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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

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N,*N*'-Dibenzyl-4-amino-2-iminopent-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**, allyl phenyl ether; **5**, stilbene; **7**, xylylisonitrile; **8**, triphenylphosphine). With diphenylacetylene (DPA) the dimeric complex $\{(nacnac^{Bn})Cu\}_2(\mu\text{-DPA})$, **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 the 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 toward the olefin.

Introduction

Copper(I) η^2-olefin complexes are involved as intermediates or resting states in a number of catalytic reactions and in industrial applications and were investigated as biomimetic 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 dominating.[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 one-sixth to one-third of the covalent bonding.[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 back-bonding 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

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

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Table 1. 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)−1.926(6)	1.941(1)	1.955(1)
Cu1−N2	1.919(2)	1.908(3)	1.922(1)		1.941(1)	1.933(1)
Cu1−X/CH_2(CHR)[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) and 2.019(1)			
X−Y[a]	1.385(4)	1.388(4)	1.391(2)	1.291(10) and 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

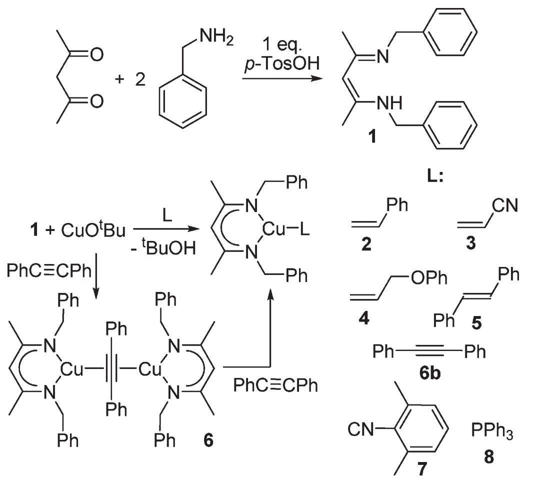
[a] C26−C27 (**2**); C20−C21 (**3**); C32−C33 (**5**); C28−N3 (**7**); P1−C20/C26/C32 (**8**). [b] Cu1−C26 (**2**); Cu1−C20 (**3**). [c] Cu1−C27 (**2**); Cu1−C21 (**3**); Cu1−C32, Cu1−C33 (**5**). [d] Torsion angle: Cu1−C26−C27−C20 (**2**); Cu1−C20−C21−C22 (**3**); Cu−C33−C32−C20, Cu1−C32−C33−C26 (**5**).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

π back-bonding and a clear preference to coordinate electron-deficient olefins.

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 yields of 80% by direct condensation of benzylamine and acetylacetone in the presence of 1 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 CuO*t*Bu with **1** in the presence of the respective olefin/Lewis base in toluene or ether (Scheme 1). The use of copper mesityl as an alternative copper source in the presence of catalytic amounts of CuO*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 recrystallization). Complexes **2−8** are colorless to yellow solids, which are sensitive to air, but 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 the presence of acetonitrile led to decomposition products. We have previously shown that for the related di(methylbenzyl)diketimine ligand a lack of reactivity toward 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 1



Crystal Structure Studies. The crystal structures of complexes **2**, **3**, and **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** and **8** and an *anti* conformation in **2**, **3**, **5**, and **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 1) 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 1) do not correlate with the steric demand of the coordinated Lewis base.

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The olefinic bond of coordinated styrene in **2** (1.385(4) Å, Figure 1, Table 1) is significantly elongated compared to that of the free olefin (1.318(2) and 1.325(2) Å).[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$_{\mathrm{Ph}}$ 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 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 stronger 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.

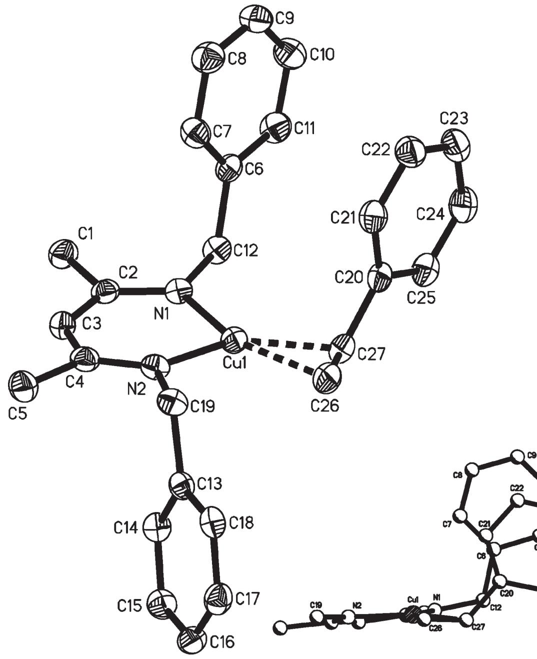

Figure 1. Crystal structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. The inset shows the π-stacking interaction between styrene and one benzyl substituent.

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 2, Table 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) and 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-squares planes of 20° and without any superposition of nitrile and phenyl substituents. The reason for this apparent repulsion is the formation of a

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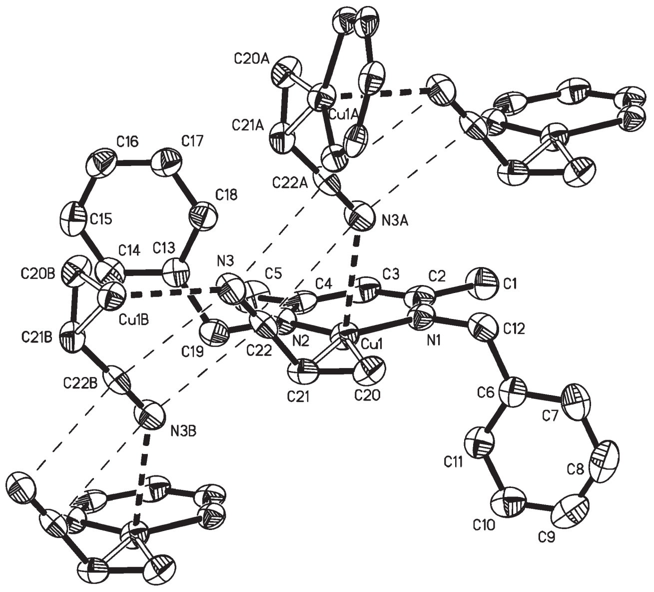

Figure 2. Crystal structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Additional fragments were generated using the symmetry operations 1−*x*, *y*−0.5, 0.5−*z* (A) and 1−*x*, 0.5+*y*, 0.5−*z* (B).

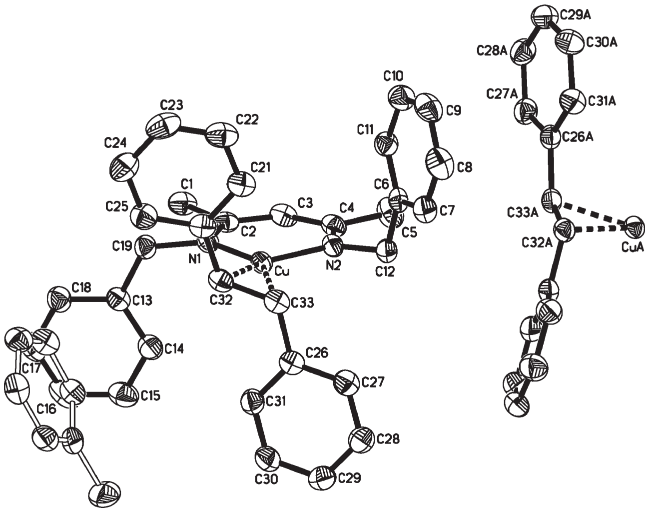

Figure 3. Crystal structure of **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. The cocrystallized toluene molecule is disordered around an inversion center. The π-stacked fragment was generated by 0.5−*x*, 0.5+*y*, 0.5−*z*.

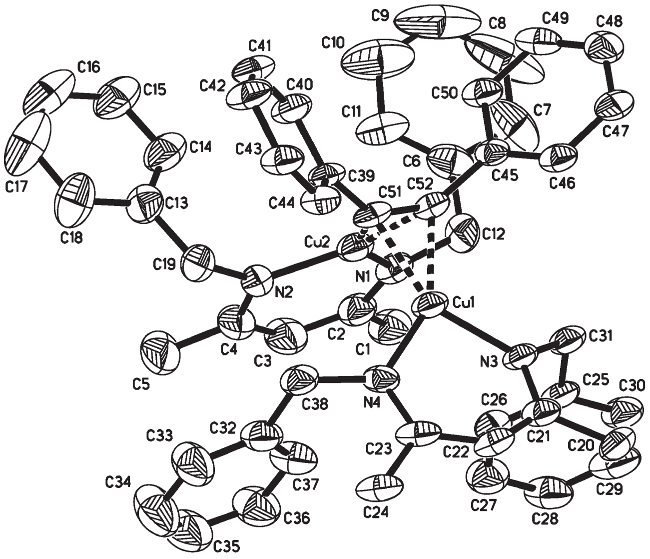

Figure 4. Crystal structure of **6**. Only one of two independent molecules in the unit cell is shown. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

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 copper 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 1, 7°) indicate that the interaction is probably mostly electrostatic in character and of minor importance.

The coordination of *trans*-stilbene in **5** (Figure 3, Table 1) 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 cocrystallized toluene molecule is sandwiched between two benzyl substituents not involved in π-stacking interactions with stilbene in an edge-on CH−π interaction.

The crystal structure of **6** (Figure 4, Table 1) 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

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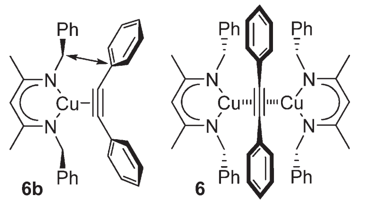
(35) Castonguay, A.; Sui-Seng, C.; Zargarian, D.; Beauchamp, A. L. *Organometallics* **2006**, *25*, 602. Tasker, P.; Parkin, A.; Higgs, T. C.; Parsons, S.; Messenger, D. *Private communication to the CSD database*, **2005**, CCDC 278228. Davidson, J. L.; Richtzenhein, H.; Thiebaut, B. J. S.; Landskron, K.; Rosair, G. M. *J. Organomet. Chem.* **1999**, *592*, 168. Chin, C. S.; Chong, D.; Lee, S.; Park, Y. J. *Organometallics* **2000**, *19*, 4043. Kumar, P. G. A.; Pregosin, P. S.; Vallet, M.; Bernardinelli, G.; Jazzar, R. F.; Viton, F.; Kundig, E. P. *Organometallics* **2004**, *23*, 5410. Yang, Z.; Ebihara, M.; Kawamura, T. *J. Mol. Catal. A: Chem.* **2000**, *158*, 509.

(36) Based on 15 structures for free *trans*-stilbene and 19 stilbene complexes in the CSD database.

(37) Doyle, G.; Eriksen, K. A.; Van Engen, D. *Inorg. Chem.* **1983**, *22*, 2892. Reger, D. L.; Huff, M. F. *Organometallics* **1992**, *11*, 69. Schmidt, G.; Behrens, U. *J. Organomet. Chem.* **1996**, *509*, 49.

Scheme 2



(1.29(1) and 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) and 2.635(2) Å) are slightly shorter (cf. 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 that 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 potential 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 and the *ipso*-carbon atom of diphenylacetylene when the latter is located in the mean ligand plane (Scheme 2). A complex comparable to **6b**, (N,N'-di-(iBu)diketiminato)Cu($Me_3SiCCSiMe_3$), showed a strongly increased bending between the mean diketiminato−copper and acetylene−copper planes of 22°, which is absent in the corresponding acetylacetonate complex.[12]

Structures **7** and **8** (Figures 5 and 6, Table 1) 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 toward the benzyl groups, indicating that the *syn*-orientation of the benzyl substituents observed in **7** is caused by an attractive $CH_3-\pi$ 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 and 2.20 Å, respectively)[13] that are longer than those in corresponding *N*-aryl-substituted diketiminato 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.

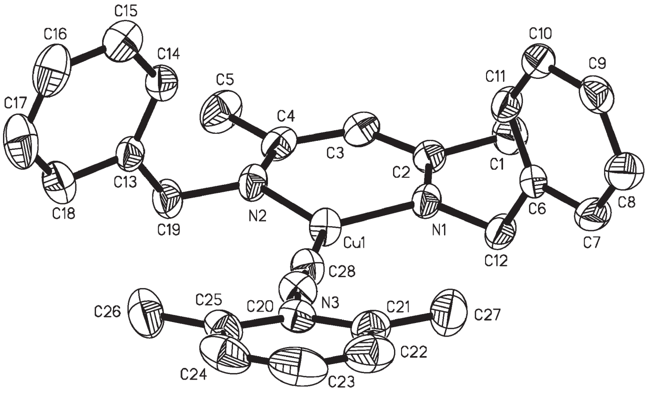


Figure 5. Crystal structure of **7**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

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 cross-peaks 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 free 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 1 and 2). 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; that is, 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 nonsymmetric complex featuring two methyl resonances and four 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)

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[38] Villacorte, G. M.; Gibson, D.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6732. Villacorta, G. M.; Gibson, D.; Williams, I. D.; Whang, E.; Lippard, S. J. *Organometallics* **1987**, *6*, 2426. Aalten, H. L.; Van Koten, G.; Riethorst, E.; Stam, C. H. *Inorg. Chem.* **1989**, *28*, 4140. Reger, D. L.; Huff, M. F.; Wolfe, T. A.; Adams, R. D. *Organometallics* **1989**, *8*, 848. Olbrich, F.; Behrens, U.; Gröger, G.; Weiss, E. *J. Organomet. Chem.* **1993**, *448*, C10.

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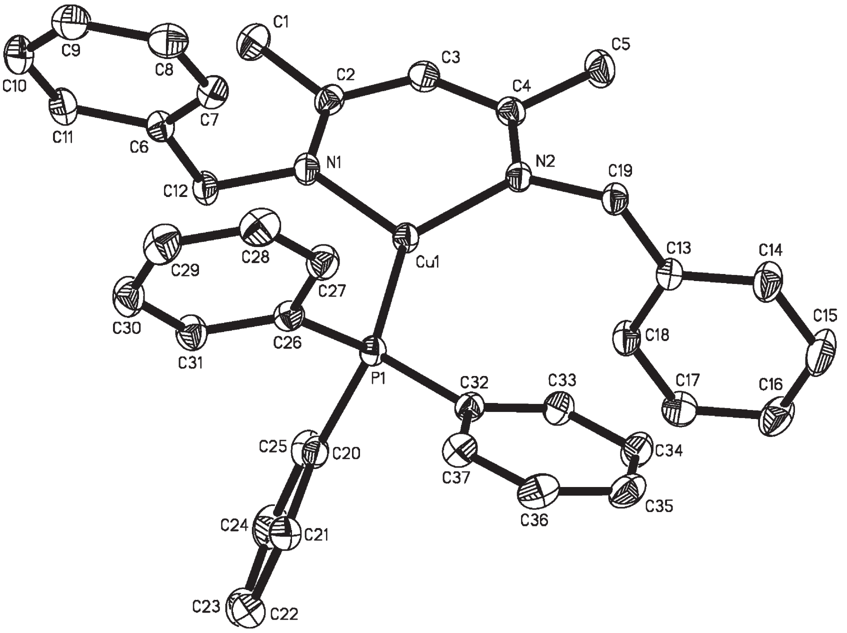

Figure 6. Crystal structure of **8**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

(see Supporting Information). 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 2). 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 by electronic reasons and might be related either to decreased π back-bonding in this system[44] or to the sterically undemanding four-membered metallacycle.

Table 2. Olefin Rotation Barriers in LCu^{I}(styrene) complexes with Bidentate Ligands L

LCu	styrene rotation	$k/k(\mathbf{2})^a$	reference
nacnac^{Xyl}Cu	$\Delta G^{\ddagger}_{215K}$ = 10.7(3) kcal/mol	50	25
tBu$_2$P{(Me$_3$Si)N}$_2$Cu	$\Delta G^{\ddagger}_{180K}$ = 37.0 kJ/mol	6×10^4	43
(bipyridine)Cu$^+$	fast at 180 K	$> 10^5$	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, 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. 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 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**, and **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 spectrum is in the fast exchange region). Since olefin exchange with traces of free olefin was already notable at this temperature for **2** and would be expected to be even faster for **3**, we cannot delineate 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

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(43) Straub, B. F.; Gruber, I.; Rominger, F.; Hofmann, P. *J. Organomet. Chem.* **2003**, *684*, 124.

(44) Srebro, M.; Mitoraj, M. *Organometallics* **2009**, *28*, 3650.

(45) Bryan, S. J.; Huggett, P. G.; Wade, K.; Daniels, J. A.; Jennings, J. R. *Coord. Chem. Rev.* **1982**, *44*, 149.

(46) Rosenblum, M.; Turnbull, M. M.; Kohinoor Begum, M. *J. Organomet. Chem.* **1987**, *321*, 67. del Rio, I.; Gossage, R. A.; Hannu, M. S.; Lutz, M.; Spek, A. L.; van Koten, G. *Organometallics* **1999**, *18*, 1097.

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 poorly 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 the form of the M−C=C−C_{Ph} torsion angle) for structurally characterized styrene complexes (Figure 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 7, back-bonding in **2** is still rather weak, but more important than in other reported Cu(I) styrene complexes.

In ^{13}C NMR spectra of **2**, resonances of the olefinic carbon atoms are displaced by 47−48 ppm toward higher field when compared to those of the free olefin. The amount of this displacement is a measure of the amount of charge delocalization toward 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 8). The olefinic carbon atoms of the coordinated styrene in **2** show $^1J_{CH}$ coupling constants of 172 and 161 Hz, significantly higher than those in free styrene (CH(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

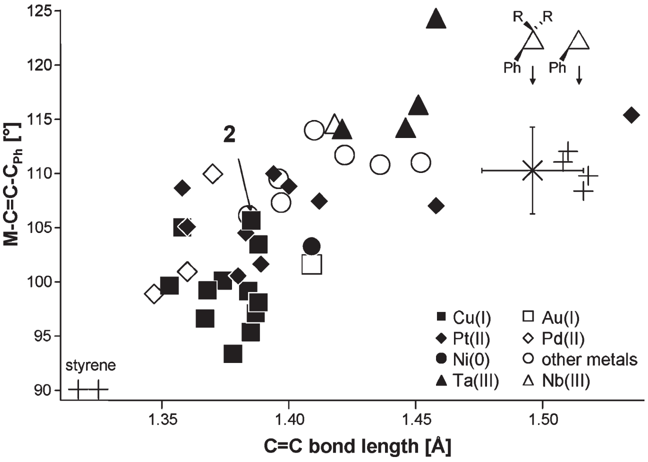

Figure 7. Correlation between the length of the coordinated double bond and the bending of the phenyl substituent out of the olefinic plane in structurally characterized transition metal styrene complexes. Only high-quality structures with R1 values lower than 5% were considered. Outliers with double 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.

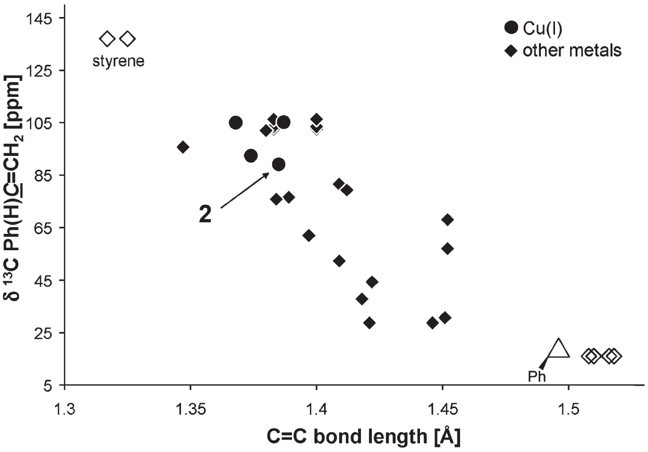

Figure 8. Correlation between crystallographically determined lengths of the olefinic bond and the displacement of the benzylic carbon atom in ^{13}C NMR spectra of transition metal styrene complexes.

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

(48) Averages of the P−C bond distances in six structures for triphenylphosphine in the CSD database.

(49) Based on seven $(R_3P)_3NiPPh_3$ and 33 $L_nCr^0PPh_3$ structures in the Cambridge Structural Database.

(50) Reedy, B. J.; Murthy, N. N.; Karlin, K. D.; Blackburn, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 9826. Rhames, F. C.; Murthy, N. N.; Karlin, K. D.; Blackburn, N. J. *JBIC, J. Biol. Inorg. Chem.* **2001**, *6*, 567. Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Le Pape, L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307. Petrovic, D.; Bannenberg, T.; Randoll, S.; Jones, P. G.; Tamm, M. *Dalton Trans.* **2007**, 2812. Petrovic, D.; Hill, L. M. R.; Jones, P. G.; Tolman, W. B.; Tamm, M. *Dalton Trans.* **2008**, 887.

(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 $\Delta\delta$ 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 δ(CHPh) in ^{13}C spectra. Relative errors in the latter two were too 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.

(52) Boer, J. S. A. M. d.; Loopstra, B. O.; Stam, C. H. *Rec. Trav. Chim. Pays-Bas* **1987**, *106*, 537.

(53) Averages from 55 structures of 1-phenyl, 2-R, 2-R′-cyclopropanes in the Cambridge Structural Database.

(54) Straub, B. F.; Eisenträger, F.; Hofmann, P. *Chem. Commun.* **1999**, 2507.

(55) Christine, H. *Chem.−Eur. J.* **2004**, *10*, 5888.

(56) Koole, N. J.; Bie, M. J. A. d.; Hansen, P. E. *Org. Magn. Reson.* **1984**, *22*, 146.

Table 3. Chemical Displacement of Coordinated Olefins in ^{13}C NMR Spectra and Equilibrium Constants of Olefin Exchange Reactions (benzene-d_6, room temperature)

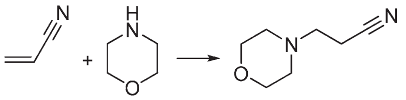
complex	coordinated olefin	δ CH_2, ppm	δ CH(R), ppm	$\Delta\delta$,[a] ppm	K = [Cu-olefin][styrene]/[Cu-styrene][olefin]
3	acrylonitrile	70.6	54.0	53−66	6.2 ± 20%[b]
2	styrene	67.1	89.1	47−48	1
4	$H_2C{=}C(H)CH_2OPh$	71.7	84.8	45−49	0.9 ± 20%[b]
	$H_2C{=}C(H)OEt$				< 0.01
5	*trans*-stilbene		85.0	20	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 (CHPh); acrylonitrile, 136.5 (CH_2), 107.4 (CHCN); $H_2C{=}C(H)CH_2OPh$, 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**.

upfield shift (Figure 8) indicate, however, that **2** has relatively little metallacyclopropane character.

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 3. The smallest displacement is observed for the stilbene complex **5**, followed by allyl phenyl ether 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 3 indicate 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 that 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 allyl phenyl ether yielded comparable binding constants.[58] No free styrene was observed even in the presence of a large excess of ethyl vinyl ether, 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 3)[59] and indicate a preferential binding of electron-poor olefins to the diketiminato copper complex investigated here. While acrylonitrile binds only moderately stronger 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.

Scheme 3



The reduced coordination constant for *trans*-stilbene indicates that, as usually observed in copper olefin complexes, steric interactions are more important than electronic differences. In agreement with the importance of steric effects, diketiminato 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 ethyl vinyl ether). While intramolecular π−π interactions were observed only 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 dominating influence on the olefin binding strength.

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** toward nucleophilic attack. Uncatalyzed reaction of acrylonitrile and morpholine in benzene-d_6 for 24 h at 60 °C led to 30−50% hydroamination of acrylonitrile (Scheme 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 catalyzes 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 1 equiv of morpholine in benzene-d_6 at 60 °C for 24 h yielded only unreacted **3** and morpholine. Thus not only does the presence of the diketiminate ligand favor 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

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(57) Navon, N.; Masarwa, A.; Cohen, H.; Meyerstein, D. *Inorg. Chim. Acta* **1997**, *261*, 29.

(58) *Para*-substitution of the phenyl substituent in styrene proved to be an effect too subtle to be determined with high accuracy, and values for 4-methoxystyrene and 4-fluorostyrene were in the margin of error difficult to distinguish from styrene. A reduced binding for 4-methoxystyrene compared to 4-fluorostyrene was indicated, however.

(59) The averaged upfield shift of the olefinic protons in ^{1}H NMR spectra correlates neither with the $\Delta\delta$ in the ^{13}C spectra nor with the exchange constants K. Given the aromatic rings in varying orientations close to the olefinic protons, this is hardly surprising.

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

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.

The ability of β-diketiminate ligands to favor metal–ligand back-donation has been previously noted by others. Holland and co-workers 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 diketiminato 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*$^{\mathrm{Mes}}$ ligand (Mes = 2,4,6-Me$_3$C$_6$H$_2$) they prepared.[39] Tolman and co-workers 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 toward nucleophilic attack. In summary, the observed high degree of π back-donation in *nacnac*$^{\mathrm{Bn}}$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 toward 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, for example, 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 toward nucleophilic attack and the slow olefin rotation justify describing **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 glovebox techniques. Solvents were dried by passage through activated aluminum oxide (MBraun SPS) and deoxygenated by repeated extraction with nitrogen. C$_6$D$_6$ was distilled from Na and deoxygenated by three freeze–pump–thaw cycles. CuO*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$_6$D$_5$*H*, δ 7.15; *C*$_6$D$_6$, δ 128.02) or external reference (^{31}P, 75% H$_3$PO$_4$). ^{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-iminopent-3-ene, *nacnac*$^{\mathrm{Bn}}$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$_2$CO$_3$ (30 g in 150 mL of H$_2$O). The aqueous phase was extracted with 3 × 100 mL of toluene. The combined organic phases were dried over Na$_2$SO$_4$, filtered, and evaporated to give a beige solid, which was recrystallized from hot EtOH (4.4 g of colorless 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 C*H*$_2$), 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

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meta Bn), 126.4 (*para* Bn), 95.1 (H*C*(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 one-eighth of its volume and layered with 2 mL of hexane. A colorless 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 and styrene), 4.75−4.52 (m, 6H, C*H$_2$*Ph, HC(C=N)$_2$ and Ph*H*C=), 3.45 (d, J = 14 Hz, 1H, *cis* H$_2$C=), 3.19 (d, J = 9 Hz, 1H, *trans* H$_2$C=), 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 ($^1J_{CH}$ = 172 Hz, Ph*HC*=), 67.1 ($^1J_{CH}$ = 161 Hz, H$_2$*C*=), 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$_2$C=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 and *cis* H$_2$C=), 2.39 (d, J = 9 Hz, 1H, *trans* H$_2$C=), 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$_2$*C*=), 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 two drops of DMSO were added to the toluene solution before layering with hexane at −35 °C for 24 h.

(*Nacnac*^{Bn})Cu(H$_2$C=CHCH$_2$OPh), 4. CuO*t*Bu (137 mg, 1.0 mmol), **1** (300 mg, 1.1 mmol), and allyl phenyl ether (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 and OPh), 4.68−4.79 (m, 5H, Bn CH$_2$ and 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$_2$C=), 3.16 (d, J = 9 Hz, 1H, *trans* H$_2$C=), 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$_2$*C*=), 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 of **1** (200 mg, 0.72 mmol), CuO*t*Bu (100 mg, 0.73 mmol), and *trans*-stilbene (130 mg, 0.72 mmol) was added toluene (4 mL) 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 and 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). CuO*t*Bu (49 mg, 0.36 mmol) was dissolved in ether (4 mL) to give a yellow solution and added to the original solution. 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 and 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 and 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 of hexanes yielded a white solid (760 mg, 70%). After 1 day, additional colorless crystals were obtained from the hexane wash. ^{1}H NMR (C_6D_6 400 MHz): δ 7.22−6.86 (m, 25H, PPh$_3$ and 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 missing). ^{31}P NMR (C_6D_6, 101 MHz): δ 3.5. Anal. Calcd for $C_{37}H_{36}N_2PCu$: C, 73.67; H, 6.02; N, 4.69. Found: C, 73.82; H, 6.52; N, 4.91.

(*nacnac*^{Bn})CuCN(C$_6$Me$_2$H$_3$), 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 from the NMR

Table 4. Details of X-ray Diffraction Studies

	2	**3**	**5**	**6**	**7**	**8**
formula	$C_{27}H_{29}N_2Cu$	$C_{22}H_{24}N_3Cu$	$C_{33}H_{33}N_2Cu \cdot 0.5\ C_7H_8$	$C_{26}H_{26}N_2Cu_2$	$C_{28}H_{30}N_3Cu$	$C_{37}H_{36}N_2PCu$
M_w (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
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$C2/c$	$P\bar{1}$
unit cell: a (Å)	24.5143(5)	14.3009(7)	11.3531(4)	11.317(2)	17.3118(6)	11.1477(11)
b (Å)	5.6499(1)	6.0688(3)	11.6674(4)	11.331(2)	17.0767(6)	11.2906(11)
c (Å)	15.9542(3)	22.7308(11)	21.9442(7)	36.015(7)	15.9761(5)	12.9378(13)
α (deg)				93.520(6)		101.041(3)
β (deg)	101.0520(10)	102.916(2)	94.6670(10)	98.623(6)	93.694(2)	107.854(2)
γ (deg)				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 (deg); 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
reflns: 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 $I > 2\sigma(I)$; wR(F^2) and GoF(F^2) based on all data.

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 ensure an unchanged olefin/styrene ratio. Diphenylacetylene:[Cu] ratios were > 10, to avoid the presence of **6** instead of **6b**.

(*nacnac*$^{\mathbf{Bn}}$)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, $-C_6H_4F$ and Bn), 4.43−4.75 (m, 6H, Bn CH$_2$, =C(*H*)C$_6$H$_4$F and HC(C=N)$_2$), 3.32 (d, J = 14 Hz, 1H, *cis* H$_2$C=), 3.12 (d, J = 9 Hz, 1H, *trans* H$_2$C=) 1.82 (s, 6H, Me(C=N)$_2$).

(*nacnac*$^{\mathbf{Bn}}$)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 and $-C_6$*H*$_4$OMe), 4.51−4.77 (m, 6H, Bn CH$_2$, =C(*H*)C$_6$H$_4$OMe and HC(C=N)$_2$), 3.43 (d, J = 14 Hz, 1H, *cis* H$_2$C=), 3.38 (s, 3H, OMe), 3.15 (d, J = 9 Hz, 1H, *trans* H$_2$C=) 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** and **5**−**7**), and a Bruker Microstar-Proteum with Helios optics (**2**), 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 isotropically on calculated positions using a riding model. Further experimental details are listed in Table 4 and given in the Supporting Information.

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Supporting Information Available: Details of the X-ray diffraction studies (CIF). VT-NMR specta. This material is available free of charge via the Internet at http://pubs.acs.org.

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