, respectively, show only minor changes in their absorption maxima between toluene and ether solution. In comparison to **5b**, ^{13}C NMR spectra of **1b-4b** show a high-field shift of C10A/C10B (C30 and C31 in the crystal structure of **4b**, Figure 7.3), which qualitatively correlates with the observed π stacking and might be attributed to the ring current effect of the π-stacked benzyl substituent. The effect is however minor ($\Delta\delta < 2$ ppm) and could not be reliably reproduced in ether/acetone-d_6 mixtures.

Conclusions

Heteroleptic diketiminate copper phenanthroline complexes can be prepared readily through protonation of CuO*t*Bu by diketimines in the presence of the desired phenanthroline ligand. The complexes are stable and show no evidence of undergoing ligand redistribution reactions. Intramolecular π stacking interactions between the *N*-benzyl substituents and the phenanthroline ligand suppress complex flattening in the ground state and reduced Stokes shifts in solution (compared to copper bisphenanthroline complexes) are indicative of reduced distortions in the excited states. Comparatively sharp luminescence peaks with FWHM values well below 100 nm (Figure 7.6) also support the notion that the investigated complexes do not undergo extensive exited state distortions.

For comparison, typical FWHM values for $[Cu(dmp_2]^+$ complexes in solution range from 120 – 240 nm [27, 30, 32].

Luminescence intensities, however, were low and lifetimes were shorter than 60 ns for all complexes, which might be partly due to the low energies of the emission (up to 830 nm). We are currently investigating if luminescence properties can be improved by shifting the emission to shorter wavelengths or by further increasing π stacking interactions between *N*-substituents and phenanthroline.

Experimental section

All operations, except ligand synthesis, were carried out under nitrogen atmosphere using Schlenk or glove box techniques. Solvents were dried by passage through activated aluminum oxide (MBraun SPS) and de-oxygenated by repeated extraction with nitrogen. C_6D_6 was distilled from Na and de-oxygenated by three freeze-pump-thaw cycles. CuO*t*Bu [53], dpp [54], monomesityl phenanthroline [55], **1** [10, 28], **2** [9, 28], and *nacnac*$^{i\text{Bu}}$H [28] were synthesized according literature procedures. Dmp was purchased as the hemihydrate and dried by allowing a solution in dry toluene to stand overnight over activated molecular sieves (4 Å), followed by decantation and evaporation of the solvent. All other chemicals were obtained from commercial suppliers and used as received. Elemental analyses were performed by the Laboratoire d'Analyse Elémentaire (Université de Montréal). NMR spectra were recorded on a Bruker ARX 400 MHz spectrometer and referenced to residual solvent (C_6D_5H: δ 7.15, C_6D_6: δ 128.02, $CHCl_3$: δ 7.26, $CDCl_3$: δ 77.0). NMR coupling constants are provided in Hz. UV/vis spectra were recorded on a Cary 500i UV/vis/NIR spectrometer in dry and oxygen-free ether or toluene using a sealable UV cell. Emission and excitation spectra in solution were obtained on a Cary Eclipse Fluorescence spectrometer. The luminescence spectra of the solid state samples were measured using a Renishaw 3000 imaging microscope system equipped with a CCD detector. The excitation source was a 514.5 nm line of Argon ion laser. All measurements were undertaken at ambient temperature.

***Nacnac*$^{\text{Bn}}$Cu(phen), 1a**. A flask was charged with **1** (100 mg, 0.36 mmol), CuO*t*Bu (44 mg, 0.33 mmol) and 1,10-phenanthroline (58 mg, 0.33 mmol). Toluene (15 mL) was added

and the mixture was stirred for 1 h to give a dark-green suspension. The suspension was filtered and the resulting dark green solution was evaporated to dryness. The residue was washed twice with hexane (6 mL). Residual solvent was removed under vacuum to obtain dark-blue powder (104 mg, 60%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 8.84 (d, *J* = 4 Hz, 2H, phen), 7.36 (d, *J* = 8, 2H, phen), 7.05 (s, 2H, phen), 6.91 (d, *J* = 6, 4H, Bn), 6.85 (dd, *J* = 4, 8, 2H, phen), 6.73-6.76 (m, 6H, Bn), 4.83 (s, 1H, CH(C=N)$_2$), 4.53 (s, 4H, Bn CH_2), 2.16 (s, 6H, C(=N)Me). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 162.5 (C=N), 146.7, 144.1, 142.9, 131.4, 128.6, 128.3, 127.0, 125.8, 125.0, 124.0, 94.3 (*C*H(C=N)$_2$), 57.5 (Bn CH_2), 22.4 (C(=N)*Me*). Anal. Calcd for $C_{31}H_{29}N_4Cu$: C, 71.45; H, 5.61; N, 10.75. Found: C, 70.80; H, 5.74; N, 10.43. X-Ray quality crystals were obtained by slow evaporation of a diethyl ether solution (20 mg, 1 mL).

***Nacnac*^{Bn}Cu(dmp), 1b**. Preparation analogous to **1a** from **1** (100 mg, 360 μmol), CuO*t*Bu (49 mg, 0.36 mmol), 2,9-dimethyl-1,10-phenanthroline (84 mg, 0.36 mmol) and ether (10 mL) gave a crude product, which was recrystallised from diethyl ether (5 mL) at -30 °C. Dark-blue plates formed after 1 day (72 mg, 35%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.48 (d, *J* = 8 Hz, 2H, dmp 4/7), 7.18 (s, 2H, dmp 5/6), 6.94 (d, *J* = 8 Hz, 2H, dmp 3/8), 6.65 (d, *J* = 6 Hz, 4H, Bn), 6.36-6.37 (m, 6H, Bn), 4.78 (s, 1H, CH(C=N)$_2$), 4.38 (s, 4H, Bn CH_2), 2.79 (s, 6H, dmp Me), 2.16 (s, 6H, C(=N)Me). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.7 (C=N), 155.5 (dmp 2/9), 143.5 (*ipso* Bn), 142.6 (dmp 10A/10B), 132.1 (dmp 4/7), 128.2 (*meta* Bn), 126.8 (dmp 4A/6A), 126.7 (*ortho* Bn), 124.9 (*para* Bn), 124.7 (dmp 5/6), 124.2 (dmp 3/8), 94.0 (*C*H(C=N)$_2$), 57.8 (Bn CH_2), 25.7 (dmp Me), 22.4 (C(=N)*Me*). Anal. Calcd for $C_{33}H_{33}N_4Cu$: C, 71.45; H, 5.61; N, 10.75. Found: C, 70.80; H, 5.74; N, 10.43.

***Nacnac*^{Bn}Cu(dpp), 1c.** Preparation analogous to **1a** from **1** (100 mg, 0.36 mmol), CuO*t*Bu (49 mg, 0.36 mmol), 2,9-diphenyl-1,10-phenanthroline (128 mg, 0.36 mmol) and ether (10 mL) afforded a dark-blue solid (143 mg, 59%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 8.68 (d, *J* = 8, 2H, phen Ph), 7.22-7.65 (m, 16H), 6.45 (d, *J* = 4, 2H), 6.20-6.22 (m, 6H), 4.66 (s, 1H, CH(C=N)$_2$), 3.84 (s, 4H, Bn C*H*$_2$), 1.91 (s, 6H, C(=N)Me). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.5 (C=N), 142.9, 140.3, 133.0, 129.9, 129.1, 129.0, 128.6, 128.5, 128.4, 127.8, 127.5, 126.4, 124.6, 124.1, 94.0 (*C*H(C=N)$_2$), 56.8 (Bn *C*H$_2$), 22.9 (C(=N)*Me*). Anal. Calcd for $C_{43}H_{37}N_4Cu$: C, 76.70; H, 5.54; N, 8.32. Found: C, 77.17; H, 5.44; N, 8.24.

Crystals suitable for a X-ray diffraction study were obtained by slow evaporation of a diethyl ether solution (20 mg, 1 mL).

***Nacnac*^{Bn}Cu(monomesityl phenanthroline), 1d.** Diketimine **1** (44 mg, 0.16 mmol) and CuO*t*Bu (24 mg, 0.18 mmol) were dissolved in toluene (2 mL) to afford a yellow solution. A solution of 2-mesityl-1,10-phenanthroline (47 mg, 0.16 mmol) in toluene (2 mL) was added drop-wise to give a dark-blue suspension. After stirring for 1 h, the suspension was filtered and the resulting dark green solution was evaporated to dryness. The crude product was dissolved in Et_2O (3 mL) and kept at –30 ºC. Dark-green crystals (20 mg, 20%) formed after 2 months. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 8.20 (d, *J* = 4, 1H), 7.64 (d, *J* = 8, 1H), 7.32 (d, *J* = 8, 1H), 7.28 (d, *J* = 8, 1H), 6.89-7.19 (m, 12H), 6.59 (dd, *J* = 4, 8, 1H), 4.55 (d, *J* = 15, 2H, Bn C*H*$_2$), 4.27 (s, 1H, HC(C=N)$_2$), 3.93 (d, 2H, *J* = 15, Bn C*H*$_2$), 2.36 (s, 3H, Mes *p*-CH_3), 2.17 (s, 6H, Mes *o*-CH_3), 1.86 (s, 6H, Me(C=N)$_2$). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.8 (C=N), 158.8, 146.1, 145.0, 144.2, 142.3, 138.4, 137.3, 135.8, 129.9, 129.4, 128.6, 127.4 126.9, 126.8, 125.9, 125.8, 125.6, 125.4, 124.6, 105.4, 94.3 (H*C*(C=N)$_2$), 57.1 (Bn *C*H$_2$), 22.0 (Mes *o*-*C*H$_3$), 21.3 (Mes *p*-*C*H$_3$), 20.6 (*Me*(C=N)$_2$). Anal. Calcd for $C_{40}H_{39}N_4Cu$: C, 75.15; H, 6.15; N, 8.76. Found: C, 74.82; H, 6.12; N, 8.67.

***SS-nacnac*$^{CH(Me)Ph}$Cu(phen), 2a.** A flask was charged with *SS*-**2** (100 mg, 330 μmol), CuO*t*Bu (45 mg, 0.33 mmol) and 1,10-phenanthroline (60 mg, 0.33 mmol). Toluene (15 mL) was added and the mixture was stirred to give a dark-blue solution. After stirring for 1 h, the solution was concentrated to 1/5th of its volume and layered with hexane (3 mL). Dark-green crystals (80 mg, 44%) formed after 3 days. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 8.70 (d, *J* = 4, 2H, phen), 7.36 (d, *J* = 8, 2H, phen), 7.03 (s, 1H, phen), 6.91 (d, *J* = 6, 4H, Ph), 6.85 (dd, *J* = 4, 8, 2H, phen), 6.55-6.57 (m, 6H, Ph), 4.98 (q, *J* = 6, 2H, C*H*(Me)Ph), 4.73 (s, 1H, CH(C=N)$_2$), 2.17 (s, 6H, C(=N)Me), 1.03 (d, *J* = 6, 6H, CH(*Me*)Ph). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.5 (C=N), 149.0, 147.5, 142.6, 132.0, 129.1, 127.3, 127.1, 126.1, 125.1, 124.2, 94.6 (*C*H(C=N)$_2$), 59.0 (*C*HMePh), 24.0 (C(=N)*Me*), 23.2 (CH*Me*Ph). Anal. Calcd for $C_{33}H_{33}N_4Cu$: C, 72.17; H, 6.06; N, 10.20. Found: C, 71.75; H, 6.19; N, 10.24.

***N,N'*-Bis(3,4,5-trimethoxyphenylmethyl)-2-amino-4-imino-pent-2-ene, 3**. Acetylacetone (0.4 mL, 4 mmol), *p*-toluenesulfonic acid monohydrate (0.7 g, 4 mmol) and 3,4,5-trimethoxybenzylamine (1.5 g, 7.6 mmol) were suspended in toluene (175 mL) and refluxed under azeotropic removal of water (Dean-Stark apparatus). A white suspension formed immediately, which turned yellow after 6 h and finally became orange after 5 days. The reaction mixture was cooled to room temperature and then transferred to a solution of KOH (0.4 g in 150 mL H_2O). The organic layer was separated and the aqueous phase was extracted with 2 x 100 mL of toluene. The combined organic phases were dried over Na_2SO_4, filtered and evaporated to give a yellow solid. Washing of the yellow solid with MeOH (15 mL) afforded 900 mg (65%) of a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 6.50 (s, 4H, $C_6H_2(OMe)_3$), 4.68 (s, 1H, $HC(C=N)_2$), 4.43 (s, 4H, CH_2Ar), 3.80 (s, 6H, *p*-$C_6H_2(OMe)_3$), 3.68 (s, 6H, *m*-$C_6H_2(OMe)_3$), 1.96 (s, 6H, $Me(C=N)_2$). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.3 (C=N), 153.1, 138.8, 136.3, 103.6 (*o*-$C_6H_2(OMe)_3$), 95.7 ($HC(C=N)_2$), 60.7 (*p*-$C_6H_2(OMe)_3$), 55.7 (*m*-$C_6H_2(OMe)_3$), 50.8 (CH_2Ar), 19.6 ($Me(C=N)_2$). Anal. Calcd. for $C_{25}H_{34}N_2O_6$: C, 65.48; H, 7.47; N, 6.11. Found C, 65.20; H, 7.48; N, 6.14. X-Ray quality crystals were obtained by slow evaporation of a CH_2Cl_2 solution.

***N,N'*-Bis($C_6H_2(OMe)_3$)-*nacnac*Cu(dmp), 3b**. Diketimine **3** (70 mg, 0.15 mmol) and 2,9-dimethyl-1,10-phenanthroline (45 mg, 0.15 mmol) were dissolved in toluene (5 mL) to give a colourless solution. A solution of CuO*t*Bu (26 mg, 0.15 mmol) in toluene 2 (mL) was added, affording a dark-green solution, which was stirred for 1 h, filtered and evaporated to dryness (109 mg, 98%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.54 (d, *J* = 8, 2H, dmp), 7.20 (s, 2H, dmp 5/6), 7.01 **(**d, *J* = 8, 2H, dmp), 5.88 (s, 4H, $C_6H_2(OMe)_3$), 4.78 (s, 1H, $CH(C=N)_2$), 4.36 (s, 4H, NCH_2), 3.54 (s, 6H, *para* OMe), 2.96 (s, 12H, *meta* OMe), 2.85 (s, 6H, dmp Me), 2.23 (s, 6H, C(=N)Me). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.3 (C=N), 155.3 (dmp 2/9), 152.7 (*meta* Ar), 142.4 (dmp 10A/10B), 139.1 (Ar), 136.6 (Ar), 132.4 (dmp 4/7), 126.8 (dmp 4A/6A), 125.0 (dmp), 124.3 (dmp), 105.6 (*ortho* Ar), 93.9 ($CH(C=N)_2$), 60.1 (*para* OMe), 58.2 (NCH_2), 55.0 (*meta* OMe), 25.8 (dmp Me), 22.5 (C(=N)*Me*). Anal. Calcd for $C_{39}H_{45}N_4O_6Cu$: C, 64.22; H, 6.22; N, 7.68. Found: C, 64.22; H, 6.17; N, 7.56. X-ray quality crystals were obtained by layering a toluene solution (20 mg, 1 mL) with an equal amount of hexane and keeping the mixture at –30 °C for 3 days.

***N,N'*-Bis($C_6H_2(OMe)_3$)-*nacnac*Cu(dpp), 3c.** Preparation analogous to **3b** afforded 118 mg (90%) of **3c**, which contained approximately 15% of dpp. Recrystallisation from toluene/hexane at –30 °C yielded crystalline material, still contaminated however with dpp and elemental analyses were not satisfactory. Handpicking of a suitable crystal allowed an X-ray diffraction study. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 8.86 (d, J = 8, 2H, dpp), 7.29-7.75 (m, 12H, dpp), 7.28 (s, 2H, dpp), 5.71 (s, 4H, $C_6H_2(OMe)_3$), 4.69 (s, 1H, $CH(C{=}N)_2$), 3.77 (s, 4H, NCH_2), 3.34 (s, 6H, *para* OMe), 2.89 (s, 12H, *meta* OMe), 2.85 (s, 6H, dmp Me), 1.98 (s, 6H, C(=N)Me). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.4 (C=N), 154.2 (*meta* Ar), 152.3, 143.4, 139.9, 138.4, 136.4, 133.5, 129.9, 128.6, 128.2, 127.9, 127.5, 126.0, 123.7, 119.8, 111.3 (o-$C_6H_2(OMe)_3$), 93.9 ($CH(C{=}N)_2$), 60.0 (*para* OMe), 57.2 (NCH_2), 54.9 (*meta* OMe), 23.0 (C(=N)*Me*).

***N,N'*-Bis(pentafluorophenylmethyl)-2-amino-4-imino-pent-2-ene, 4**. To a flask containing pentafluorobenzylamine (310 mg, 1.6 mmol) in toluene (5 mL) were added acetylacetone (80 µL, 0.8 mmol) and HCl (196 µL, 12 M, 2.4 mmol) to give white precipitate. The mixture was refluxed under azeotropic removal of water for 5 days during which the reaction mixture turned yellow. By cooling to room temperature, yellow precipitate formed. The solvent was decanted and KOH solution (1.5 g in 5 mL of water) was added to the solid, followed by toluene (5 mL). After stirring for 15 min, the mixture was separated and the aqueous phase was extracted with toluene (5 mL). The combined organic phases were dried over Na_2SO_4, filtered and evaporated to afford 40 mg (6%) of a beige solid in 85-90% purity. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 11.08 (bs, 1H, NH), 4.58 (s, 1H, $HC(C{=}N)_2$), 4.44 (s, 4H, $CH_2C_6F_5$), 1.98 (s, 6H, $Me(C{=}N)_2$). ^{13}CNMR ($CDCl_3$, 101 MHz): δ 161.2 (C=N), 145.1 (dm, $^1J_{CF}$ = 250, ortho), 140.5 (dm, $^1J_{CF}$ = 250), 137.5 (dm, $^1J_{CF}$ = 250), 113.7 (t, $^2J_{CF}$ = 2, *ipso*), 95.9 ($HC(C{=}N)_2$), 37.9 ($CH_2C_6F_5$), 19.3 ($Me(C{=}N)_2$). Three aromatic peaks are missing. ^{19}F NMR ($CDCl_3$, 377 MHz, 298 K) δ –144.9 (dd, J = 9, 22), –156.5 (t, J = 22), –162.9 (td, J = 9, 22). Anal. Calcd for $C_{19}H_{12}N_2F_{10}$: C, 49.79; H, 2.64; N, 6.11. Found: C, 50.58; H, 2.76; N, 6.13. MS ESI-HRMS (hexane) (m/z): $[M+H]^+$ for $C_{19}H_{12}N_2F_{10}$ calcd. 459.0919; found 459.0915.

***N,N'*-Bis(pentafluorophenylmethyl)-*nacnac*Cu(dmp), 4b.** Preparation analogous to **3b** and recrystallisation in Et_2O at -30 °C afforded black crystals after 1 day (18 mg, 56%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.56 (d, *J* = 8, 2H, dmp), 7.22 (s, 2H, dmp 5/6), 7.04 (d, *J* = 8, 2H, dmp), 4.73 (s, 1H, $CH(C{=}N)_2$), 4.20 (s, 4H, NCH_2), 2.92 (s, 6H, dmp Me), 2.06 (s, 6H, C(=N)Me). ^{19}F NMR (C_6D_6, 377 MHz, 298 K) δ –144.6 (dd, *J* = 9, 22), –160.5 (t, *J* = 22), –165.7 (td, *J* = 9, 22). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 162.7 (C=N), 156.5 (dmp 2/9), 145.0 (dm, $^1J_{CF}$ = 240, *ortho* C_6F_5), 141.2 (dmp 10A/10B), 140.4 (dm, $^1J_{CF}$ = 180, *para* C_6F_5), 135.9 (dm, $^1J_{CF}$ = 240, *meta* C_6F_5), 133.6 (dmp 4/7), 126.3 (dmp 4A/6A), 125.2 (dmp), 124.4 (dmp), 116.0 (t, $^2J_{CF}$ = 2, *ipso* C_6F_5), 94.5 (*C*H(C=N)$_2$), 43.7 (CH_2), 25.4 (dmp Me), 22.8 (C(=N)*Me*). Anal. Calcd for $C_{33}H_{23}N_4F_{10}Cu$: C, 54.36; H, 3.18; N, 7.68. Found: C, 54.73; H, 3.53; N, 7.65.

***Nacnac*$^{i\text{Bu}}$Cu(dmp), 5b.** *Nacnac*$^{i\text{Bu}}$H (60 mg, 0.29 mmol), CuO*t*Bu (39 mg, 0.29 mmol) and 2,9-dimethyl-1,10-phenanthroline (66 mg, 0.29 mmol) were dissolved in Et_2O (4 mL) to give a dark-green solution. After stirring for 10 min, the solvent was evaporated and the residue was washed with hexane (2 x 2 mL) and dried under vacuum to yield 109 mg (84%) of a dark-blue solid. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.55 (d, *J* = 8, 2H, dmp), 7.17 (s, 2H, dmp 5/6), 7.07 (d, *J* = 8, 2H, dmp), 4.67 (s, 1H, $CH(C{=}N)_2$), 3.12 (m, 4H, NCH_2) 3.08 (s, 6H, dmp Me), 2.16 (s, 6H, C(=N)Me), 1.24 (sp, *J* = 7, 2H, C*H*Me_2), 0.58 (d, *J* = 7, 12H, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 161.1 (C=N), 155.8 (dmp 2/9), 142.6 (dmp 10A/10B), 132.4 (dmp 4/7), 127.8 (dmp 4A/6A), 125.2 (dmp), 124.7(dmp), 93.8 (*C*H(C=N)$_2$), 61.7 (NCH_2), 30.8 (*C*HMe_2), 25.8 (dmp Me), 22.9 (C(=N)*Me*), 20.6 (CH*Me*$_2$). Anal. Calcd for $C_{27}H_{37}N_4Cu$: C, 67.40; H, 7.75; N, 11.64. Found: C, 67.70; H, 7.96; N, 11.32.

X-ray diffraction studies

All data sets were recorded on a Bruker SMART 6000 with Montel 200 monochromator, except that of compound **1b** which was collected on a Bruker Microstar-Proteum with Helios optics, both equipped with a rotating anode source for Cu Kα radiation (λ = 1.54178 nm). Cell refinement and data reduction were performed using APEX2 [56]. Absorption corrections were applied using SADABS [57]. Structures were solved by direct methods

using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97 [58]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on calculated positions using a riding model.

Table VII-4:

	3	**1a**	**2a**	**1c**	**1b**	**1d**	**3c**	**3b**
Formula	$C_{25}H_{34}N_2O_6$	$C_{31}H_{29}N_4Cu$	$C_{33}H_{33}N_4Cu$	$C_{43}H_{37}N_4Cu$	$C_{33}H_{33}N_4Cu$	$C_{40}H_{39}N_4Cu$	$C_{49}H_{49}N_4O_6Cu$	$C_{39}H_{45}N_4O_6Cu$
Mw (g/mol); $d_{calcd.}$ (g/cm^3)	458.54; 1.291	521.12; 1.342	549.17; 1.317	673.31; 1.312	549.17; 1.328	639.29; 1.292	853.47; 1.377	729.33; 1.361
T (K); F(000)	175; 984	200; 1088	150; 1152	150; 1408	150; 1152	200; 672	150; 1792	150; 1528
Crystal System	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space Group	Pbcn	$P2_1/n$	$P2_12_12_1$	$Pca2_1$	$P2_1/c$	P-1	C2/c	$P2_1/c$
Unit Cell: *a* (Å)	14.865(2)	12.9479(5)	11.9865(3)	19.4278(5)	14.3783(7)	10.6782(2)	24.122(2)	15.9441(3)
b (Å)	21.753(2)	13.3925(6)	13.2064(4)	9.2147(2)	8.7026(4)	12.4794(2)	14.137(1)	13.4855(3)
c (Å)	7.2959(9)	15.6737(6)	17.4969(5)	19.0384(5)	22.2668(10)	12.8421(2)	14.689(1)	16.8628(3)
α(°)	90	90	90	90	90	104.773(1)	90	90
β(°)	90	108.18(2)	90	90	98.534(2)	92.322(1)	124.751(4)	101.081(1)
γ(°)	90	90	90	90	90	94.659(1)	90	90
V (Å^3); Z	2359.2(5)	2578.95(18); 4	2769.73(13); 4	3408(15); 4	2755.4(2); 4	1643.63(5); 2	4115.7; 4	3558.1(1); 4
θ range (°); completeness	3.60-73.39; 0.984	3.88-72.42; 0.994	4.19-72.51 0.990	4.55-63.67; 0.980	3.11-67.83; 0.991	3.57-68.26; 0.976	3.84-67.85; 0.992	2.82-68.30; 0.998
Refl.: collec./indep.; R_{int}	30741/2347; 0.071	33584/5068; 0.045	36033/4712; 0.044	45919/5514; 0.057	54048/4961; 0.064	20597/5875; 0.032	43433/3707; 0.068	45237/6505; 0.048
μ (mm^{-1})	0.753	1.391	1.321	1.180		1.190	1.207	1.295
R1(F); wR(F^2); GoF(F^2) [a]	0.053; 0.157; 1.06	0.056; 0.155; 1.02	0.038; 0.098; 1.04	0.030; 0.056; 0.89	0.034; 0.96; 1.12	0.039; 0.118; 1.11	0.034; 0.099; 1.07	0.034; 0.103; 1.07
Residual electron density	0.23	0.78	0.29	0.20	0.32	0.23	0.26	0.31

[a] R1(F) based on observed reflections with I>2s(I), wR(F^2) and GoF(F^2) based on all data.

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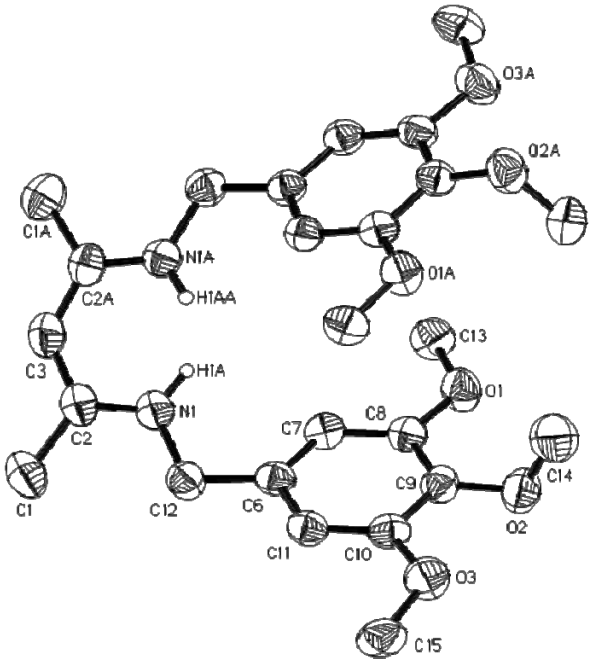
Supplementary material

Intramolecular π-Stacking in Copper(I) Diketiminate Phenanthroline complexes



3

Figure 7.S1: Crystal structures of **3**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

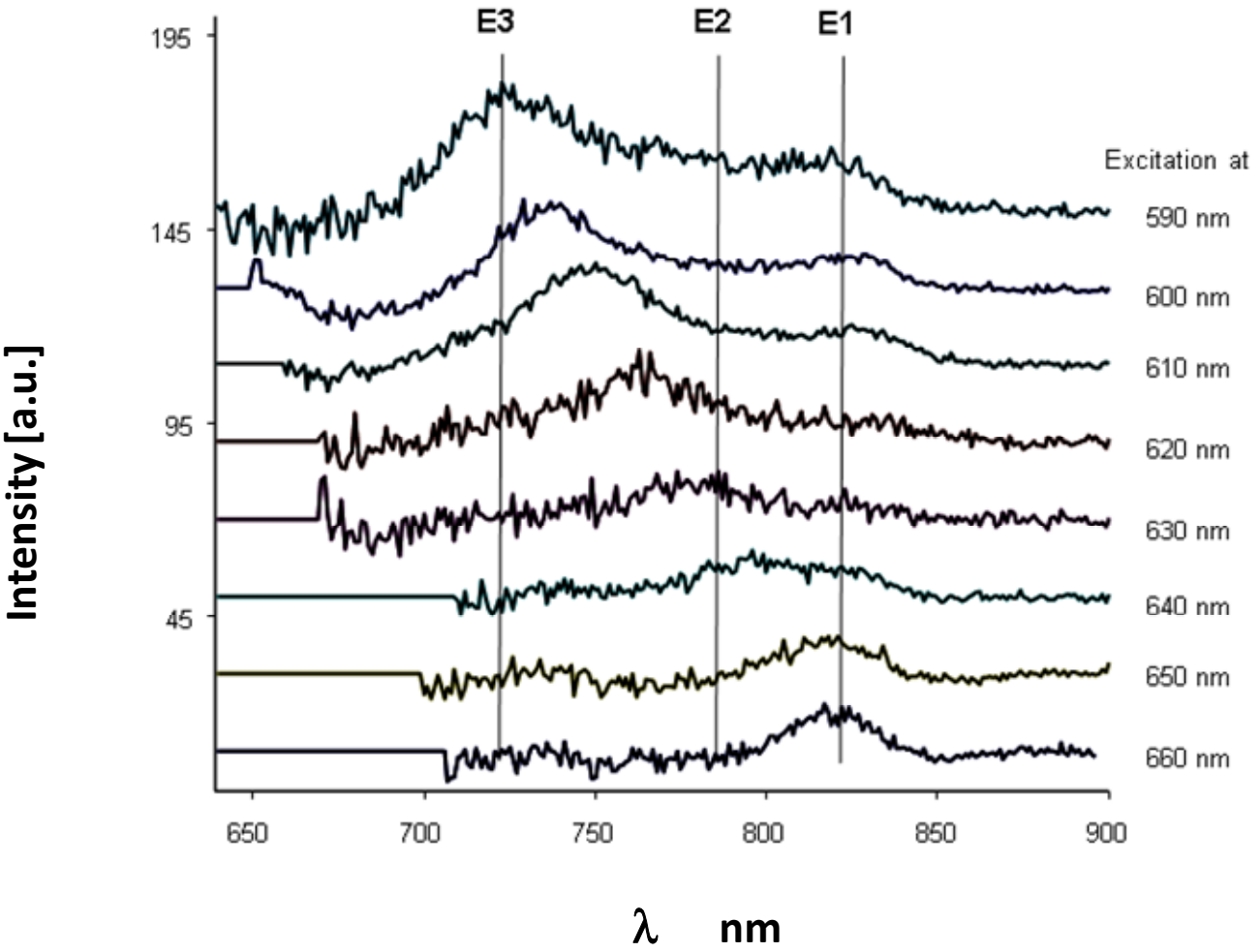


Figure 7.S2: Emission spectra upon excitation at different wavelengths in the longest wavelength transition of **3b**. A Gaussian function was used to subtract the baseline, originating from stray light from the excitation beam. Intensity of **E1** diminishes between 610 and 640 nm. Emissions **E2** and **E3** are obtained as superimposed peaks in varying ratios, resulting in an apparent displacement of the obtained maximum.

Solid state emission spectra

Obtained emission spectra displayed asymmetric peak profiles, which could not be fitted with a single Gaussian function, or even a second maximum at lower wavelength ($\Delta\nu$ = 50-110 nm). The relative intensities of both peaks and the peak profiles varied in repeated experiments (different target spots chosen on the solid) or with different excitation energies using the same target spot. Lower excitation energies generally favoured the longer-wavelength emission and we ascribed this emission tentatively to a decomposition of the air-sensitive compounds on the surface. Its location of the surface and different absorption coefficient of both species could be responsible for the variations

in the intensities of both peaks. The overlap of two emission (in combination with the fact that multiple luminescent states were observed in solution), would require rather intensive investigations before reliable λ_{max} values could be extracted from the data, thus, we refrain from reporting λ_{max} values for solid state emissions and limit us to the statement that all complexes are emissive in the solid state.

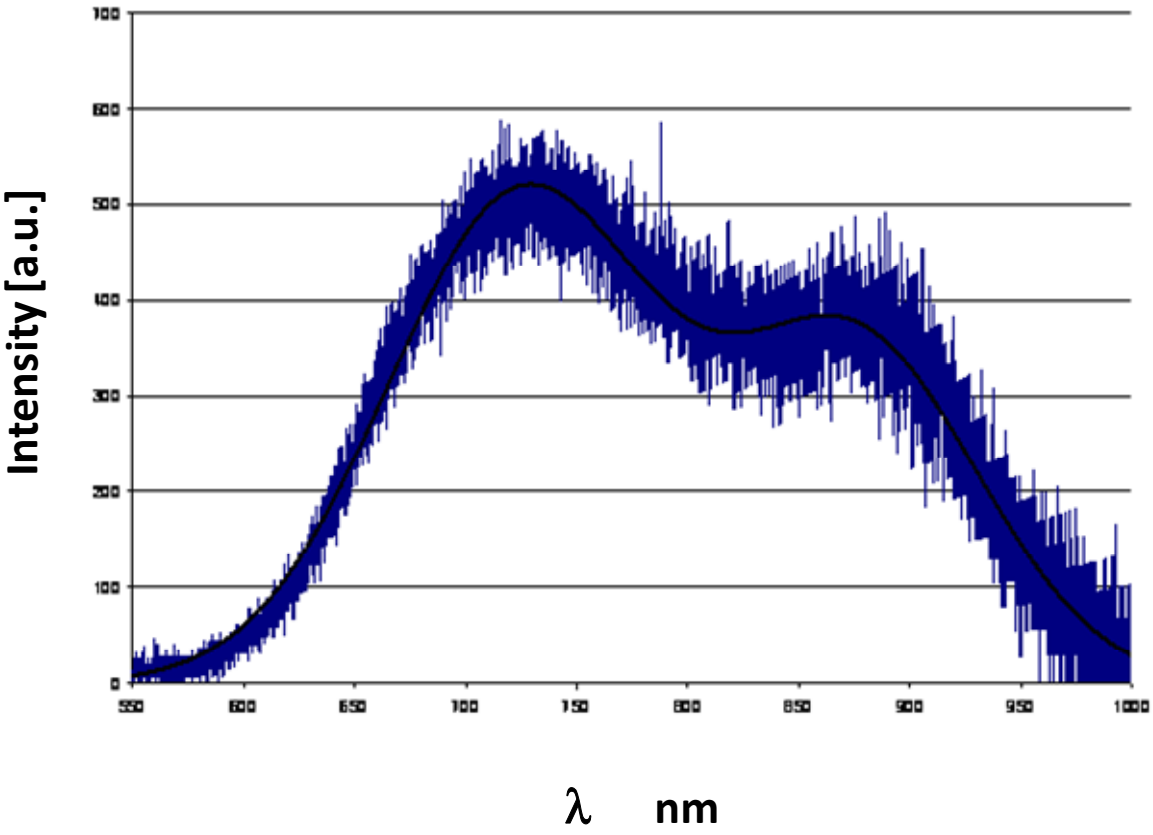


Figure 7.S3: Solid state emission spectrum of **4b** with 5% beam intensity.

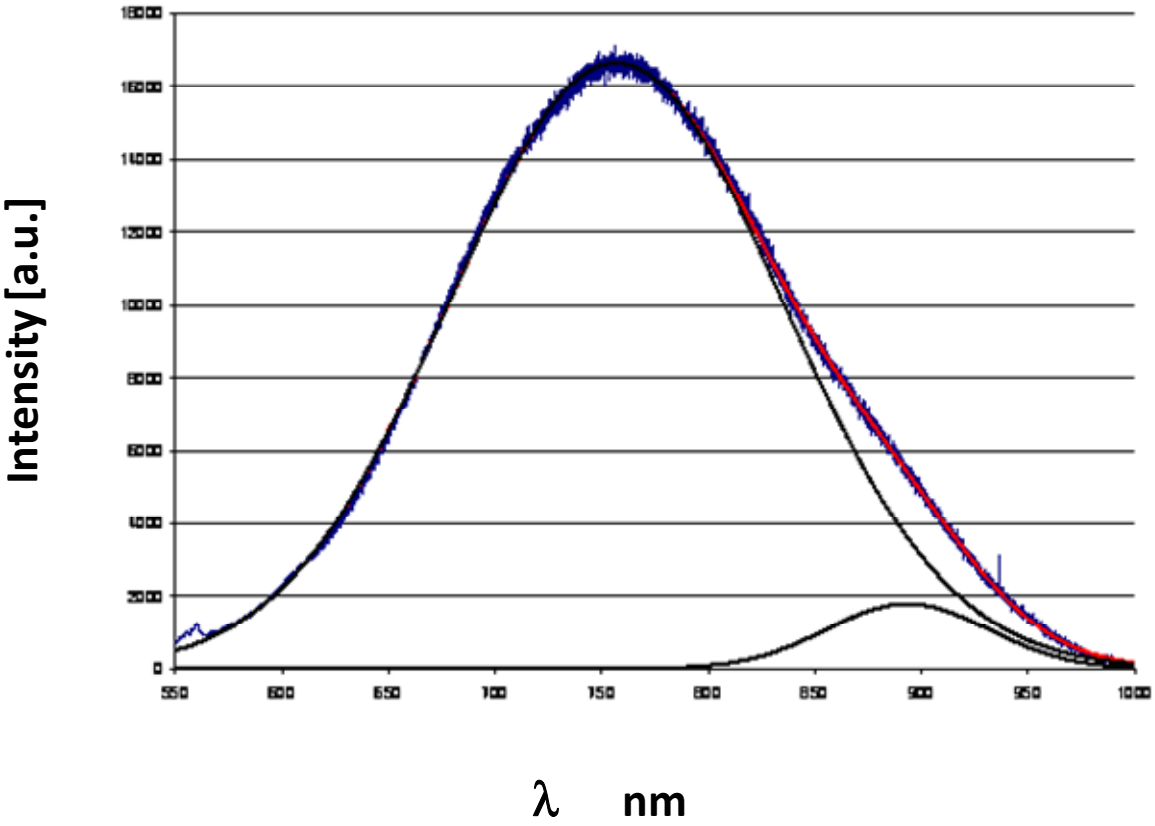
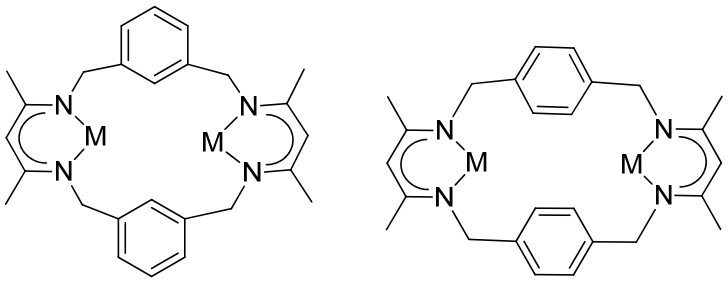


Figure 7.S4: Solid state emission spectrum of **4b** with 100% beam intensity.

Conclusion and Perspectives

N_2O activation

The toluene complex (*nacnac*^{xylyl}Cu)$_2$(μ-toluene), which is labile in C_6D_6 solution and forms an equilibrium mixture of bridged and terminal bound C_6D_6 adducts, neither coordinates nor reacts with N_2O, even after exposure for thirteen days at 60 °C in Et_2O solution. N_2O is a poor ligand and lack of coordination is not surprising. The high stability of the Cu(I) complex towards N_2O was less expected and might be related to the fact that at least two copper centers have been proposed to be involved in its activation.[1] For future studies, systems such as the macrocyclic ligands prepared by Vela *et al*.[2] might be worth investigating as they can incorporate two copper(I) centers for N_2O activation (Scheme 8.1).



Scheme 8.1

Synthesis of *N*-alkyl β-diketimines

N-alkyl β-diketimines are now accessible through a one-step procedure by condensation of acetylacetone with the appropriate amine in the presence of *p*-TsOH with the help of a Dean-Stark apparatus as opposed to multi-step procedures which most often employ toxic, air- and moisture sensitive activating agents such as Meerwein's salt or Me_2SO_4. Through this novel method, the ligands can be easily prepared on a multi-gram scale. However, diketimine ligands with secondary alkyls as *N*-substituents require longer reaction times.

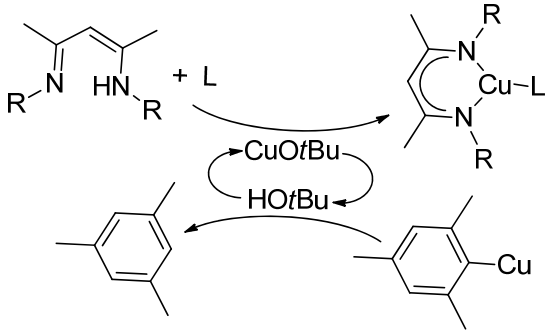
The *nacnac*^{R}H (R = alkyl) ligands were functionalized on the β-carbon by reaction of their lithium salts with N-bromosuccinimide. The succinimido substituted ligands were obtained in place of the brominated ligands. The mass spectrum showed traces of the

brominated ligand which is probably formed first and subsequently displaced by the succinimido moiety. The reaction with N-chlorosuccinimide afforded the chlorinated ligand in 80% purity but without the succinimide substituted ligand.[3]

_N_-alkyl substituted copper(I) β-diketiminates

β-Diketiminato copper(I) complexes with *N*-alkyl substituents have been prepared using the methods employed for *N*-aryl substituents,[4] but supporting Lewis bases are required to stabilize the complexes. Another method, involving the use of MesCu and 5-10% CuO*t*Bu was developed and though no major difference was observed in the yields when either method was used, complexes prepared *via* the catalytic cycle crystallized more easily due to small amounts of HO*t*Bu released in the reaction (Scheme 8.2). MesCu alone did not furnish the desired copper complexes, despite being a stronger base than CuO*t*Bu. Close examination of the solution behavior of MesCu, reveals that it exists in solution as an equilibrium mixture of the dimer and the pentamer.[5] Cupration of *N*-aryl β-diketimines has been effected with MesCu.[6] Thus, the inability of MesCu to deprotonate *N*-alkyl β-diketimines might be due to the ligand environment, which is completely different compared to the *N*-aryl substituted ligands, coupled with the kinetic barrier associated to steric bulk of MesCu or due to the lower acidity of *N*-alkyl substituted diketimines.

Like most copper(I) complexes, these complexes are sensitive to air and moisture. They exhibit colors ranging from pale yellow to bright yellow, except the four-coordinate β-diketiminato copper(I) phenathroline complexes, which are dark-blue.



Scheme 8.2: Proposed catalytic cycle for the preparation of the copper complexes.

Steric effects of *nacnac*^{R}CuL complexes

While *nacnac*^{Bn}H form complexes *nacnac*CuL, where L is either a κ-coordinated or an η^2-coordinated Lewis base, ligands with secondary alkyl *N*-substituents (*nacnac*$^{CH(Me)Ph}$H and *nacnac*^{iPr}H) form only complexes with ancilliary ligands in κ-coordination. Analysis of the space-filling model of the solid state structure of *nacnac*^{Bn}Cu(styrene) reveals that this is most likely related to steric interactions between the olefin carbon atoms and the substituents on the C_N directly attached to the nitrogen atoms (Figure 8.1). Thus, a Me group in place of a hydrogen atom prevents any side-on coordination on the metal center. This is in line with behavior observed by Drouin *et al*. in the reaction of *nacnac*^{R}H (R = Bn, CH(Me)Ph) with $ZnEt_2$. While the homoleptic complex (*nacnac*^{Bn})$_2$Zn is formed, the bulkier secondary *nacnac* ligand afforded, however, only *nacnac*$^{CH(Me)Ph}$ZnEt.[7]

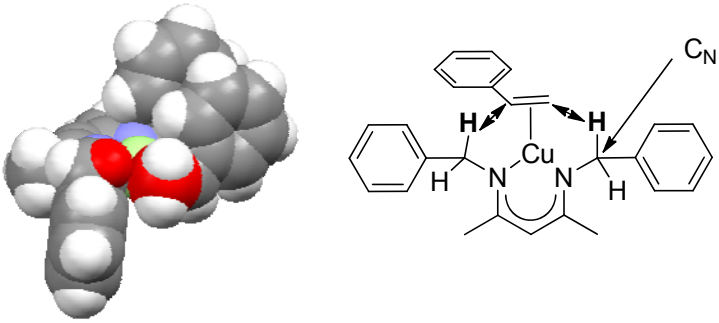
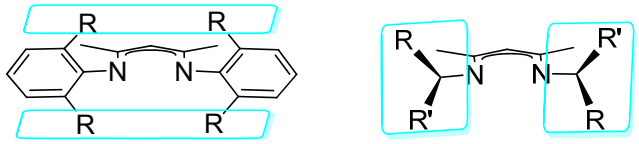


Figure 8.1: Steric interactions in copper styrene complex.

N-Aryl β-diketimines, such as *nacnac*^{dipp}H and *nacnac*^{Mes}H, which are among the most sterically demanding *N*-aryl substituted ligands, form copper styrene complexes,[8] while *N*-alkyl substituted derivatives with secondary alkyl groups do not. In addition P-C bond distances in *nacnac*CuPPh$_3$ complexes are longer in the *N*-secondary alkyl substituted complexes than in their *N*-aryl congeners (Aryl: 2.16-2.18 Å; *sec*-Alkyl: 2.191-2.195 Å).[4,9,10,11] This indicates that the *N*-*sec*-alkyl substituted β-diketimines are sterically more demanding than even *nacnac*^{dipp}H. On the other hand, Nikiforov *et al*. have demonstrated through intramolecular π coordination that *nacnac*^{dipp}H is bulkier than *nacnac*^{iPr}H.[12] These differences are most likely due to the completely different steric enviroments in *N*-aryl and *N*-alkyl substituted ligands. The steric interactions in the *N*-aryl substituted diketimines extend up and down as shown in their neutral α-diimine analogues,[13] while that of their

aliphatic counterparts extend equatorially, perpendicular to the NCCCN plane (Figure 8.2). *N-sec*-Alkyl substituted β-diketimines, thus, provide steric protection close to the metal center but none above and below the NCCCN plane, while the reverse is true for *N*-aryl substituted β-diketimines. The ready formation of four-coordinate *nacnac* copper phenanthroline complexes even with *nacnac*$^{CH(Me)Ph}$, supports this fact as the supporting Lewis bases can only be coordinated perpendicular to the NCCCN plane.



A **B**

Figure 8.2: Steric influence in β-diketimine ligand (**A**) parallel and (**B**) perpendicular to the NCCCN plane.

Substituents on the β-carbon of the diketimine ligand increase the steric bulk around the copper center by interacting with the Me substituents on the α-carbon atoms which in turn pushes *N*-substituents towards the metal center, in the same way as bulky α-carbon substituents do in *N*-aryl substituted β-diketiminates.[14,15] The geometrical changes which occur in *nacnac*$^{CH(Me)Ph}$$CuCNC_6H_3(Me)_2$ and ^{succ}*nacnac*$^{CH(Me)Ph}$$CuCNC_6H_3(Me)_2$ complexes are illustrated below (Figure 8.3). This has a profound effect on the rate of complex formation (Table VIII-1).

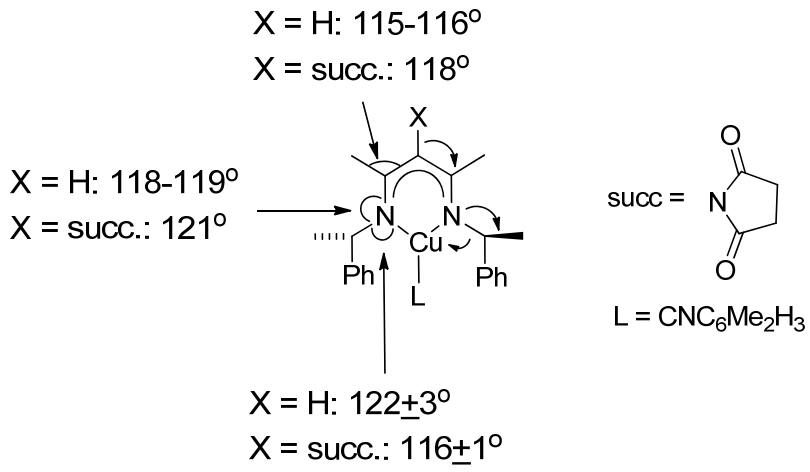
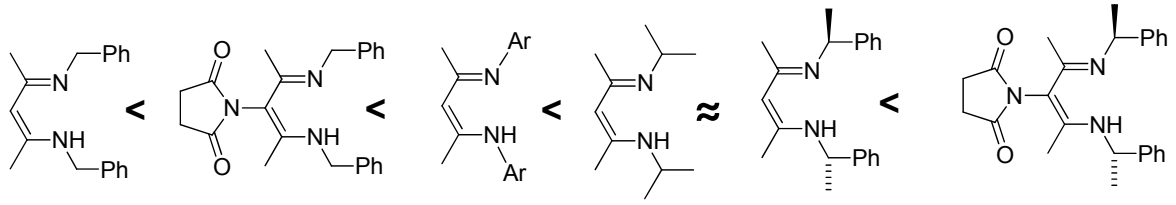


Figure 8.3: Geometric changes in β-carbon substituted copper complex

Table VIII-1: Relative reactivities in complex formation.

Lewis bases	X = H	X = succ
olefin	none	none
PhCCPh	none	none
acetone	none	none
THF	none	none
MeCN	slow, complete	none
pyridine	fast, complete	slow, incomplete
DMAP	fast, complete	
PPh_3	fast, complete	slow, complete
$CNC_6Me_2H_3$	fast, complete	fast, complete

At least for copper(I) complexes, steric congestion can thus be arranged in the following order:

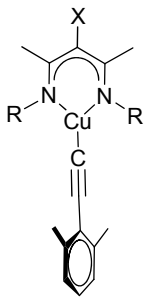


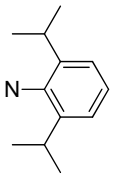
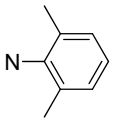
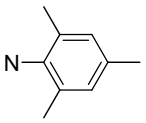
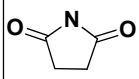
Electronic effects of *nacnac*^{R}CuL complexes

Electronic differences between *N*-aryl and *N*-alkyl β-diketiminato copper complexes are subtle. The C-N bond distances in *nacnac*$CuCNC_6H_3Me_2$, the chemical displacement of *nacnac*$CuPPh_3$ in ^{31}P NMR and the average P-C bond distances, which are all influenced by the amount of charge transfer to the coordinated Lewis base, are not significantly different (C-N: 1.157(3)-1.172(4) Å,[4,16] ^{31}P NMR: 3.5-5.4 ppm[4,9,13,14,16] and average P-C: 1.825(1)-1.839(2) Å.[4,9,13,14,16] IR studies on *nacnac*$CuCNC_6H_3Me_2$ complexes also show a narrow range (2105-2126 cm^{-1})[4,13,14] for the C-N stretching frequency. While the variations are small, they show nevertheless a clear trend; *N*-aryl substituted β-diketiminate complexes have ν_{CN} higher than the free isocynide (ν_{CN} = 2119 cm^{-1}), *N*-alkyl substituted complexes have frequencies lower than 2119 cm^{-1}, with secondary alkyls lower than primary alkyls. The electron withdrawing succinimido substituent increases ν_{CN} by 6

cm^{-1}. The *N-i*Pr substituted complex having the lowest value ever reported for 2,6-xylyl isocyanide copper(I) complexes (Table VIII-2).

Table VIII-2: IR stretching frequencies of C-N bond in *nacnac* xylylisocynide copper complexes.



	N-aryl			N-alkyl			
R =							
X =	H	H	H		H	H	H
ν(C-N) [cm^{-1}]	2126[9]	2123[16]	2121[4]	2117	2114	2111	2105

In terms of electron donor properties, diketiminate ligands can thus be arranged as shown in figure 8.4, based on the increase in π back donation from the metal center to the π* orbitals of the C-N unit in the copper complexes, indicative of the high electron donor properties of β-diketiminate ligands in general and *N-sec*-alkyl substituted β-diketiminates in particular.

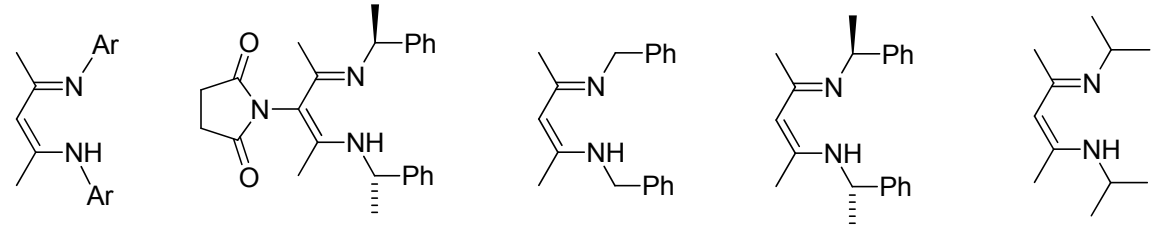


Figure 8.4: Electronic influence of various β-diketimine ligands.

π Backbonding

The Lewis basic nature of *N*-alkyl β-diketimine ligands governs also the chemistry of their olefin complexes. The rotational barrier of the olefin moiety in *nacnac*^{Bn}Cu(styrene) is the highest reported for copper styrene complexes. In *nacnac*^{Bn}Cu(acrylonitrile) π backbonding to the coordinated olefin occurs to an extent that nucleophilic attack on acrylonitrile is prevented and the complex does not yield the hydroamination product in the presence of morpholine (Figure 8.5). The same reaction proceeds to 30% when free acrylonitrile and morpholine are reacted and to 100% conversion in the presence of catalytic amounts of $Cu(CNMe)_4PF_6$, a cationic copper source.

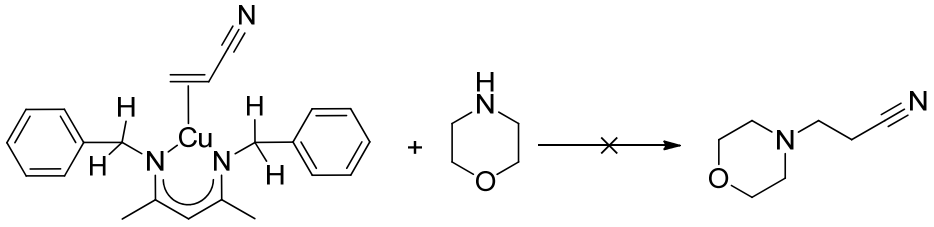
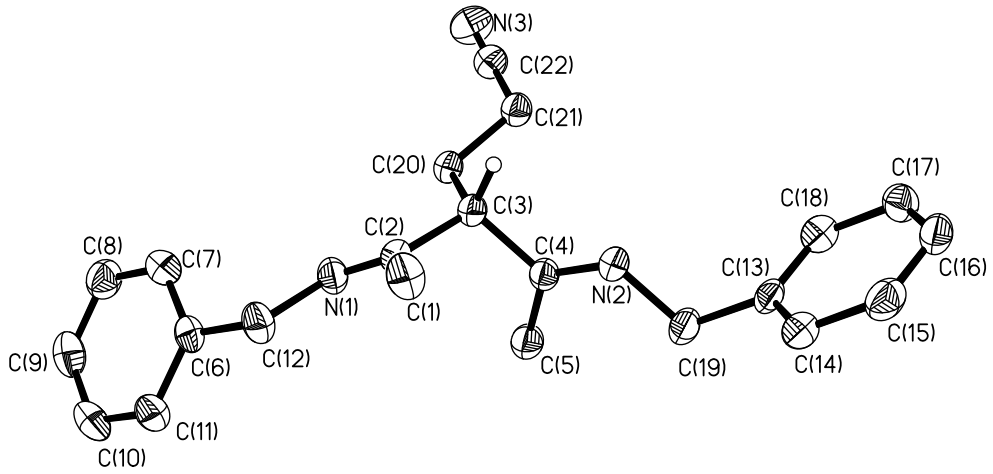


Figure 8.5: Reaction of *nacnac*^{Bn}Cu(acrylonitrile) complex with morpholine.

Stability of copper *nacnac* complexes

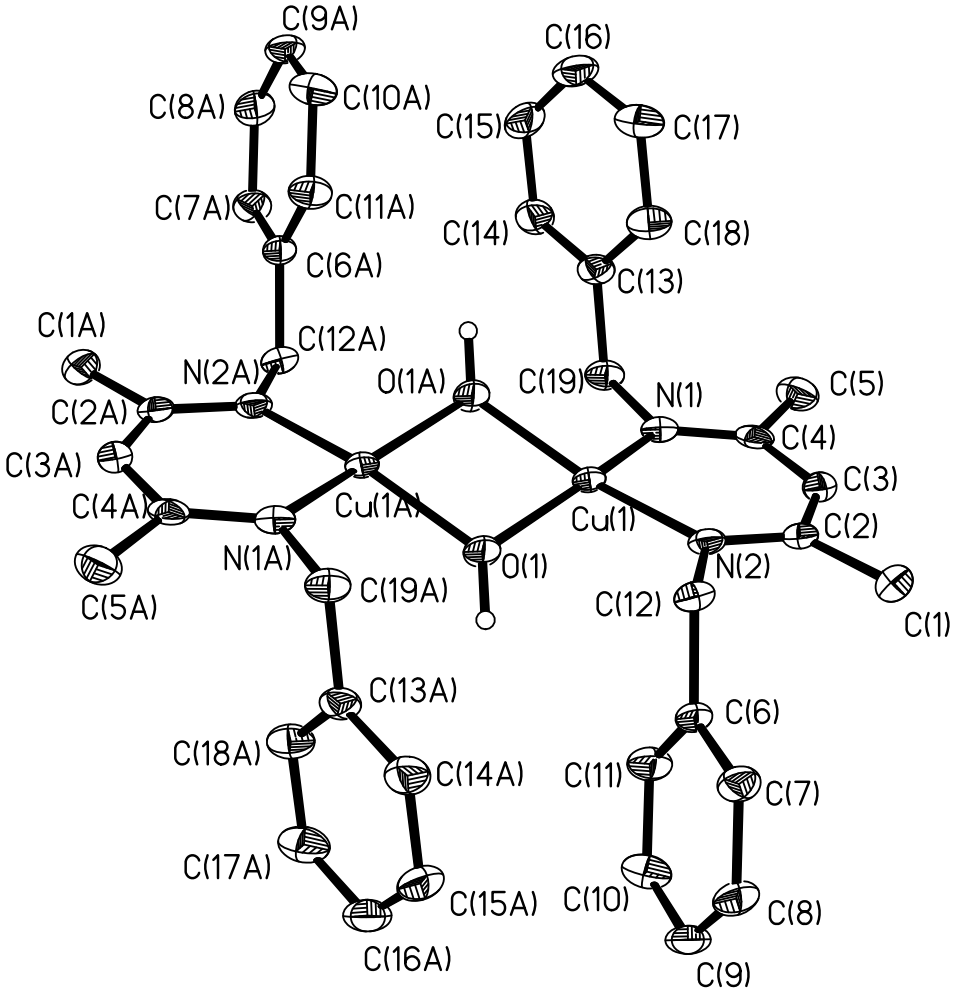
It has been observed in *N*-aryl diketiminato complexes that the β-carbon is prone to oxidation.[17] The β-carbon attacked acrylonitrile in *N*-alkyl substituted *nacnac* ligands while preparing *nacnac*^{Bn}Cu(acrylonitrile). The side product, which was only crystallographically characterized (Annex I), shows an acrylonitrile moiety bonded to the β-carbon, with the resulting ligand disposed in an open conformation. Most β-diketimines exist as the enamine tautomer. This side product is a rare case where the ligand adopts the diimine form (Figure 8.6). Attempts to obtain this side product in sufficient amount for complete characterization were unsuccessful.



8.1

Figure 8:6: Ortep representation of the solid state structure of side product obtained while preparing the *nacnac*^{Bn}Cu(acrylonitrile) complex. Most H atoms have been omitted for clarity. Thermal ellipsoids are set at 50% probability level. Selected bond distances (Å) and angles (deg.) for the molecule shown: C(2)-C(3) = 1.527(2), C(3)-C(4) = 1.532(2), C(3)-C(20) = 1.530(2), N(1)-C(2) = 1.275(2), N(2)-C(4) = 1.277(2), N(2)-C(3)-C(4) = 116.7(1), N(1)-C(2)-C(3) = 119.2(1), C(2)-C(3)-C(4) = 108.4(1), C(3)-C(4)-C(5) = 116.7(1).

Like most copper(I) complexes, the *N*-alkyl substituted β-diketiminato copper(I) complexes are susceptible to oxygenation, to afford copper(II) species. In an attempt to synthesize *nacnac*^{Bn}Cu(stilbene), the dimer [*nacnac*^{Bn}Cu(μ-OH)]$_2$ was serendipitously obtained by oxygen contamination and was characterized by X-ray diffraction studies (Annex 1). While similar copper complexes with *N*-aryl substituents have been isolated by reaction of the appropriate precursors with oxygen,[11,14,18] this is the first time such a species has been isolated with *N*-alkyl β-diketimine ligand.

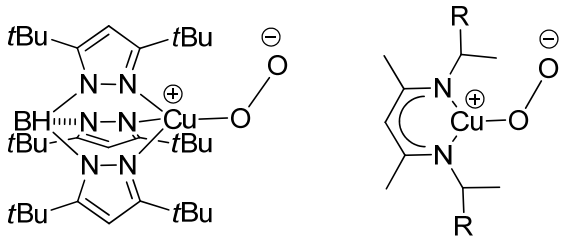


8.2

Figure 8.7: Ortep plot of the [*nacnac*^{Bn}Cu(μ-OH)]$_2$ complex. Most H atoms are omitted for clarity. Ellipsoids are drawn at 50% probability level. Selected bond distances (Å) and angles (deg.) for the molecule shown: Cu(1)-N(1) = 1.931(2), Cu(1)-N(2) =1.937(2) , Cu(1)-O(1) = 1.947(2), N(1)-Cu1-N(2) = 96.1(1), Cu(1)-O(1)-Cu(1A) = 104.9(1).

The 1:1 Cu-O_2 motive is a very important unit in the field of biochemistry. While many such complexes with side-on coordination mode have been isolated,[14,20] only one complex with end-on coordination mode is known.[21] β-Diketimines with secondary *N*-alkyl substituents do not allow side-on coordination of supporting ligands in their copper

complexes and the electron richness coupled with a different steric surrounding relative to their *N*-aryl counterparts might stabilize such oxygen adducts with end-on coordination mode Figure (8.8).



A **B**

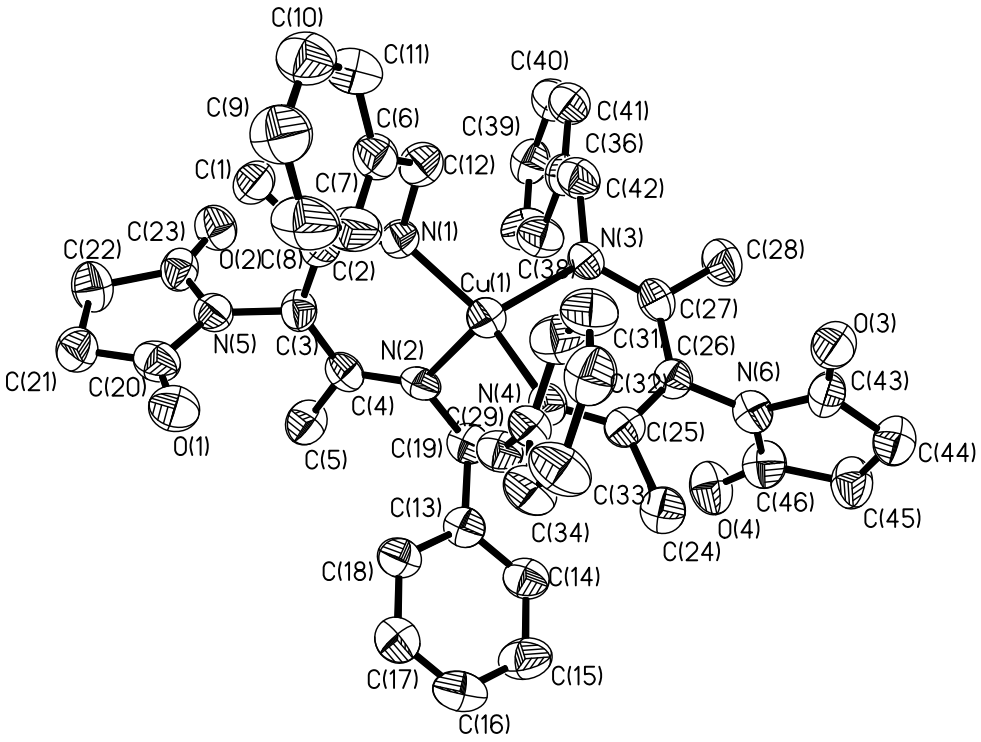
Figure 8.8: Known end-on $Tp^{tBu,tBu}Cu\text{-}O_2$ complex (**A**) and proposed end-on $nacnac^{R}Cu\text{-}O_2$ complex (**B**).

A general problem in Cu(I) chemistry is its possible disproportionation to Cu(0) and Cu(II), which is strongly influenced by the stability of the respective complexes formed. Cu(I) diketiminate complexes with *N*-alkyl substituents tend to disproportionate more readily than their *N*-aryl analogues. This lability towards disproportionation might be partly related to the inability of *sec*-alkyl *N*-substituted complexes to coordinate olefins; while this is not a problem for *N*-aryl diketiminates. In the absence of additional ligands, intermolecular coordination of the *N*-aryl substituent to another Cu center is thus possible.[22] This does not explain, however, the instability of primary alkyl *N*-substituted complexes, which do coordinate olefins.

Another explanation involves the increased electron density properties of *N*-alkyl diketimines. The reduction potential **ΔE** for the disproportionation reaction (Scheme 8.3) is given by $\Delta E = \Delta E(Cu/Cu^{+}) - \Delta E(Cu^{+}/Cu^{2+})$. Increases Lewis basicity of the ligand will increase $\Delta E(Cu/Cu^{+})$ more than $\Delta E(Cu^{+}/Cu^{2+})$, thus rendering the disproportionation more favorable. While disproportionation products were in general not characterized in detail, $^{succ}nacnac^{Bn}$Cu(styrene) or $^{succ}nacnac^{Bn}$Cu(1-hexene) afforded crystals of the Cu(II) complex $[^{succ}nacnac^{Bn}]_2$Cu which was characterized by X-ray diffraction studies (**Figure 8.9**).

$$2\ nacnacCu \rightleftharpoons nacnac_2Cu + Cu^0$$

Scheme 8.3



8.3

Figure 8.9: Ortep plot of the [^{succ}*nacnac*^{Bn}]$_2$Cu complex. H atoms are omitted for clarity. Ellipsoids are drawn at 50% probability level. Selected bond distances (Å) and angles (deg) for the molecule shown: Cu(1)-N(1) = 1.924(3), Cu(1)-N(2) = 1.960(3), Cu(1)-N(3) = 1.957(3), Cu(1)-N(4) = 1.915(4), C3(1)-N(5) = 1.445(5), C26(1)-N(6) = 1.438(5), N(1)-Cu(1)-N(2) = 95.3(2), N(3)-Cu(1)-N(4) = 92.8(2), C(27)-N(3)-C(42) = 118.4(4), C(25)-N(4)-C(35) = 117.8(4), C(4)-N(2)-C(19) = 121.0(4).

Catalytic applications

Despite the ease of synthesis and introduction of chirality, *N*-alkyl β-diketimines are not very suitable for catalytic applications, with Cu(I) as the central metal. No chiral induction was observed in cyclopropanation of styrene with ethyldiazoacetate and conjugate addition of $ZnEt_2$ to 2-cyclohexenone from which it was concluded that the ligand is lost prior to entering the catalytic cycle. The chiral ligand and other secondary *N*-

alkyl substituted β-diketimines do not form side-on coordinated copper(I) complexes which are key intermediates in catalytic processes such as 1,4-conjugate addition reactions. In addition, Drouin et al. observed C-N bond rotation in the solid state structure of the complex $[(nacnac^{CH(Me)Ph}Zn)(\mu\text{-}OC(CH_3)_2]_2$[7] and this complex failed to induce enantioselectivity in lactide polymerisation while El-Zoghbi et al. also observed C-N bond rotation and C-H bond activation in an octahedral Zr complex, which is a pathway to epimerization.[22] The chiral *nacnac* CH(Me)Ph seems neither rigid enough, nor sufficiently bound to Cu(I) for the desired application.

Applications as structural motifs

Some of the complexes studied during the course of this thesis show intra- and or intermolecular π-stacking interactions in their solid state structures. This property has been exploited to stabilize *nacnac* copper complexes with phenanthroline ligands which are useful in light harvesting. Appending substituents on the *N*-Bn group enhances intramolecular π-π interactions and prevents flattening distortions of the phenanthroline ligand. Absorption and emission studies show lower Stoke shifts (129-159 nm in toluene and 122-166 nm in diethylether) and narrow transition bands (FWHM < 100 nm), indicating smaller excited state distortions. Despite these, lifetimes were still lower than 60 ns, probably due to the low energy of the transitions. Modification of the ligand framework with π-enhancing substituents or introducing electron-withdrawing substituents on the ligand backbone which will increase the donor-acceptor gap is worth investigating in the future. The anthranylmethyl substituent might be of special interest to equilibrate the excited state with an organic auxillary.

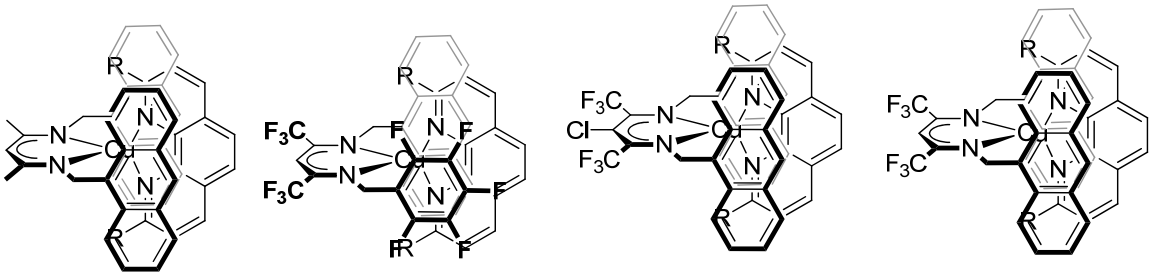


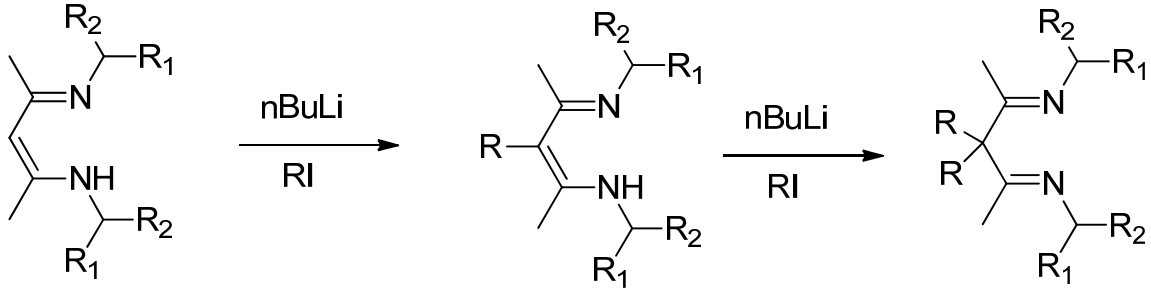
Figure 8.10: Proposed complexes with possibly high energy MLCT transitions.

In summary, many *N*-alkyl β-diketimines can be prepared easily by the optimized one-step procedure. More Cu(I) complexes supported by these ligands are now accessible, but they are not ideal complexes for catalytic applications:

(i) η^2-Coordinated complexes are not formed with *N-sec*-alkyl substitutued ligands, in particular *nacnac*$^{CH(Me)Ph}$, due to steric interactions between the η^2-coordinated ligand and the substituents on the sp^3 C_N atoms. Most catalytic reactions require at some point co-planar arrangement of the metal center and the ligands for subsequent reactions to proceed, which might have contributed to ligand loss in the catalytic reactions investigated. Although all structurally characterized *nacnac*^{R}Cu complexes show comparable ligand conformations with a hydrogen substituent of the C_N atom oriented towards the ligand backbone, results from other *nacnac*^{R} metal complexes let suspect that the ligand geometry is not rigid enough to induce enantioselectivity.

(ii) The electron richness of β-diketimines and in particular *N-sec*-substituted β-diketimines, renders their Cu(I) complexes very susceptible to disproportionation. Strong Lewis bases are required to prevent this and these block the coordination site required for catalytic reactions. Competition between the strong supporting ligand and diketimine for the copper center probably led to loss of the diketimine prior to entering the catalytic cycle.

Appending substitents by double substitution on the β-carbon atom on the diketiminate backbone could be a way out to attenuate the unrequired electron density by transforming the anionic ligand into a neutral ligand, while keeping the general framework unchanged (Scheme 8.4). It should be noted that most of the limitations encountered here might be specific to Cu(I) and not be present with other metal complexes.



Scheme 8.4

Despite their limitations in catalytic applications, *N*-alkyl diketimines provide an additional, complementary structural motif in Cu(I) chemistry. The *N*-substituent can extend

extend far out in the mean ligand plane. In applications which aim at narrowing the accessible space around the metal center, i.e. a big Tolman angle of the ligand, they offer access to a ligand environment which can not be obtained with their *N*-aryl counterparts. One example is their application in *nacnac*Cu(phenanthroline) complexes described in chapter 7.

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Annex 1

Table I. Crystal data and structure refinement for C22 H25 N3, chapter 8

Identification code	paul13
Empirical formula	C22 H25 N3
Formula weight	331.45
Temperature	150K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 9.7742(3) Å α = 90° b = 17.6962(6) Å β = 90.060(2)° c = 10.9336(4) Å γ = 90°
Volume	1891.14(11)Å^3
Z	4
Density (calculated)	1.164 Mg/m^3
Absorption coefficient	0.532 mm^{-1}
F(000)	712
Crystal size	0.14 x 0.12 x 0.12 mm
Theta range for data collection	4.75 to 72.39?
Index ranges	$-12 \leq h \leq 11$, $-20 \leq k \leq 17$, $-13 \leq l \leq 13$
Reflections collected	24544
Independent reflections	3213 [R_{int} = 0.062]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9382 and 0.6755
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3213 / 0 / 229
Goodness-of-fit on F2	0.920
Final R indices [I>2sigma(I)]	R_1 = 0.0419, wR_2 = 0.1053
R indices (all data)	R_1 = 0.0585, wR_2 = 0.1111
Largest diff. peak and hole	0.185 and -0.182 e/Å^3

Table II. Bond lengths [Å] and angles [°] for C22 H25 N3

N(1)-C(2)	1.275(2)
N(1)-C(12)	1.4739(18)
N(2)-C(4)	1.2773(19)
N(2)-C(19)	1.4736(19)
N(3)-C(22)	1.143(2)
C(1)-C(2)	1.511(2)
C(2)-C(3)	1.5273(19)
C(3)-C(20)	1.5302(19)
C(3)-C(4)	1.5316(19)
C(4)-C(5)	1.508(2)
C(6)-C(7)	1.388(2)
C(6)-C(11)	1.391(2)
C(6)-C(12)	1.511(2)
C(7)-C(8)	1.390(3)
C(8)-C(9)	1.382(2)
C(9)-C(10)	1.378(3)
C(10)-C(11)	1.390(2)
C(13)-C(14)	1.387(2)
C(13)-C(18)	1.393(2)
C(13)-C(19)	1.509(2)
C(14)-C(15)	1.393(2)
C(15)-C(16)	1.383(2)
C(16)-C(17)	1.383(2)
C(17)-C(18)	1.392(2)
C(20)-C(21)	1.5377(19)
C(21)-C(22)	1.469(2)
C(2)-N(1)-C(12)	117.41(13)
C(4)-N(2)-C(19)	118.61(12)
N(1)-C(2)-C(1)	126.26(13)
N(1)-C(2)-C(3)	119.17(13)
C(1)-C(2)-C(3)	114.57(13)
C(2)-C(3)-C(20)	113.27(12)
C(2)-C(3)-C(4)	108.38(11)
C(20)-C(3)-C(4)	113.00(12)
N(2)-C(4)-C(5)	126.61(13)
N(2)-C(4)-C(3)	116.68(13)
C(5)-C(4)-C(3)	116.70(12)
C(7)-C(6)-C(11)	118.43(15)
C(7)-C(6)-C(12)	121.17(14)
C(11)-C(6)-C(12)	120.39(14)
C(8)-C(7)-C(6)	120.67(15)
C(9)-C(8)-C(7)	120.41(16)
C(10)-C(9)-C(8)	119.35(16)
C(9)-C(10)-C(11)	120.44(16)
C(10)-C(11)-C(6)	120.70(16)
N(1)-C(12)-C(6)	111.65(12)
C(14)-C(13)-C(18)	118.35(14)
C(14)-C(13)-C(19)	121.13(14)
C(18)-C(13)-C(19)	120.52(14)
C(13)-C(14)-C(15)	120.81(15)
C(16)-C(15)-C(14)	120.21(15)
C(17)-C(16)-C(15)	119.70(15)
C(16)-C(17)-C(18)	119.89(15)
C(17)-C(18)-C(13)	121.03(15)
N(2)-C(19)-C(13)	110.03(12)
C(3)-C(20)-C(21)	110.04(12)
C(22)-C(21)-C(20)	112.14(12)
N(3)-C(22)-C(21)	178.51(17)

Table III. Crystal data and structure refinement for C38 H44 Cu2 N4 O2.

Identification code	shap41
Empirical formula	C38 H44 Cu2 N4 O2
Formula weight	715.85
Temperature	150 K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 5.4783(3) Å α = 73.210(2)? b = 11.8231(5) Å β = 85.367(2)? c = 13.4079(5) Å γ = 87.491(2)?
Volume	828.51(7)Å^3
Z	1
Density (calculated)	1.435 Mg/m^3
Absorption coefficient	1.893 mm^{-1}
F(000)	374
Crystal size	0.25 x 0.20 x 0.16 mm
Theta range for data collection	3.45 to 67.95?
Index ranges	$-5 \leq h \leq 5$, $-14 \leq k \leq 14$, $-16 \leq l \leq 16$
Reflections collected	13328
Independent reflections	2604 [R_{int} = 0.055]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7387 and 0.7852
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2604 / 0 / 210
Goodness-of-fit on F2	1.043
Final R indices [I>2sigma(I)]	R_1 = 0.0405, wR_2 = 0.1120
R indices (all data)	R_1 = 0.0447, wR_2 = 0.1145
Largest diff. peak and hole	0.334 and -0.768 e/Å^3

Table IV. Bond lengths [Å] and angles [deg.]for C38 H44 Cu2 N4 O2

Cu(1)-N(1)	1.931(2)
Cu(1)-N(2)	1.937(2)
Cu(1)-O(1)	1.9362(17)
Cu(1)-O(1)	1.9465(17)
O(1)-Cu(1)	1.9465(17)
O(1)-H(2)	0.9064
N(1)-C(4)	1.331(3)
N(1)-C(19)	1.465(3)
N(2)-C(2)	1.333(3)
N(2)-C(12)	1.475(3)
C(1)-C(2)	1.513(3)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.391(4)
C(3)-C(4)	1.403(4)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.512(4)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(11)	1.383(4)
C(6)-C(7)	1.393(4)
C(6)-C(12)	1.522(3)
C(7)-C(8)	1.394(4)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.367(5)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.390(4)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.391(4)
C(10)-H(10A)	0.9500
C(11)-H(11A)	0.9500
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(18)	1.379(4)
C(13)-C(14)	1.396(4)
C(13)-C(19)	1.524(4)
C(14)-C(15)	1.386(4)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.368(5)
C(15)-H(15A)	0.9500
C(16)-C(17)	1.386(4)
C(16)-H(16A)	0.9500
C(17)-C(18)	1.389(4)
C(17)-H(17A)	0.9500
C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900

N(1)-Cu(1)-N(2)	96.08(9)
N(1)-Cu(1)-O(1)	158.29(10)
N(2)-Cu(1)-O(1)	98.16(8)
N(1)-Cu(1)-O(1)	97.21(8)
N(2)-Cu(1)-O(1)	157.42(11)
O(1)-Cu(1)-O(1)	75.10(7)
Cu(1)-O(1)-Cu(1)	104.90(7)
Cu(1)-O(1)-H(2)	122.6
Cu(1) 1-O(1)-H(2)	129.1
C(4)-N(1)-C(19)	118.0(2)
C(4)-N(1)-Cu(1)	124.65(18)
C(19)-N(1)-Cu(1)	117.15(17)
C(2)-N(2)-C(12)	117.9(2)
C(2)-N(2)-Cu(1)	123.78(19)
C(12)-N(2)-Cu(1)	118.22(16)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
N(2)-C(2)-C(3)	123.9(2)
N(2)-C(2)-C(1)	120.0(3)
C(3)-C(2)-C(1)	116.1(2)
C(2)-C(3)-C(4)	128.6(2)
C(2)-C(3)-H(3A)	115.7
C(4)-C(3)-H(3A)	115.7
N(1)-C(4)-C(3)	122.9(2)
N(1)-C(4)-C(5)	120.8(2)
C(3)-C(4)-C(5)	116.3(2)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(11)-C(6)-C(7)	118.9(2)
C(11)-C(6)-C(12)	122.2(2)
C(7)-C(6)-C(12)	118.9(2)
C(8)-C(7)-C(6)	120.2(3)
C(8)-C(7)-H(7A)	119.9
C(6)-C(7)-H(7A)	119.9
C(9)-C(8)-C(7)	120.5(3)
C(9)-C(8)-H(8A)	119.7
C(7)-C(8)-H(8A)	119.7
C(8)-C(9)-C(10)	119.8(2)
C(8)-C(9)-H(9A)	120.1
C(10)-C(9)-H(9A)	120.1
C(11)-C(10)-C(9)	119.8(3)
C(11)-C(10)-H(10A)	120.1
C(9)-C(10)-H(10A)	120.1
C(6)-C(11)-C(10)	120.8(3)
C(6)-C(11)-H(11A)	119.6
C(10)-C(11)-H(11A)	119.6
N(2)-C(12)-C(6)	114.3(2)
N(2)-C(12)-H(12A)	108.7
C(6)-C(12)-H(12A)	108.7
N(2)-C(12)-H(12B)	108.7
C(6)-C(12)-H(12B)	108.7
H(12A)-C(12)-H(12B)	107.6
C(18)-C(13)-C(14)	118.6(3)
C(18)-C(13)-C(19)	122.6(2)
C(14)-C(13)-C(19)	118.8(3)
C(15)-C(14)-C(13)	120.5(3)
C(15)-C(14)-H(14A)	119.7
C(13)-C(14)-H(14A)	119.7
C(16)-C(15)-C(14)	120.4(3)
C(16)-C(15)-H(15A)	119.8
C(14)-C(15)-H(15A)	119.8
C(15)-C(16)-C(17)	119.7(3)
C(15)-C(16)-H(16A)	120.2
C(17)-C(16)-H(16A)	120.2
C(18)-C(17)-C(16)	120.1(3)
C(18)-C(17)-H(17A)	120.0
C(16)-C(17)-H(17A)	120.0
C(13)-C(18)-C(17)	120.7(3)
C(13)-C(18)-H(18A)	119.6
C(17)-C(18)-H(18A)	119.6
N(1)-C(19)-C(13)	113.3(2)
N(1)-C(19)-H(19A)	108.9
C(13)-C(19)-H(19A)	108.9
N(1)-C(19)-H(19B)	108.9
C(13)-C(19)-H(19B)	108.9
H(19A)-C(19)-H(19B)	107.7

Table V. Crystal data and structure refinement for C46 H48 Cu N6 O4.

Identification code	paul09
Empirical formula	C46 H48 Cu N6 O4
Formula weight	812.45
Temperature	150K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 20.1736(6) α = 90° b = 9.6549(2) β = 102.363(1)° c = 45.6035(10) γ = 90°
Volume	8676.4(4)A^3
Z	8
Density (calculated)	1.244 mg/m^3
Absorption coefficient	1.096 mm^{-1}
F(000)	3416
Crystal size	0.16 x 0.12 x 0.12 mm
Theta range for data collection	1.98 to 72.62°
Index ranges	$-24 \leq h \leq 24$, $-11 \leq k \leq 11$, $-55 \leq l \leq 56$
Reflections collected	56369
Independent reflections	8531, R_{int} = 0.175
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8182 and 0.5300
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8531 / 0 / 520
Goodness-of-fit on F^2	0.868
Final R indices [I>2sigma(I)]	R_1 = 0.0775, wR_2 = 0.1690
R indices (all data)	R_1 = 0.1375, wR_2 = 0.1862
Extinction coefficient	0.00041(3)
Largest diff. peak and hole	0.509 and -0.493 e/A^3

Table VI. Bond lengths [Å]and angle [deg.] for C46 H48 Cu N6 O4

Cu(1)-N(4)	1.915(4)
Cu(1)-N(1)	1.924(3)
Cu(1)-N(5)	1.957(3)
Cu(1)-N(2)	1.960(3)
O(1)-C(20)	1.204(5)
O(2)-C(23)	1.207(5)
O(3)-C(43)	1.220(5)
O(4)-C(46)	1.209(5)
N(1)-C(2)	1.349(5)
N(1)-C(12)	1.480(5)
N(2)-C(4)	1.327(5)
N(2)-C(19)	1.476(5)
N(3)-C(20)	1.393(5)
N(3)-C(23)	1.402(6)
N(3)-C(3)	1.445(5)
N(4)-C(25)	1.317(5)
N(4)-C(35)	1.483(5)
N(5)-C(27)	1.343(5)
N(5)-C(42)	1.483(5)
N(6)-C(43)	1.384(6)
N(6)-C(46)	1.396(6)
N(6)-C(26)	1.438(5)
C(1)-C(2)	1.529(6)
C(2)-C(3)	1.414(6)
C(3)-C(4)	1.410(6)
C(4)-C(5)	1.508(6)
C(6)-C(7)	1.359(6)
C(6)-C(11)	1.392(6)
C(6)-C(12)	1.525(6)
C(7)-C(8)	1.385(6)
C(8)-C(9)	1.386(7)
C(9)-C(10)	1.371(7)
C(10)-C(11)	1.401(7)
C(13)-C(14)	1.386(6)
C(13)-C(18)	1.400(6)
C(13)-C(19)	1.511(6)
C(14)-C(15)	1.386(6)
C(15)-C(16)	1.387(7)
C(16)-C(17)	1.365(7)
C(17)-C(18)	1.380(6)
C(20)-C(21)	1.493(6)
C(21)-C(22)	1.514(6)
C(22)-C(23)	1.508(6)
C(24)-C(25)	1.516(6)
C(25)-C(26)	1.417(6)
C(26)-C(27)	1.408(6)
C(27)-C(28)	1.533(5)
C(29)-C(30)	1.391(6)
C(29)-C(34)	1.403(6)
C(29)-C(35)	1.518(6)
C(30)-C(31)	1.374(6)
C(31)-C(32)	1.373(6)
C(32)-C(33)	1.383(6)
C(33)-C(34)	1.368(6)
C(36)-C(41)	1.386(6)
C(36)-C(37)	1.387(6)
C(36)-C(42)	1.512(6)
C(38)-C(37)	1.373(6)
C(38)-C(39)	1.374(6)
C(39)-C(40)	1.379(7)
C(40)-C(41)	1.398(6)
C(43)-C(44)	1.514(6)
C(44)-C(45)	1.508(6)
C(45)-C(46)	1.499(6)

N(4)-CU1-N(1)	137.39(15)	C(27)-C(26)-N(6)	115.7(4)
N(4)-CU1-N(5)	92.83(15)	C(25)-C(26)-N(6)	115.6(4)
N(1)-CU1-N(5)	110.73(16)	N(5)-C(27)-C(26)	122.6(4)
N(4)-CU1-N(2)	99.84(15)	N(5)-C(27)-C(28)	120.4(4)
N(1)-CU1-N(2)	95.26(16)	C(26)-C(27)-C(28)	116.9(4)
N(5)-CU1-N(2)	124.47(14)	C(30)-C(29)-C(34)	116.2(5)
C(2)-N(1)-C(12)	118.0(4)	C(30)-C(29)-C(35)	122.7(4)
C(2)-N(1)-CU1	125.0(3)	C(34)-C(29)-C(35)	121.1(4)
C(12)-N(1)-CU1	117.0(3)	C(31)-C(30)-C(29)	122.1(5)
C(4)-N(2)-C(19)	121.0(4)	C(32)-C(31)-C(30)	120.4(5)
C(4)-N(2)-CU1	126.5(3)	C(31)-C(32)-C(33)	119.1(5)
C(19)-N(2)-CU1	112.3(3)	C(34)-C(33)-C(32)	120.4(5)
C(20)-N(3)-C(23)	112.9(4)	C(33)-C(34)-C(29)	121.8(5)
C(20)-N(3)-C(3)	122.1(4)	N(4)-C(35)-C(29)	112.0(4)
C(23)-N(3)-C(3)	125.0(4)	C(41)-C(36)-C(37)	117.5(4)
C(25)-N(4)-C(35)	117.8(4)	C(41)-C(36)-C(42)	118.6(4)
C(25)-N(4)-CU1	127.5(3)	C(37)-C(36)-C(42)	123.7(4)
C(35)-N(4)-CU1	114.7(3)	C(37)-C(38)-C(39)	120.4(5)
C(27)-N(5)-C(42)	118.4(4)	C(38)-C(39)-C(40)	118.6(5)
C(27)-N(5)-CU1	122.2(3)	C(39)-C(40)-C(41)	121.1(5)
C(42)-N(5)-CU1	118.5(3)	C(36)-C(41)-C(40)	120.2(5)
C(43)-N(6)-C(46)	112.2(4)	N(5)-C(42)-C(36)	115.1(4)
C(43)-N(6)-C(26)	123.1(4)	C(38)-C(37)-C(36)	122.2(5)
C(46)-N(6)-C(26)	124.6(4)	O(3)-C(43)-N(6)	124.5(5)
N(1)-C(2)-C(3)	122.0(4)	O(3)-C(43)-C(44)	126.8(5)
N(1)-C(2)-C(1)	120.3(4)	N(6)-C(43)-C(44)	108.8(4)
C(3)-C(2)-C(1)	117.7(4)	C(45)-C(44)-C(43)	104.6(4)
C(4)-C(3)-C(2)	130.6(4)	C(46)-C(45)-C(44)	106.1(4)
C(4)-C(3)-N(3)	115.1(4)	O(4)-C(46)-N(6)	124.4(5)
C(2)-C(3)-N(3)	114.3(4)	O(4)-C(46)-C(45)	127.4(5)
N(2)-C(4)-C(3)	120.3(4)	N(6)-C(46)-C(45)	108.1(4)
N(2)-C(4)-C(5)	121.6(4)		
C(3)-C(4)-C(5)	118.1(4)		
C(7)-C(6)-C(11)	117.6(5)		
C(7)-C(6)-C(12)	123.6(5)		
C(11)-C(6)-C(12)	118.8(5)		
C(6)-C(7)-C(8)	122.9(5)		
C(7)-C(8)-C(9)	119.3(5)		
C(10)-C(9)-C(8)	119.3(5)		
C(9)-C(10)-C(11)	120.3(5)		
C(6)-C(11)-C(10)	120.6(5)		
N(1)-C(12)-C(6)	115.9(4)		
C(14)-C(13)-C(18)	117.8(5)		
C(14)-C(13)-C(19)	118.7(4)		
C(18)-C(13)-C(19)	123.5(4)		
C(15)-C(14)-C(13)	121.0(5)		
C(14)-C(15)-C(16)	120.1(5)		
C(17)-C(16)-C(15)	119.5(5)		
C(16)-C(17)-C(18)	120.8(5)		
C(17)-C(18)-C(13)	120.8(5)		
N(2)-C(19)-C(13)	115.4(3)		
O(1)-C(20)-N(3)	123.9(5)		
O(1)-C(20)-C(21)	128.2(5)		
N(3)-C(20)-C(21)	107.8(4)		
C(20)-C(21)-C(22)	106.3(4)		
C(23)-C(22)-C(21)	105.1(4)		
O(2)-C(23)-N(3)	124.6(5)		
O(2)-C(23)-C(22)	127.8(5)		
N(3)-C(23)-C(22)	107.6(4)		
N(4)-C(25)-C(26)	119.7(4)		
N(4)-C(25)-C(24)	121.5(4)		
C(26)-C(25)-C(24)	118.7(4)		
C(27)-C(26)-C(25)	128.3(4)		

Experimental

^{succ}*Nacnac*^{Bn}H. (*Nacnac*)^{Bn}Li(THF) (3.0 g, 68 mmol) and NBS (1.8 g, 97 mmol) were mixed in THF (150 mL) to give a yellow-brown suspension. After stirring for 24h at 60 °C under static vacuum a brown suspension was obtained. The reaction mixture was cooled to room temperature and 1, 4-dioxane (5 mL) was added to complete the precipitation of LiCl. After stirring for a further 30 minute, the mixture was filtered through a pad of celite. The resulting brown solution was evaporated to give a brown solid. The product was extracted in toluene (200 mL). Evaporation of the solvent gave brown solid (1.5 g, 60%). Crystals suitable for X-ray were grown by dissolving the brown solid in a DCM and then layering with equal amount of hexane. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 12.84 (bs, 1H, NH), 7.20 (m, 10H, C_6H_5), 4.46 (s, 4H, Bn CH_2), 2.84 (s, 4H, $CH_2C(=O)$), 1.73 (s, 6H, MeC(=N)).). ^{1}13C NMR ($CDCl_3$, 101 MHz, 298 K): δ 178.3 (C=O), 159.9 (C=N), 139.9 (*ipso* Ph), 128.4 (*ortho* Ph), 127.3 (*para* Ph), 126.6 (*meta* Ph), 97.0 ($C(C=N)_2$), 50.9 (Bn CH_2), 28.0 ($Me(C=N)_2$), 14.5 ($CH_2C(=O)$). Anal. Calcd. for $C_{23}H_{25}N_3O_2$: C, 73.58; H, 6.71; N, 11.19. Found: C, 73.08; H, 6.69; N, 10.64.

^{succ}*Nacnac*^{Bn}Cu(styrene)

^{succ}*Nacnac*^{Bn}H (100 mg, 0.29 mmol), CuO*t*Bu (40 mg, 0.30 mmol) and styrene (94 mg, 0.90 mmol) were dissolved in toluene (6 mL). The resulting brown solution was stirred for 30 minutes. The solution was evaporated and the residue washed twice with hexane (10 mL). Residual solvent was removed on the vacuum line to obtain dark-brown solid (139 mg, 89%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.12-7.16 (m, 10H, C_6H_5), 4.15-4.70 (m, 4H, Bn CH_2 & 1H, CH olefin), 3.45 (d, 1H, J = 14 Hz CH_2 olefin), 3.19 (d, 1H, J = 9 Hz CH_2 olefin) 1.92 (s, 4H, $CH_2C(=O)$), 1.64 (s, 6H, CH_3 MeC(=N)). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 177.7 (C=O), 164.7(C=N), 142.2 (*ipso* Bn), 139.6 (*ipso*, styrene) 129.3 (*ortho*, styrene), 128.8 (*meta or ortho* Bn), 126.9 (*para*, styrene) , 126.4 (*meta or ortho* Bn), 125.7 (*meta*, styrene), 98.8 ($C(C=N)_2$), 90.2 (CH, styrene), 67.1 (CH_2, styrene), 58.2 (Bn CH_2), 27.9 ($CH_2C(=O)$), 16.4 ($Me(C=N)_2$). One peak (*para* Bn) is missing.

^{succ}*Nacnac*^{Bn}Cu(1-hexene)

^{succ}*Nacnac*^{Bn} (100 mg, 0.29 mmol) was dissolved in toluene (6 mL) to afford a brown solution. 1-hexene (140 mg, 1.6 mmol) and CuO*t*Bu (40 mg, 0.30 mmol) were added. After stirring for 30 min, the brown solution was layered with hexane (6 mL) and kept at -30 °C from which few crystals of compound **3** were obtained.

For NMR characterization, ^{succ}*nacnac*^{Bn}H (10 mg, 27 μmol) was dissolved in C_6D_6 (0.7 mL) to afford a brown solution. 1-hexene (3.5 mg, 41 μmol) and CuO*t*Bu (4.0 mg, 30 μmol) were added. The resulting solution was transferred to an A. J. Young tube. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.10-7.23 (m, 10H, C_6H_5) , 4.80 (s, 4H, CH_2 Bn), 3.97-3.91 (m, 1H, olefinic CH 1-hexene), 3.12 (m, 2H, olefinic CH_2, 1-hexene), 1.95 (s, 4H, $CH_2C(=O)$) 1.71 (s, 6H, *Me*$(C=N)_2$), 1.24-0.70 (m, 9H, Butyl of 1-hexene). ^{13}C NMR (C_6D_6, 101 MHz, 298 K): δ 177.9 (C=O), 164.8(C=N), 142.2 (*ipso* Bn), 128.8 (*ortho* Bn), 126.5 (*para* Bn), 126.3 (*meta*, Bn), 98.7 (*C*$(C=N)_2$), 93.4 (CH, styrene), 72.3 (CH_2, styrene), 58.7 (CH_2, Bn), 33.1, 32.8. 28.0 (*C*$H_2C(=O)$), 22.3, 16.5 (*Me*$(C=N)_2$), 14.0.

X-ray diffraction studies. Compounds **1** and **3** were crystallized from a toluene and dichloromethane solution at –30 °C during attempts to recrystallize *nacnac*^{Bn}Cu(acrylonitrile) and ^{succ}*nacnac*^{Bn}Cu(1-hexene) or *nacnac*^{Bn}Cu(styrene) respectively while compound **2** crystallized from an oxygen contaminated THF solution at –30 °C in the course of preparing *nacnac*^{Bn}Cu(*trans*-stilbene). Data sets for **1** and **3** were recorded on a Bruker SMART 6000 with Montel 200 monochromator, while that of compound **2** was collected on a Bruker Microstar-Proteum with Helios optics, both equipped with a rotating anode source for Cu Kα radiation (λ = 1.54178 Å). Cell refinement and data reduction were performed using APEX2.[1] Absorption corrections were applied using SADABS.[2] Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on calculated positions using a riding model. The co-crystallized solvent was identified as dichloromethane based on electron count but could not be resolved and was thus suppressed by application of SQUEEZE.

Table VII: Details of X-ray diffraction studies

		8.1	**8.2**	**8.3**
Formula		$C_{22}H_{25}N_3$	$C_{38}H_{44}N_4O_2Cu_2$	$C_{46}H_{48}N_6O_4Cu$
Mw(g/mol); $d_{calcd.}$(g/cm^3)		331.45; 1.162	715.85; 1.435	285.89; 1.277
CCDC N^o		773446	773445	773447
T (K); F(000)		150 ; 712	150; 374	150; 3416
Crystal System		Monoclinic	Triclinic	Monoclinic
Space Group		$P2_1/n$	P-1	C2/c
Unit Cell:	*a* (Å)	9.7742(3)	5.4783(3)	20.1736(6)
	b (Å)	17.6962(6)	11.8231(5)	9.6549(2)
	c (Å)	10.9336(4)	13.4079(5)	45.6035(10)
	α (°)	90	72.210(2)	90
	β (°)	90.060(2)	85.367(2)	102.361(1)
	γ(°)	90	87.367(2)	90
V (Å^3); Z		1891.14(11); 4	828.51(7); 1	8676.4(4); 8
θ range (°); completeness		4.75-72.39; 0.86	3.45-67.95; 0.86	1.98-72.64
Refl.: collec./indep.; R_{int}		24544/3213; 0.062	13326/2604; 0.055	56558/3833; 0.175
μ (mm^{-1}); abs. corr		0.532; SADABS	1.893; SADABS	1.096; SADABS
R1(F); wR(F^2); GoF(F^2) [a]		0.0419; 0.1111; 0.912	0.0405; 0.1145; 1.043	0.0775; 0.1862; 0.868
Residual electron density		0.185; -0.182	0.334, -0.768	0.509; -0.493

[a] R1(F) based on observed reflections with I>2σ(I), wR(F^2) and GoF(F^2) based on all data.

References

(1) *APEX2*, Release 2.1-0; Bruker AXS Inc.: Madison, USA, 2006.

(2) Sheldrick, G. M. *SADABS*, Bruker AXS Inc.: Madison, USA, 1996 & 2004.

(3) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.