ORGANOMETALLICS
Article

Organometallics **2009,** *28,* 4089–4097 4089
DOI: 10.1021/om9002279

Bis(2-phenylethyl)-*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

Received March 25, 2009

The chiral diketiminate ligand bis-*N*,*N*′-(2-phenylethyl)-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 were obtained by reaction of the ligand with a basic copper source in the presence of coordinating Lewis bases, and **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) have been prepared 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 past 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-diisopropylphenyl 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 economical way to introduce chirality into diketiminate ligands. We report here the synthesis of *N*,*N*′-bis(2-phenylethyl)-*nacnac*H, **1**H, 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 acetyl acetone with a primary amine yielded the monosubstituted product 4-ketiminpropan-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

*Corresponding author. E-mail: Frank.Schaper@umontreal.ca.

(1) Kim, W. K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541.
(2) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031.
(3) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.
(4) York, J. T.; Llobet, A.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2007**, *129*, 7990. Brown, E. C.; Bar-Nahum, I.; York, J. T.; Aboelella, N. W.; Tolman, W. B. *Inorg. Chem.* **2007**, *46*, 486.
(5) York, J. T.; Young, V. G.Jr.; Tolman, W. B. *Inorg. Chem.* **2006**, *45*, 4191.
(6) Badiei, Y. M.; Krishnaswamy, A.; Melzer, M. M.; Warren, T. H. *J. Am. Chem. Soc.* **2006**, *128*, 15056. Kogut, E.; Wiencko, H. L.; Zhang, L.; Cordeau, D. E.; Warren, T. H. *J. Am. Chem. Soc.* **2005**, *127*, 11248.
(7) Badiei, Y. M.; Warren, T. H. *J. Organomet. Chem.* **2005**, *690*, 5989.
(8) Park, K.-H.; Bradley, A. Z.; Thompson, J. S.; Marshall, W. J. *Inorg. Chem.* **2006**, *45*, 8480. Thompson, J. S.; Bradley, A. Z.; Park, K.-H.; Dobbs, K. D.; Marshall, W. *Organometallics* **2006**, *25*, 2712.
(9) Oguadinma, P. O.; Schaper, F. *Inorg. Chim. Acta* **2008**, *362*, 570.
(10) Dorman, L. C. *Tetrahedron Lett.* **1966**, 459. Bradley, A. Z.; Thorn, D. L.; Glover, G. V. *J. Org. Chem.* **2008**, *73*, 8673.
(11) Budzelaar, P. H. M.; de Gelder, R.; Gal, A. W. *Organometallics* **1998**, *17*, 4121.

Published on Web 07/02/2009

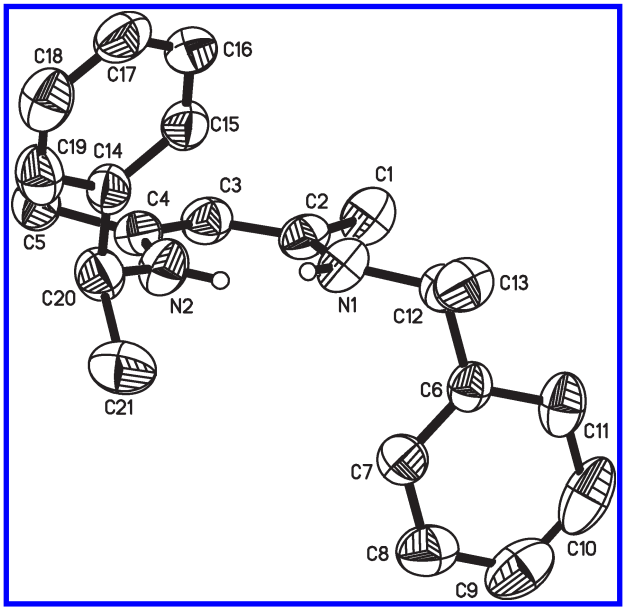
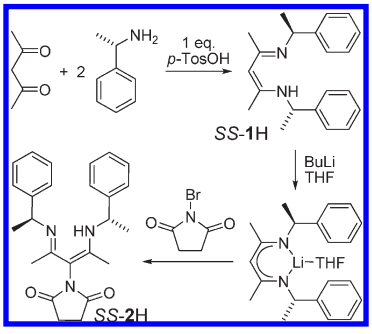


Figure 1. Crystal structure of *SS*-**1**H. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except the disordered NH, were omitted for clarity.

Scheme 1



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.

Crystals suitable for an X-ray diffraction study of *SS*-**1**H and *RR*-**2**H were obtained from ethanol at −20 °C (Figure 1, Table 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-iminopent-2-enes[13−16] ranged from apparent delocalization (Δ_{C-C}, $\Delta_{C-N} < 0.01$ Å)[13] to clear bond alternation ($\Delta_{C-C} = 0.08$ Å, $\Delta_{C-N} = 0.06$ Å).[16] For **1**H, small differences in the C3−C2/C4 and C−N bond lengths ($\Delta_{C-C} = 0.02$ Å, $\Delta_{C-N} = 0.02$ 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 to orientate its hydrogen atom toward the methyl group of the ligand backbone. Ligand **2**H displays, as expected, the same general geometry (Figure 2, Table 2), with the methine-hydrogen toward the ligand backbone. In contrast to **1**H, the double bonds are substantially localized, as indicated by differences in the C3−C2/C4 and C−N bond lengths of $\Delta_{C-C} = 0.06$ Å and $\Delta_{C-N} = 0.05$ 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 2).

Table 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

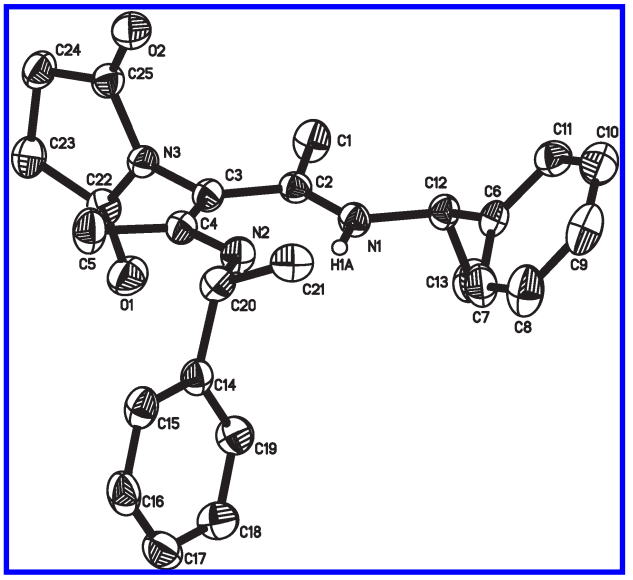


Figure 2. Crystal structure of *RR*-**2**H. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except NH, were omitted for clarity.

Complex Syntheses. Protonation of CuO^tBu 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^tBu 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

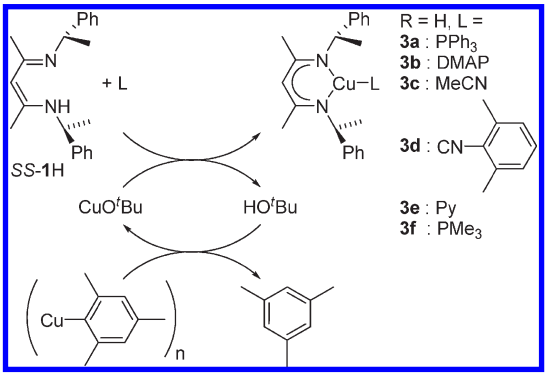
(12) Buch, F.; Harder, S. *Z. Naturforsch., B: Chem. Sci.* **2008**, *63*, 169.
(13) Bailey, P. J.; Liddle, S. T.; Parsons, S. *Acta Crystallogr., Sect. E* **2001**, *57*, o661.
(14) Stender, M.; Wright, R. J.; Eichler, B. E.; Prust, J.; Olmstead, M. M.; Roesky, H. W.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **2001**, 3465. Brownstein, S.; Gabe, E. J.; Prasad, L. *Can. J. Chem.* **1983**, *61*, 1410. Hsu, S. H.; Chang, J. C.; Lai, C. L.; Hu, C. H.; Lee, H. M.; Lee, G. H.; Peng, S. M.; Huang, J. H. *Inorg. Chem.* **2004**, *43*, 6786. Cole, S. C.; Coles, M. P.; Hitchcock, P. B. *Organometallics* **2004**, *23*, 5159.
(15) Aboelella, N. W.; Gherman, B. F.; Hill, L. M. R.; York, J. T.; Holm, N.; Young, V. G.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2006**, *128*, 3445.
(16) Hamaki, H.; Takeda, N.; Yamasaki, T.; Sasamori, T.; Tokitoh, N. *J. Organomet. Chem.* **2007**, *692*, 44.
(17) Dai, X.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 10085.

Table 2. Selected Bond Distances [Å] and Bond Angles [deg] for *SS*-1H, *SS*-2H, *SS*-3a−c, and *SS*-4d[a]

	SS-1H	*RR*-2H	*SS*-3a	*SS*-3b[b]	*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[c]			2.195(1)	1.97 ± 0.02	1.890(1)	1.813(4)
X−Y[c]			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[c]			129.85(4)	124 - 134	120.63(5)	130.73(13)
N2−Cu1−X[c]			130.37(4)		138.07(5)	130.75(14)
tors. C=N−C_{Bn}−H[d]	34 ± 10	34 ± 2	15 ± 12	17 ± 29	14 ± 26	11 ± 1
complex bending[e]			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[f]	118.5 ± 0.9	119.3 ± 2.1	114.8 ± 0.4	116 ± 1	114.7 ± 0.4	118 ± 1
C2/C4=N−C[g]	124.2 ± 0.6	124.0 ± 1.2	118.3 ± 0.4	119 ± 3	118.4 ± 1.3	121 ± 1
Cu−N−C12/20[h]			121.5 ± 0.3	122 ± 3	121.7 ± 1.6	115.8 ± 0.6

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

Scheme 2



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-tetramer.[18] CuMes could be employed as a copper source, however, in the presence of catalytic amounts of either *tert*-butanol or CuO^{t}Bu. We propose a catalytic cycle, where CuO^{t}Bu reacts with **1**H and is regenerated by reaction of *tert*-butanol with CuMes (Scheme 2). While no difference in reactivity between CuO^{t}Bu and CuMes/CuO^{t}Bu was observed in any reactions, we found that products obtained by reaction with CuMes/CuO^{t}Bu were sometimes easier to isolate by crystallization, probably due to the absence of large amounts of *tert*-butanol.

Reaction of *SS*-**1**H with CuMes/CuO^{t}Bu or with CuO^{t}Bu in the presence of PPh_3, *N*,*N*′-dimethylaminopyridine (DMAP), or MeCN in toluene at room temperature yielded after crystallization from toluene/hexane at −30 °C the corresponding ligand-coordinated copper complexes *SS*-**3a**−**c** in 65−80% yield (Scheme 2). While **3a**+**b** 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-xylylisonitrile 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-$Me_2C_6H_3$-NC)Cu(O^{t}Bu)}$_4$ by X-ray crystallography (Figure 3). Since reactions were usually complete

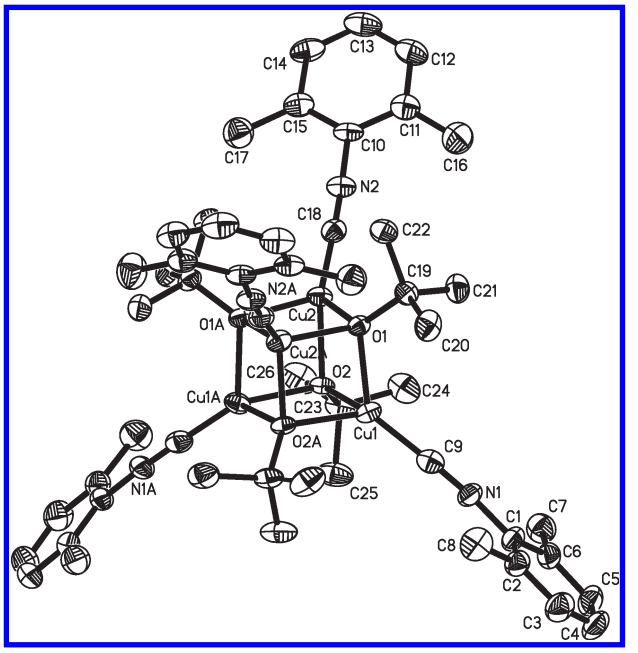


Figure 3. Crystal structure of {(2,6-$Me_2C_6H_3$-NC)Cu(O^{t}Bu)}$_4$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

(18) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

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-xylylisonitrile yielded the Lewis-base-coordinated complexes **2**Cu(PPh_3), **4a**, and **2**Cu($CNC_6Me_2H_3$), **4d**, respectively.

Since copper complexes **3** and **4** could not, in contrast to their aryl-substituted analogues, be obtained 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. ^{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 if CuMes/CuO^{t}Bu was employed as a copper source. After 1 h, NMR spectra became difficult to interpret due to the instability of **3c**. Complete conversion to the complexes **3a,b**+**d** and the putative complexes **3e**+**f** was observed in the presence of PPh_3, DMAP, 2,6-xylylisocyanide, pyridine, or PMe_3 (Scheme 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 styrene did not yield any Cu(I) complex, but strongly colored suspensions. In the presence of 2,6-xylylisonitrile, 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 toward 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 that have proved unreactive toward 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. 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** in only 8% conversion (compared to unreacted **2**H). Further addition of 4 equiv of pyridine increased the percentage of **4e** to 23%, while addition of 2 equiv of *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 (cf. Figure 3). Reactions with 2,6-xylylisonitrile 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 1).

Dynamic Processes in Solution. The coordinated Lewis base in complexes **3a**−**f** exchanges fast on the NMR time scale at room temperature with excess base present, and only average 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 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 average 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 and B, in a 2:1 ratio for the *nacnac* ligand. Only one signal was observed for MeCN, corresponding to 1 equiv of 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 for **3a**−**c** 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 4, Table 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 (Δ_{C-C} = 0.016 Å, Δ_{C-N} = 0.017 Å, Table 2). Similar to the free ligand **1**H, the chiral N-substituent orients its

(19) Oguadinma, P. O.; Schaper, F. Unpublished results.

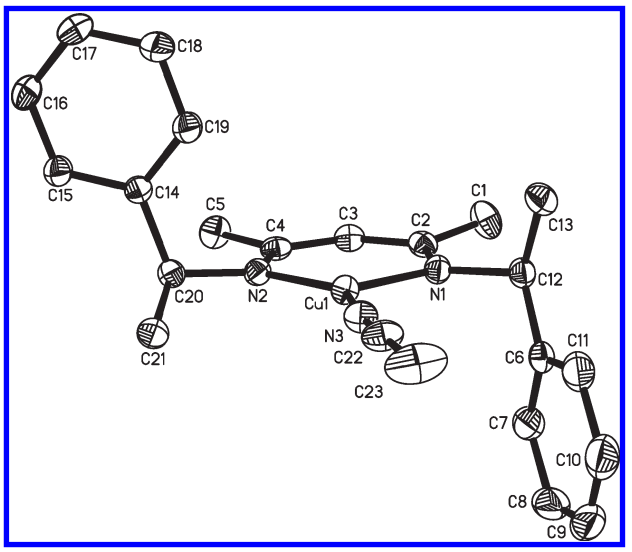


Figure 4. Crystal structure of *SS*-**3c**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

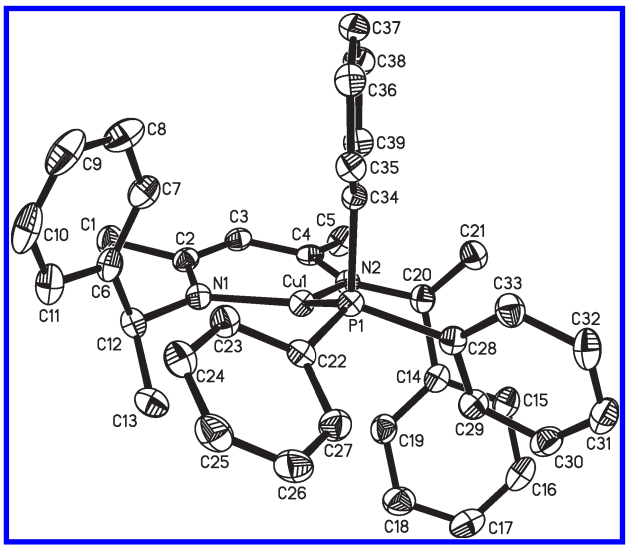


Figure 5. Crystal structure of *SS*-**3a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

hydrogen substituent toward 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 **1H** 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 toward the ligand backbone (C=N−C_{Ar} 117−122°) with values for C_{Ar}−N−Cu of 114−122°.[21] Corresponding values of the average Me−N−C12/22 and the C12/22−N−Cu angles in **3c** (and as well as in **3a**+**b**, *vide infra*) are at the extremes of these ranges, 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 toward 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 **1H** 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 Supporting Information).

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 5, bending angle in Table 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) and 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 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-phenylethyl substituent remains orientated toward the ligand backbone (see average torsion angle in Table 2) and that average 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.

The DMAP-coordinated complex *SS*-**3b** crystallizes with four independent molecules in the asymmetric unit, each with slightly different torsion angles (Figure 6). The structural data are of relatively low quality (due to the quality of the obtained single crystal), and only general structural features will be discussed (Table 2). Coordination of DMAP is comparable to acetonitrile coordination in **3c** in the rather

(20) Hill, L. M. R.; Gherman, B. F.; Aboelella, N. W.; Cramer, C. J.; Tolman, W. B. *Dalton Trans.* **2006**, 4944. Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 2108.

(21) Based on 27 *nacnac* Cu(I) complexes with nonchelating substituents found in the Cambridge Structural Database. Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *B58*, 380.

(22) Reynolds, A. M.; Lewis, E. A.; Aboelella, N. W.; Tolman, W. B. *Chem. Commun.* **2005**, 2014.

Table 3. Details of X-ray Diffraction Studies

	SS-**1**H	*RR*-**2**H	*SS*-**3c**	*SS*-**3b**	*SS*-**3a**	*SS*-**4d**	{(RNC)Cu (O^{t}Bu)}$_4$
formula	$C_{21}H_{26}N_2$	$C_{25}H_{29}N_3O_2$	$C_{23}H_{28}CuN_3$	$C_{28}H_{35}CuN_4$	$C_{39}H_{40}CuN_2P$	$C_{34}H_{37}CuN_4O_2$	$C_{52}H_{72}Cu_4N_4O_4$
M_w (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; 1.308	1071.30; 1.331
T (K); F(000)	150; 332	150; 864	150; 864	150; 2080	150; 1328	150; 1256	150; 2240
cryst syst	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 (deg)	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 (deg); completeness	3.9−71.1; 0.99	4.3−72.5; 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
reflns: collec/ indep; R_{int}	11 088/1929; 8.8%	28 674/2474; 3.2%	48 406/6597; 2.6%	68 189/19992; 4.0%	73 790/10102; 3.5%	39 607/5976; 4.8%	34 639/5249; 4.0%
μ (mm^{-1}); abs corr	0.483; multiscan	0.617; multiscan	1.062; multiscan	1.332; multiscan	0.758; multiscan	1.299; multiscan	2.133; multiscan
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-param			0.019(8)	0.05(3)	0.015(6)	−0.05(3)	0.01(2)
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 $I > 2\sigma(I)$, wR(F^2), and GoF(F^2) based on all data.

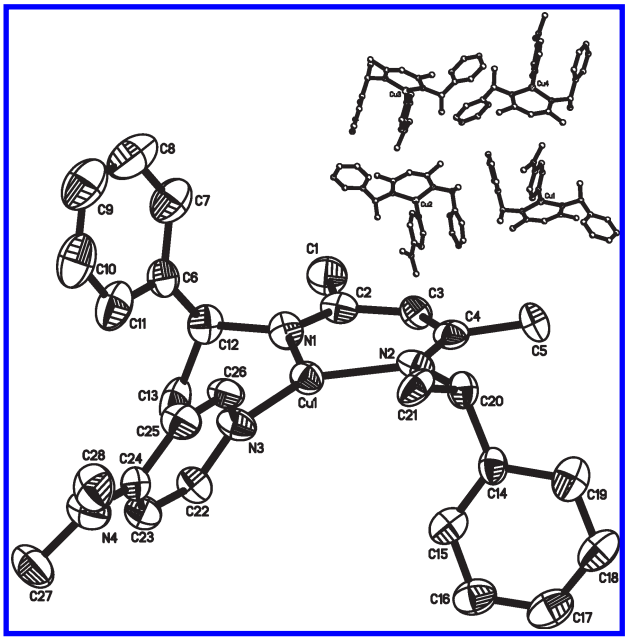


Figure 6. Crystal structure of *SS*-**3b**. Only one of four independent molecules is shown. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. The inset displays the orientation of the four independent molecules in the asymmetric unit.

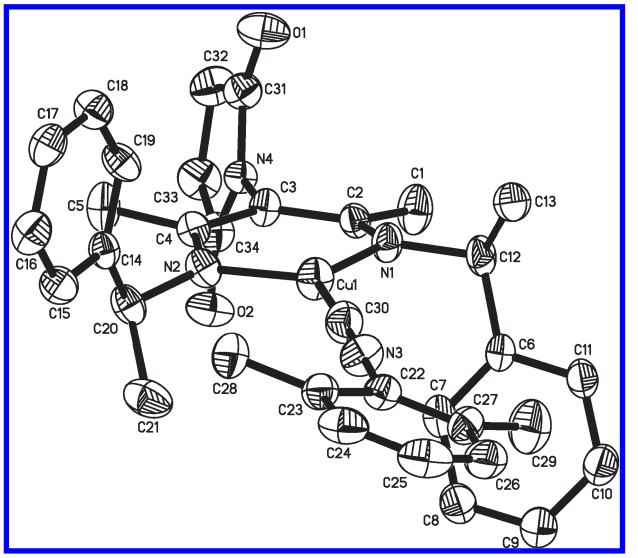


Figure 7. Crystal structure of *SS*-**4d**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

unsymmetrical binding of the DMAP ligand (Δ(N−Cu−N$_{DMAP}$) = 2−10°). The in-plane coordination of the copper atom (cf. complex bending angle of 4 ± 2° in Table 2) and the N1−Cu1−N2 angles (101.3 ± 0.5°) are also strongly comparable to those found in **3c**.

The lack of strong steric interactions in **4d** (Figure 7, Table 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 its 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**−**c** and **4d** and reduces the Me−C2/4−C3 angle by 3−4° in **3a**−**c** (Table 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

(23) Jazdzewski, B. A.; Holland, P. L.; Pink, M.; Young, V. G.; Spencer, D. J. E.; Tolman, W. B. *Inorg. Chem.* **2001**, *40*, 6097.

Cu−N−C12/20 bond angle compared to **3a**−**c** (Table 2), thus indicating an increased steric crowding around the copper center in this complex.

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 = $Me_3C_6H_2$, 5.2 ppm;[7] Ar = $Me_2C_6H_3$, 5.4 ppm;[5] Ar = $^iPr_2C_6H_3$, 3.6 ppm[22]). The signal for the succinimide-substituted complex **4a** is observed at 3.6 ppm. Average P−C bond lengths in **3a** (Table 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 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** toward disproportionation, which correlates with their reduced reactivity toward CuO^{t}Bu, seems to be of steric rather than of electronic origin. While partial, slow conversion to the acetonitrile complex **3c** and complete conversion to the 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.

(24) Orpen, A. G.; Connelly, N. G. *Chem. Commun.* **1985**, 1310.

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 deoxygenated by repeated extraction with nitrogen. C_6D_6 was distilled from Na and deoxygenated by three freeze−pump−thaw cycles. CuO^{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 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). Elemental analyses were performed by the Laboratoire d'Analyse Elémentaire (Université de Montréal).

2-(*S*-2-Phenylethyl)amino-4-(*S*-4-phenylethyl)iminopent-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 was 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%). ^{1}H NMR ($CDCl_3$ 400 MHz): 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) (*c* 10^{-3} g/mL, toluene).

2-(*R*-2-Phenylethyl)amino-4-(*R*-4-phenylethyl)iminopent-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) (*c* 10^{-3} g/mL, toluene).

2-(*S*-2-Phenylethyl)amino-3-succinimido-4-(*S*-4-phenylethyl)-iminopent-2-ene, *SS*-2H. *n*-BuLi (1.5 mL, 2.9 M, 4.4 mmol) was added dropwise over a period of 45 min 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 min. 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.)

(25) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658.

(26) Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 192.

(*SS*-1)Cu(PPh$_3$), 3a. *SS*-**1**H (250 mg, 0.82 mmol), mesityl copper (150 mg, 0.83 mmol), CuO^{t}Bu (11 mg, 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 −35 °C. 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* and 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} = 2 Hz, *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) and filtered through a plug of Celite, and the filtrate was 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* and *ortho* DMAP CH), 5.58 (bs, 2H, *meta* DMAP) 5.07 (q, 2H, J = 6 Hz C*H*(Me)Ph), 4.78 (s,1H, CH(C=N)$_2$), 2.12 (s, 6H, DMAP Me) 1.93 (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, 400 MHz, 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 (N*C*CH$_3$) 95.1 (*C*H(C=N)$_2$), 59.2 (*C*H(Me)Ph), 27.3 (*MeC*(=N)), 23.0 (CH(*Me*)Ph), 0.2 (NC*CH*$_3$). 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): ^{1}H NMR (C_6D_6, 400 MHz, 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 (N*C*CH$_3$) 95.1 *C*H(C=N)$_2$), 59.2 (*C*H(Me)Ph), 30.4 (*Me*C(=N), 26.1 (CH(*Me*)Ph), 0.2 (NC*C*H$_3$).

(*SS*-1)Cu(CNC$_6$H$_3$Me$_2$), 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 min, the solution was evaporated to give a yellow-brown oil (152 mg, 92%) (4 mL). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 6.99−7.56 (m, 10H, CHMe(*Ph*)), 6.71 (t, 1H, J = 8 Hz, *para* $C_6H_3Me_2$), 6.55 (d, 2H, J = 8 Hz, *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 (*C*H(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 6.96−7.48 (m, 25H, CH(Me)*Ph* and P*Ph*$_3$), 4.89 (q, 2H, J = 7 Hz C*H*(Me)Ph), 1.97 (s, 4H, $CH_2C(=O)$), 1.77 (s, 6H, C(=N)Me), 1.42 (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$_2$C(=O)), 24.8 (*Me*C(=N)), 17.7 (CH(*Me*)Ph). Two signals missing. ^{31}P{^{1}H} NMR (C_6D_6, 75 MHz, 298 K): 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-xylylisonitrile (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 min, 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$_2$C(=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* and 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* and 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**+**c**) 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 isotropically on calculated positions using a riding model. Further experimental details are listed in Table 3 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.

(27) *APEX2, Release 2.1-0*; Bruker AXS Inc.: Madison, WI, 2006.
(28) Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112.

Acknowledgment. Funding for this research was provided by the Natural Sciences and Engineering Research Council of Canada and the Université de Montréal. We thank Francine Bélanger and Dr. Michel Simard for their support with the crystal structure determinations, and Prof. Dr. André B. Charette for the use of his polarimeter.

Supporting Information Available: Details of the X-ray diffraction studies (CIF) and calculation of the lateral aperture angle. This material is available free of charge via the Internet at http://pubs.acs.org.