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Mononuclear Bis(imino)arylcopper(I) N-Heterocyclic Carbene Complex: Synthesis, Structure, and Reaction with Organic Azide

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Mononuclear bis(imino)arylcopper(I) N-heterocyclic carbene compound [(IPM)CuL] {**1**, L = 2,6-(RN=CH)$_2$-4-*t*BuC$_6$H$_2$, R = 2,6-*i*Pr$_2$C$_6$H$_3$, IPM = C[N(*i*Pr)CMe]$_2$} has been synthesized, structurally characterized, and its reaction with 1-adamantyl azide investigated. The reaction of a less bulky arylcopper(I) compound [(IPM)CuPh] with the azide was also studied. The formation of the corresponding products [(IPM)CuN(1-ad)-NN(L)] (**2**) and [(IPM)CuN(Ph)NN(1-ad)] (**3**) (1-ad = 1-adamantyl) reveals an aryl group transfer (L in **2** and Ph in **3**) reactivity pattern mediated at Cu^{I} with the support of the N-heterocyclic carbene. However, a Cu–N$_{1\text{-ad}}$ σ-bond and a Cu···N$_L$ weak bond were observed in the structure of **2**, significantly different to the bonding in **3** in which a Cu–N$_{Ph}$ σ-bond and a Cu···N$_{1\text{-ad}}$ weak bond were indicated. This may suggest an initial N$_T$ (N$_T$, terminal N atom of the azide) coordination of the azide at the Cu center followed by aryl group transfer to N$_T$. Complex **2** may undergo further bond rearrangement of the Cu···N bonds within a pseudo-CuN$_3$ four-membered ring as a result of the large bulk of the ligand L.

Introduction

The use of an N-heterocyclic carbene (NHC) for the formation of a cationic-type copper(I) complex was first reported by Arduengo et al. in 1993.[1] Subsequently, neutral copper(I) N-heterocyclic carbene compounds were prepared by Raubenheimer and co-workers.[2] In recent years N-heterocyclic carbenes have been extensively employed to stabilize copper(I) species, especially the more reactive organocopper(I) compounds.[3] These studies revealed interesting coordination chemistry, generated by the introduction of the N-heterocyclic carbene, and the copper(I) compounds were formed in low nuclearity with the metal center having a low coordination number. Moreover, N-heterocyclic carbenes found promise as supporting ligands in copper-mediated reactions. This led to some important catalytic applications in organic synthesis.[4,5] It was found that the reaction of copper(I) compounds, which are usually stabilized by sterically demanding ligands, with organic azides can occur by direct end-on nitrogen coordination of the azide group at Cu^{I}[6] or by further N$_2$ release to form Cu–nitrene derivatives.[7] More recently, Straub and co-workers reported the reaction of an alkynylcopper(I) N-heterocyclic carbene complex with an organic azide and the successful isolation and structural characterization of the copper(I) triazolide intermediate.[8] This clearly revealed the well-known Cu^{I}-mediated Huisgen–Sharpless 1,3-dipolar cycloaddition process.[9] Furthermore, it indicated a nontransferable reactivity of the alkynyl group at Cu^{I} when interacting with the azido functionality with the support of the N-heterocyclic carbene at Cu^{I}. This type of reactivity has also been strongly considered in conjugated addition reactions.[10] However, it contrasts with the reactivity of other organylcopper(I) compounds, such as alkyl- and arylcopper ones, which generally exhibit group-transferable reactivity with a wide range of unsaturated substrates.[11]

So far the reactions of alkyl- or arylcopper(I) compounds with organic azides have not been explored. In this context, we investigated the reactions of arylcopper(I) compounds with an 1-adamantyl azide. A new mononuclear bis(imino)arylcopper(I) N-heterocyclic carbene compound [(IPM)CuL] {**1**, L = 2,6-(RN=CH)$_2$-4-*t*BuC$_6$H$_2$, R = 2,6-*i*Pr$_2$C$_6$H$_3$, IPM = C[N(*i*Pr)CMe]$_2$}, in which L is an NCN pincer-type ligand, was synthesized as a precursor, because an N-heterocyclic-carbene-free arylcopper(I) compound reacting with the azide does not give an informative result.[12] Compound **1** exhibits two types of solid-state structures, revealing a weak intramolecular Cu···N$_{iminyl}$ interaction instead of a stable chelating coordination of L as NCN pincer ligand. Compound **1** reacted with N$_3$(1-ad) to afford a cop-

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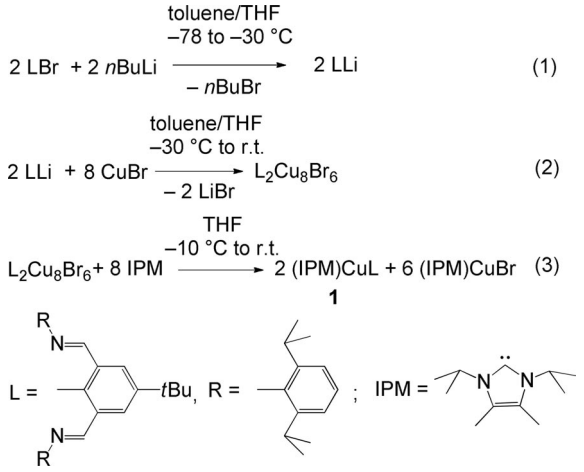
per(I) triazenide [(IPM)CuN(1-ad)NN(L)] (**2**, 1-ad = 1-adamantyl). The reaction of a less bulky (aryl)Cu^{I} compound [(IPM)CuPh] with the azide was also carried out to explore the mode of interaction between the N_3 group and the copper center under the stabilization of the N-heterocyclic carbene.

Results and Discussion

The preparation of N-heterocyclic-carbene-stabilized mononuclear compound [(IPM)CuL] {**1**, L = 2,6-(RN=CH)$_2$-4-*t*BuC_6H_2, R = 2,6-*i*Pr$_2C_6H_3$, IPM = C[N-(*i*Pr)CMe]$_2$} is illustrated in Scheme 1. Bis(imino)arylllithium (LLi) was prepared from LBr and *n*BuLi under controlled temperature (–78 to –30 °C) and directly used in the reaction with 4 equiv. of CuBr from –30 °C to room temperature. This reaction afforded a red solid product, which was identified as an octanuclear bis(imino)arylcopper(I)–copper(I) bromide cluster [$L_2Cu_8Br_6$], in good yield (75%).[13] Treatment of this cluster compound with 8 equiv. of IPM in THF smoothly led to its complete dissociation to **1** together with the byproduct [(IPM)CuBr].[14] An attempt to obtain **1** by reaction of [(IPM)CuBr] with LLi formed in situ was not successful.



Scheme 1. Synthesis of **1**.

[(IPM)CuBr] was easily separated as a colorless crystalline solid by removal of the THF solvent and precipitation using *n*-hexane. Orange crystals of **1a** were grown by maintaining the *n*-hexane solution of **1** at –10 °C for 1 week. However, these orange crystals surprisingly changed to light-yellow after being kept at –10 °C for about 1 month by decanting the solvent. Redissolving the light-yellow crystals in *n*-hexane gave an orange solution from which light-yellow crystals of **1b** were grown after being kept at –10 °C for 2 weeks. Upon measuring the melting point, the crystals of **1a** gradually changed from orange to light-yellow at 102 °C, and both **1a** and **1b** finally melted at 165 °C.

^{1}H and ^{13}C NMR analyses show that **1a** and **1b** have the same data. This indicates **1a** and **1b** are the same compound both in composition and in structure in solution. In the ^{1}H NMR spectrum, one set of resonances, which includes one doublet at δ = 1.22 ppm and one septet at δ = 4.22 ppm corresponding to the methyl and methine protons of the two *i*Pr groups, respectively, and one singlet at δ = 1.45 ppm attributed to the two methyl protons of the imidazole ring, were observed for the IPM ligand. Another set of resonances was assigned to the L ligand in which one doublet at δ = 1.18 ppm and one septet at δ = 3.37 ppm correspond to the methyl and methine protons of the four *i*Pr groups, one singlet at δ = 1.42 ppm to the *tert*-butyl, and at δ = 8.50 and 8.74 ppm to the two isophthalyl and two iminyl HC=N protons, respectively. These data suggest that in solution the groups in **1a** and **1b**, whether from the IPM or from the L ligand, are located in a symmetrically steric environment. Nonetheless, the X-ray diffraction studies clearly reveal that **1a** and **1b** have different solid-state structures. Compound **1a** crystallizes in the space group *P*2(1)/*c* and **1b** in the space group $P\bar{1}$. The crystal structures of **1a** and **1b** are illustrated in Figures 1 and 2, respectively, along with selected bond lengths and angles. In the structure of **1b**, the Cu center is coordinated by L and IPM in a nearly linear geometry [C_L–Cu–C_{IPM} 173.8(3)°]. The Cu–C_L bond of 1.916(6) Å is a little longer than that of the Cu–C_{IPM} one [1.885(7) Å]. The former distance is comparable to those found in similar arylcopper(I) N-heterocyclic carbene compounds [Cu–C_{ipso} 1.910(2)–1.922(4) Å], whereas the latter is a little shorter [Cu–C_{NHC} 1.902(3)–1.911(4) Å].[3a] Both HC=N protons of the large bulky iminyl groups point towards the Cu center. This structural feature is significantly different to that in **1a**, in which one is directed towards the Cu center and the other away from the center. Thus, in **1a** one of the iminyl groups is close to the Cu atom, giving rise to a Cu(1)···N(2) distance of 2.604 Å. This distance is significantly shorter than that of Cu(1)···N(1) (4.560 Å) and those of Cu···N_{iminyl} in **1b** (4.367–4.520 Å), but it is much longer than the distance predicted by the sum of the covalent radii (2.00 Å)[15] and also longer than that observed in [3-(2,6-diisopropylphenyl)-1-(2-pyridyl)imidazol-2-ylidene]cuprous bromide [2.454(5) Å].[16] This may indicate a weak intramolecular Cu(1)···N(2) interaction in **1a**, which may be the cause of the structural difference between **1a** and **1b** as well as the color difference in their solid states. As a result of this interaction, the Cu–C_{IPM} bond [1.901(3) Å] becomes a little longer by 0.016 Å and the C_{ipso}–Cu–C_{IPM} angle [170.26(15)°] smaller by 3.5°, although other related bond parameters remain almost unchanged [N=C: 1.265(4) and 1.271(4) Å in **1a** and 1.263(6) and 1.270(6) Å in **1b**; Cu–C_{ipso}: 1.916(3) Å in **1a**]. The ligand L normally behaves as an NCN pincer ligand and acts to stabilize mononuclear metal compounds.[17] However, in [$L_2Cu_8Br_6$] it leads to a large aggregation including an inorganic CuBr component. The use of the N-heterocyclic carbene enables the formation of the mononuclear compound, but prevents the L ligand from chelating coordination.

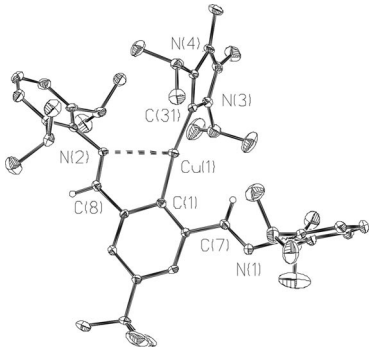


Figure 1. Crystal structure of **1a** at the 50% thermal ellipsoid level. Selected bond lengths [Å] and angles [°]: Cu(1)–C(1) 1.916(3), Cu(1)–C(31) 1.901(3), C(7)–N(1) 1.266(4), C(8)–N(2) 1.271(4), Cu(1)···N(2) 2.604, Cu(1)···N(1) 4.560, Cu(1)···H(7A)C(7) 2.845; C(1)–Cu(1)–C(31) 170.26(15).

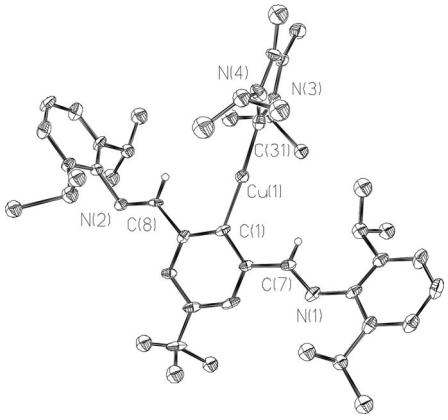


Figure 2. Crystal structure of **1b** at the 50% thermal ellipsoid level. Selected bond lengths [Å] and angles [°]: Cu(1)–C(1) 1.916(6), Cu(1)–C(31) 1.885(7), C(7)–N(1) 1.270(6), C(8)–N(2) 1.263(6), Cu(1)···H(8A)C(8) 2.860, Cu(1)···H(7A)C(7) 2.624, Cu(1)···N(1) 4.367, Cu(1)···N(2) 4.520; C(1)–Cu(1)–C(31) 173.8(3).

Compounds **1a** and **1b** show differences in the solid state although they exhibit the same structural features in solution. This could imply an equilibrium established between the structures of **1a** and **1b** in solution. However, the VT ^{1}H NMR studies of **1** recorded in [D_8]toluene showed that only one set of proton resonances for L and IPM was observed from 298 to 198 K and even from 198 back to 298 K (see the Supporting Information). This suggests that the formation of the different solid-state structures of **1** may be a result of different packing during crystallization, and this packing may give rise to the secondary Cu···N_{iminyl} interaction in **1a**. Thus, we performed density functional theory (DFT) studies to investigate in detail this issue.[18] The free-electron energy difference between **1a** and **1b** was computed to be temperature-dependent. At 0 K the structure of **1a** is predicted to be more stable than that of **1b** by around 1.15 kcal/mol, whereas at 300 K the latter is more stable by 0.61 kcal/mol. At 195 K there is almost no energy difference between them. Clearly, very low temperatures favor the structure of **1a** although these data are calculated to be small. However, further computations indicated that the entropy of the structure of **1a** is always around 5.70 cal/mol K lower than that of **1b** within this temperature range. This is in agreement with **1a** having a structure a little more compact than **1b** due to the weak Cu···N interaction. Thus, the thermal conversion of **1a** into **1b** at elevated temperatures during the melting-point measurement should be attributed to an entropy-driven process, as it is with the solid-state structural transformation of **1a** into **1b** on standing for a long time at a low temperature (–10 °C). Furthermore, the structural difference between **1a** and **1b** can be considered to be a result of a rotation of one of the iminyl groups along the C_{aryl}–C_{iminyl} bond. In solution this rotation barrier may be dynamically negligible, and the possible equilibrium between the **1a** and **1b** structures was difficult to detect. Thus, **1a** and **1b** have the same solution NMR spectroscopic data.

The reaction of **1** with 1-adamantyl azide [N_3(1-ad)] was carried out in toluene at an elevated temperature (100 °C) for 3 d. After workup, removal of the solvent under vacuum followed by extraction with *n*-hexane gave the product [(IPM)CuN(1-ad)NN(L)] (**2**). Compound **2** was characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray crystallography. The resonances at δ = 1.28–1.35 (m), 1.77 (br.), 1.93 (br.), 2.19–2.25 (m), and 2.49 (br.) ppm have been assigned to the 1-ad protons of the azide. Two separated singlets at δ = 8.28 and 9.20 ppm correspond to the two iminyl HC=N protons and at δ = 8.07 and 8.97 ppm to the two isophthalyl protons, as well as two septets at δ = 3.15 and 3.43 ppm to the methine proton resonances of the four isopropyl groups of L. These data suggest an asymmetric steric environment of these groups.

Further crystal structural analysis indicated compound **2** to be a clear L-transfer product. The molecular structure of **2** is shown in Figure 3. IPM is coordinated to Cu with a Cu–C_{IPM} bond length of 1.874(4) Å, a little shorter than those in **1a** and **1b**. The transfer of L to the terminal N atom of the azide leads to a triazenido moiety in which the N_3 functionality adopts a bent structure [N(5)–N(6)–N(7) 110.5(3)°]. The N(5)–N(6) [1.289(4) Å] bond is a little shorter than N(6)–N(7) [1.305(4) Å], but they are both longer than those in [(HB{3,5-$(CF_3)_2$Pz}$_3$)CuNNN(1-ad)] [1.136(4), 1.219(4) Å][7] with a linear N_3 group. These distances are shorter than the single N–N bond (1.45 Å).[19] This indicates electron delocalization over the bent N_3 moiety in **2**. The Cu(1)–N(7) bond length of 1.879(3) Å indicates σ-bonding, whereas the Cu(1)···N(5) distance of 2.610 Å, which is comparable to that in **1a**, suggests a weak bonding. This bonding mode is seldom observed[20] and can be described as a type of bond intermediate between mono- and bidentate bonding. Thus, Cu(1)N(5)N(6)N(7) forms an ideal plane (Δ = 0.0141 Å); however, this plane is at an angle of 46.1° to the isophthalyl ring, deviating from 90°. This array may reflect a restriction of the free rotation of the large bulky L along the C(1)N(5) axis even in solution and gives rise to the asymmetrically steric environment of L induced by different Cu–IPM and Cu–N(1-ad) structural fragments.

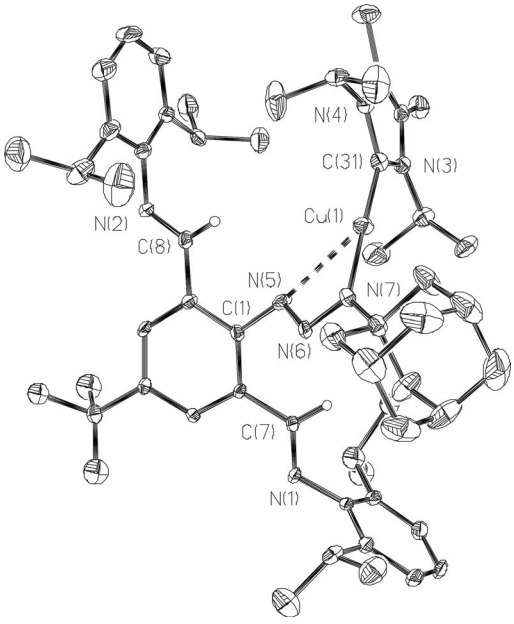
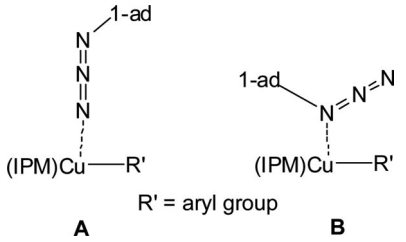


Figure 3. Crystal structure of **2** at the 50% thermal ellipsoid level. Selected bond lengths [Å] and angles [°]: Cu(1)–C(31) 1.874(4), Cu(1)–N(7) 1.879(3), N(7)–N(6) 1.305(4), N(6)–N(5) 1.289(4), Cu(1)···N(5) 2.610; C(31)–Cu(1)–N(7) 175.2(2), N(5)–N(6)–N(7) 110.5(3).

Note that in **2** Cu^{I}-mediated L transfer through the formation of a Cu(1)–N(7) σ-bond could imply CuL addition to the N_3 group at the N_A and N_T atoms (N_A is the alkylated N atom and N_T the terminal N atom of the N_3 group) and suggests an initial interaction pathway like mode B (Scheme 2). Mode B was also suggested in the Cu^{I}-mediated Huisgen–Sharpless 1,3-dipolar cycloaddition mechanism with respect to the Cu=C=CR resonance form of the alkynylcopper(I) moiety.[6] However, Dias, Marynick, and co-workers structurally characterized compound [(HB{3,5-$(CF_3)_2$Pz}$_3$)CuNNN(1-ad)], which exhibits an M–N_T bond similar to mode A, although they also computed only a small energy difference between the M–N_T and M–N_A interactions [$\Delta E = E$(Cu–N_T) – E (Cu–N_A), 4.3 kcal/mol]. Nonetheless, considering the prior chelating coordination character of the triazenido species formed, we attempted the NMR-scale reaction of **1** with N_3(1-ad) in an attempt to detect the possible existence of other coordination compounds, but **2** was formed as the sole product. In the meantime, we prepared a less bulky arylcopper(I) compound [(IPM)CuPh][21] for the reaction with N_3(1-ad) and isolated [(IPM)CuN(Ph)NN(1-ad)] (**3**, Figure 4) as the only product. Structural analysis evidences a similar Ph group transfer through the formation of a Cu–N_{Ph} σ-bond and a Cu···$N_{1\text{-}ad}$ weak bond [Cu(1)–N(3) 1.935(8) Å, Cu(1)···N(5) 2.577 Å]. Accordingly, as shown in Scheme 3, we propose that the reaction of the N-heterocyclic-carbene-stabilized arylcopper(I) compound with the organic azide may proceed through an initial N_T coordination of N_3(1-ad) at the Cu center. Subsequently, the aryl group is transferred to the N_T to form the triazenido copper(I) product. Compound **2** may be formed by further bond rearrangement of the Cu···N weak bond within the pseudo-CuN_3 four-membered ring as a result of the large bulk of the ligand L.



Scheme 2. Two possible interactions between the Cu^{I} center and the N_3 group.

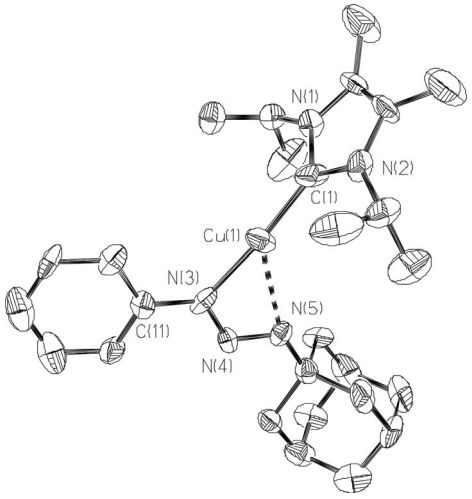
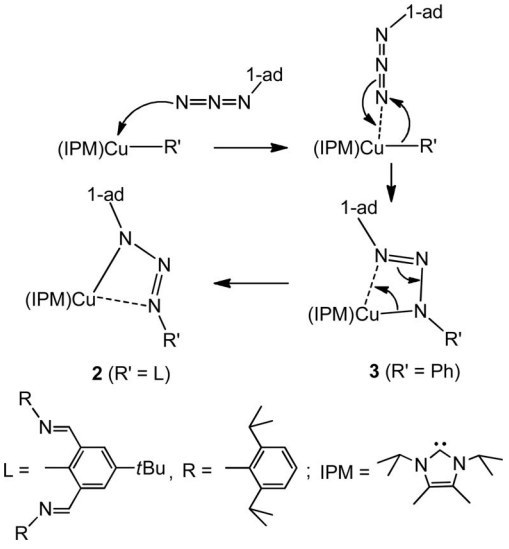


Figure 4. Crystal structure of **3** at the 50% thermal ellipsoid level. Selected bond lengths [Å] and angles [°]: Cu(1)–C(1) 1.862(10), Cu(1)–N(3) 1.935(8), N(3)–N(4) 1.319(9), N(4)–N(5) 1.261(8), Cu(1)···N(5) 2.577; C(31)–Cu(1)–N(7) 172.9(3), N(3)–N(4)–N(5) 111.7(7).



Scheme 3. Proposed mechanism for the formation of **2** and **3**.

Conclusions

By using an N-heterocyclic carbene, a mononuclear bis(imino)arylcopper(I) compound [(IPM)CuL] (**1**) has been prepared. Compound **1** exhibits two types of solid-state structures but only one structure in solution. This may be the result of different solid-state packing of **1** during crystallization giving rise to the weak intramolecular $Cu\cdots N_{iminyl}$ interaction found in **1a**. The reactions of **1** and a less bulky (aryl)Cu^{I} compound [(IPM)CuPh] with N_3(1-ad) gave [(IPM)CuN(1-ad)NNL] (**2**) and [(IPM)CuN(Ph)-NN(1-ad)] (**3**), respectively. This indicates an aryl transfer reaction pattern mediated at the Cu^{I} center with the support of an N-heterocyclic carbene.

Experimental Section

General Procedures: All syntheses and manipulations were carried out under dinitrogen by using standard Schlenk techniques or inside an MBraun Unilab glove-box filled with argon. Solvents were dried with sodium/potassium benzophenone and distilled prior to use. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded with a Bruker AF 400 spectrometer. Melting points were measured in a sealed glass tube by using a Büchi-B 540 instrument. Elemental analyses were performed with a Thermo Quest Italia SPA EA 1110 instrument. Commercially available chemicals were purchased from Aldrich, Acros, Alfa-Assar, or Lvyin Chemical Co and used as received. C[N(*i*Pr)CMe]$_2$ (IPM)[22] and LBr [L = 2,6-(RN=CH)$_2$-4-*t*BuC_6H_2, R = 2,6-*i*Pr$_2C_6H_3$][23] were prepared according to literature procedures.

Synthesis of [$L_2Cu_8Br_6$]: *n*BuLi (0.40 mL, 2.5 M in *n*-hexane, 1.0 mmol) was added dropwise to a solution of LBr (0.59 g, 1.00 mmol) in toluene (25 mL) at –78 °C. The mixture was maintained at this temperature for 1 h and then warmed to –30 °C while stirring. A dark-green solution was formed and added to a precooled (–30 °C) suspension of CuBr (0.57 g, 4 mmol) in THF (15 mL). After stirring for 4 h, a dark-red solution had developed. On removal of all solvents, the residue was extracted into toluene (15 mL). The extract was concentrated (ca. 0.5 mL) and then precipitated with *n*-hexane (10 mL). Compound [$L_2Cu_8Br_6$] was obtained as a red solid. Yield: 0.75 g, 75%. M.p. 232 °C. ^{1}H NMR (400 MHz, [D$_8$]THF, 298 K): δ = 0.10–1.34 (m, 48 H, CH*Me*$_2$), 1.37 (s, 18 H, *tBu*), 3.47 (sept, 8 H, C*H*Me$_2$), 7.08–7.21 (m, 12 H, Ar-C$_6$*H*$_3$), 7.82 (s, 4 H, Ar-C$_6$*H*$_2$), 8.61 (s, 4 H, *H*C=N) ppm. ^{13}C NMR (100 MHz, [D$_8$]THF, 298 K): δ = 21.6, 23.9, 27.4, 29.0, 29.2, 30.7, 31.4, 31.6, 32.6, 33.1, 35.3 (CH*Me*$_2$, *C*HMe$_2$, *tBu*), 124.1, 126.0, 126.1, 126.8, 129.0, 129.8, 134.4, 135.0, 135.8, 141.2, 146.9, 147.8 (Ar-*C*$_6$H$_2$, *C*$_6$H$_3$), 159.9 (Cu-*C*$_{ipso}$), 173.5 (H*C*=N) ppm. $C_{72}H_{94}Br_6Cu_8N_4$ (2003.34): calcd. C 43.17, H 4.73, N 2.80; found C 42.20, H 4.82, N 2.56.

Synthesis of [(IPM)CuL] (1): In a glove-box, a precooled (–10 °C) solution of IPM (0.22 g, 1.20 mmol) in THF (5 mL) was added dropwise to a stirred solution of [$L_2Cu_8Br_6$] (0.30 g, 0.15 mmol) in THF (20 mL) at –10 °C. After the addition, a color change from red to orange was observed. The mixture was stirred for a further 2 h. After workup, THF was removed, and *n*-hexane (30 mL) was added. An off-white crystalline solid was collected by filtration and confirmed as the byproduct [(IPM)CuBr].[14] The filtrate was dried under vacuum to give an orange solid of **1**. Yield: 0.24 g, 92%. ^{1}H NMR (400.1 MHz, [D$_8$]toluene, 298 K): δ = 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, Ar-CH*Me*$_2$), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, IPM-CH*Me*$_2$), 1.42 (s, 9 H, *tBu*), 1.45 (s, 6 H, IPM-C*Me*), 3.37 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, Ar-C*H*Me$_2$), 4.22 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, IPM-C*H*Me$_2$), 6.97–7.14 (m, 6 H, Ar-C$_6$*H*$_3$), 8.49 (s, 2 H, Ar-C$_6$*H*$_2$), 8.89 (s, 2 H, *H*C=N) ppm. ^{13}C NMR (100 MHz, [D$_8$]toluene, 298 K): δ = 23.1, 23.9, 28.3, 31.7, 32.0, 34.7 (Ar-CH*Me*$_2$, Ar-*C*HMe$_2$, *tBu*, IPM-CH*Me*$_2$, IPM-C*Me*), 51.0 (IPM-*C*HMe$_2$), 122.9, 123.6, 125.6, 127.5, 129.3, 137.4, 147.5, 147.8, 151.6 (Ar-*C*$_6$H$_2$, *C*$_6$H$_3$, IPM-*C*Me), 171.6 (H*C*=N), 176.5 (Cu-*C*$_{ipso}$), 176.9 (Cu-*C*$_{IPM}$) ppm. $C_{47}H_{67}CuN_4$ (751.61): calcd. C 75.11, H 8.99, N 7.45; found C 75.29, H 9.12, N 7.31.

Orange single crystals of **1a**·C_6H_{14}·0.5C_7H_8 suitable for X-ray analysis were grown from a toluene (trace)/*n*-hexane solution of **1** at –10 °C for 1 week. M.p. 102 °C (color change from orange to light yellow), 165 °C (melted). Light-yellow crystals of **1b** were obtained by recrystallization of **1** in *n*-hexane at –10 °C for 2 weeks. M.p. 165 °C.

Synthesis of [(IPM)Cu{N(1-ad)NN(L)}] (2): A solution of **1** (0.15 g, 0.2 mmol) and 1-adamantyl azide (0.07 g, 0.4 mmol) in toluene (20 mL) was slowly heated to 100 °C and stirred for 3 d. After cooling to room temperature, all the solvents were removed, and the residue was extracted into *n*-hexane (20 mL). The extract was concentrated (ca. 5 mL) and kept at –10 °C. One week later, light-orange crystals of **2** were obtained. Yield: 0.12 g, 65%. M.p. 195 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.17 (d, $^3J_{HH}$ = 5.6 Hz, 24 H, Ar-CH*Me*$_2$), 1.23 (d, $^3J_{HH}$ = 5.2 Hz, 12 H, IPM-CH*Me*$_2$), 1.28–1.35 (m), 1.77 (br.), 1.93 (br.), 2.19–2.25 (m), 2.49 (br.), (15 H, $C_{10}H_{15}$), 1.36 (s, 6 H, IPM-C*Me*), 1.60 (s, 9 H, *tBu*), 3.15 (sept, $^3J_{HH}$ = 5.6 Hz, 2 H), 3.43 (sept, $^3J_{HH}$ = 5.6 Hz, 2 H, Ar-C*H*Me$_2$), 5.30 (sept, $^3J_{HH}$ = 5.2 Hz, 2 H, IPM-C*H*Me$_2$), 7.01–7.20 (m, 6 H, Ar-C$_6$*H*$_3$), 8.07 (s, 1 H), 8.92 (s, 1 H, Ar-C$_6$*H*$_2$), 8.28 (s, 1 H), 9.20 (s, 1 H, *H*C=N) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 23.8, 24.3, 28.4, 30.3, 31.6, 34.6, 37.0, 44.5, 49.8, 57.1 (Ar-CH*Me*$_2$, Ar-*C*HMe$_2$, *tBu*, IPM-CH*Me*$_2$, IPM-C*Me*, *C*$_{10}$H$_{15}$), 122.8, 123.1, 123.7, 127.9, 128.4, 138.6, 143.2, 152.0, 154.1 (Ar-*C*$_6$H$_2$, *C*$_6$H$_3$, IPM-*C*Me), 163.7 (H*C*=N), 172.1 (Cu-*C*$_{IPM}$) ppm. $C_{57}H_{82}CuN_7$ (928.85): calcd. C 73.70, H 8.90, N 10.56; found C 73.66, H 8.84, N 10.36.

Synthesis of [(IPM)Cu{N(Ph)NN(1-ad)}] (3): A solution of [(IPM)-CuPh] (0.12 g, 0.38 mmol) and 1-adamantyl azide (0.14 g, 0.76 mmol) in toluene (20 mL) was heated at 100 °C for 3 d. After cooling to room temperature, the solvent was removed, and the residue was extracted into *n*-hexane (20 mL). The extract was concentrated (ca. 8 mL) and kept at –30 °C; 5 d later, **3** was obtained as colorless crystals. Yield: 0.08 g, 43%. M.p. 209 °C. ^{1}H NMR (400 MHz, [D$_8$]toluene, 298 K): δ = 1.26 (m), 1.76 (m), 2.17 (br., 15 H, $C_{10}H_{15}$), 1.42 (d, $^3J_{HH}$ = 5.2 Hz, 12 H, IPM-CH*Me*$_2$), 1.49 (s, 6 H, IPM-C*Me*), 4.11 (sept, $^3J_{HH}$ = 5.2 Hz, 2 H, IPM-C*H*Me$_2$), 6.88 (m), 7.35 (m), 7.78 (m, 5 H, *Ph*) ppm. ^{13}C NMR (100 MHz, [D$_8$]toluene, 298 K): δ = 24.8, 25.0, 31.0, 31.2, 38.0, 44.6, 51.1 (IPM-CH*Me*$_2$, IPM-C*Me*, *C*$_{10}$H$_{15}$), 59.4 (IPM-*C*HMe$_2$), 117.3, 118.7, 123.5, 156.5 (*Ph*, IPM-*C*Me), 173.7 (Cu-*C*$_{IPM}$) ppm. $C_{27}H_{40}CuN_5$ (498.18): calcd. C 65.09, H 8.09, N 14.06; found C 65.37, H 7.98, N 13.89.

X-ray Structure Determination and Refinement: The crystallographic data of compounds **1a**, **1b**, **2**, and **3** were collected with an Oxford Gemini S Ultra system. In all cases graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used. Absorption corrections were applied by using the spherical harmonics program (multiscan type). The structures were solved by direct methods (SHELXS-90)[24] and refined against F^2 using SHELXL-97.[25] In general, non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were in-

Table 1. Crystallographic data for **1a**, **1b**, **2**, and **3**.

	1a·C_6H_{14}·0.5C_7H_8	**1b**	**2**	**3**
Empirical formula	$C_{56.5}H_{81}CuN_4$	$C_{47}H_{67}CuN_4$	$C_{57}H_{82}CuN_7$	$C_{27}H_{40}CuN_5$
Formula mass	879.79	751.59	928.84	498.18
Temperature [K]	173(2)	173(2)	173(2)	173(2)
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic
Space group	$P2(1)/c$	$P\bar{1}$	$P2(1)/c$	$P2(1)2(1)2(1)$
a [Å]	13.0681(5)	12.2317(13)	18.2638(16)	11.1284(12)
b [Å]	20.9797(6)	13.3655(12)	11.0757(9)	12.8518(9)
c [Å]	20.0707(7)	13.7915(9)	27.324(2)	18.6147(14)
α [°]		98.939(7)		
β [°]	105.071(4)	90.965(7)	98.198(8)	
γ [°]		104.101(9)		
V [Å^3]	5313.4(8)	2156.7(3)	5470.8(8)	2662.3(4)
Z	4	2	4	4
$\rho_{calcd.}$ [Mg/m^3]	1.100	1.157	1.128	1.243
μ [mm^{-1}]	0.449	0.542	0.440	0.843
$F(000)$	1908	812	2008	1064
θ range [°]	2.21–26.00	2.21–26.00	2.16–26.00	2.19–26.00
Index ranges	$-16 \le h \le 16$	$-15 \le h \le 14$	$-22 \le h \le 22$	$-11 \le h \le 13$
	$-25 \le k \le 25$	$-16 \le k \le 16$	$-13 \le k \le 13$	$-15 \le k \le 15$
	$-23 \le l \le 24$	$-14 \le l \le 17$	$-33 \le l \le 33$	$-22 \le l \le 22$
No. of reflns. collected	48516	19483	51098	20462
No. of indep. reflns. (R_{int})	10410 (0.0925)	8198 (0.1198)	10738 (0.1219)	5216 (0.1277)
No. of data/restraints/params.	10410/13/589	8198/0/450	10738/0/603	5216/0/292
GoF/F^2	1.007	0.913	0.937	0.954
$R1$,[a] $wR2$[b] [$I > 2\sigma(I)$]	0.0663, 0.1411	0.0844, 0.1479	0.0692, 0.1185	0.0928, 0.1912
$R1$,[a] $wR2$[b] (all data)	0.1309, 0.1583	0.2107, 0.1818	0.1801, 0.1445	0.1655, 0.2154
Largest diff. peak/hole [e/Å^3]	0.814/–0.365	0.472/–0.309	0.996/–0.466	2.530/–0.415

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$.

cluded using the riding model with U_{iso} tied to the U_{iso} of the parent atoms unless otherwise specified. A summary of cell parameters, data collection, and structure solution and refinement is given in Table 1. CCDC-738439 (**1a**), -738440 (**1b**), -773274 (**2**), and -738443 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): VT NMR studies of compound **1**.

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[1] J. Arduengo III, H. V. R. Dias, J. C. Calabrese, F. Davidson, *Organometallics* **1993**, *12*, 3405–3409.

[2] a) H. G. Raubenheimer, S. Gronje, P. H. van Rooyen, P. J. Olivier, J. G. Toerien, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 672–673; b) H. G. Raubenheimer, S. Cronje, P. J. Olivier, *J. Chem. Soc., Dalton Trans.* **1995**, 313–316.

[3] a) M. Niemeyer, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1535–1540; b) N. P. Mankad, T. G. Gray, D. S. Laitar, J. P. Sadighi, *Organometallics* **2004**, *23*, 1191–1193; c) N. P. Mankad, D. S. Laitar, J. P. Sadighi, *Organometallics* **2004**, *23*, 3369–3371; d) L. A. Goj, E. D. Blue, C. Munro-Leighton, T. B. Gunnoe, J. L. Petersen, *Inorg. Chem.* **2005**, *44*, 8647–8649; e) L. A. Goj, E. D. Blue, S. A. Delp, T. B. Gunnoe, T. R. Cundari, J. L. Petersen, *Organometallics* **2006**, *25*, 4097–4104; f) L. A. Goj, E. D. Blue, S. A. Delp, T. B. Gunnoe, T. R. Cundari, A. W. Pierpont, J. L. Petersen, P. D. Boyle, *Inorg. Chem.* **2006**, *45*, 9032–9045; g) H. Ren, X. Zhao, S. Xu, H. Song, B. Wang, *J. Organomet. Chem.* **2006**, *691*, 4109–4113.

[4] a) V. Jurkauskas, J. P. Sadighi, S. L. Buchwald, *Org. Lett.* **2003**, *5*, 2417–2420; b) H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *Organometallics* **2004**, *23*, 1157–1160; c) H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *Organometallics* **2004**, *23*, 1157–1160; d) T. Ohishi, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.* **2008**, *47*, 5792–5795; e) J. Herron, Z. T. Ball, *J. Am. Chem. Soc.* **2008**, *130*, 16486–16487.

[5] For selected reviews, see: a) P. L. Arnold, *Heteroat. Chem.* **2002**, *13*, 534–539; b) S. Díez-González, S. P. Nolan, *Synlett* **2007**, *14*, 2158–2167; c) C. Deutsch, N. Krause, B. H. Lipshutz, *Chem. Rev.* **2008**, *108*, 2916–2927; d) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; e) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* **2009**, *109*, 3561–3598.

[6] H. V. R. Dias, S. A. Polach, S.-K. Gob, E. F. Archibong, D. S. Marynick, *Inorg. Chem.* **2000**, *39*, 3894–3901.

[7] a) Y. M. Badiei, A. Krishnaswamy, M. M. Melzer, T. H. Warren, *J. Am. Chem. Soc.* **2006**, *128*, 15056–15057; b) Y. M. Badiei, A. Dinescu, X. Dai, R. M. Palomino, F. W. Heinemann, T. R. Cundari, T. H. Warren, *Angew. Chem. Int. Ed.* **2008**, *47*, 9961–9964.

[8] C. Nolte, P. Mayer, B. F. Straub, *Angew. Chem. Int. Ed.* **2007**, *46*, 2101–2103.

[9] a) H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021.

[10] a) E. J. Corey, D. J. Beames, *J. Am. Chem. Soc.* **1972**, *94*, 7210–7211; b) E. J. Corey, D. Floyd, B. H. Lipshutz, *J. Org. Chem.* **1978**, *43*, 3418–3420.

[11] a) G. H. Posner, *An Introduction to Synthesis Using Organocopper Reagents*, Wiley, New York, **1980**; b) B. H. Lipshutz, S. Sengupta, *Org. React. (N.Y.)* **1992**, *41*, 135–631.

[12] We have even tried the reaction with [(CuMes)$_4$] (Mes = 2,4,6-$Me_3C_6H_2$) and N_3(1-ad) in toluene by heat treatment (90 °C) for 3 d. This reaction was accompanied by color changes from light-yellow to orange, and the ^{1}H NMR analysis of the residue – after removal of all volatiles – gave a messy spectrum from which it was difficult to determine whether the reaction had occurred. [(CuMes)$_4$] was prepared according to following references {in reference b it is in the form of [(CuMes)$_5$]: a) H. Eriksson, M. Håkansson, *Organometallics* **1997**, *16*, 4243–4244; b) E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *Organometallics* **1989**, *8*, 1067–1079.

[13] The cluster compound [$L_2Cu_8Br_6$] was clearly determined by X-ray crystal structural analysis. This result will be published elsewhere.

[14] [(IPM)CuBr] was confirmed by NMR (^{1}H and ^{13}C) spectroscopy and elemental analyses measurements. ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): δ = 1.65 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 2.14 (s, 6 H, C*Me*), 4.46 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 9.4 (C*Me*), 24.6 (CH*Me*$_2$), 50.3 (*C*HMe$_2$), 123.7 (*C*Me), 170.6 (Cu-*C*) ppm. $C_{11}H_{20}BrCuN_2$ (323.74): calcd. C 40.81, H 6.23, N 8.85; found C 40.58, H 6.30, N 8.73.

[15] J. E. Huheey, *Inorganic Chemistry*, 3rd ed., Harper and Row, New York, **1983**, p. 258.

[16] D. Tulloch, A. A. Danopoulos, S. Kleinhenz, M. E. Light, M. B. Hursthouse, G. Eastham, *Organometallics* **2001**, *20*, 2027–2031.

[17] For selected examples, see: a) W. J. Hoogervorst, C. J. Elsevier, M. Lutz, A. L. Spek, *Organometallics* **2001**, *20*, 4437–4440; b) J. Fossey, C. Richards, *Organometallics* **2002**, *21*, 5259–5264; c) J. Fossey, C. Richards, *Tetrahedron Lett.* **2003**, *44*, 8773–8776; d) W. J. Hoogervorst, K. Goubitz, J. Fraanje, M. Lutz, A. L. Spek, J. M. Ernsting, C. J. Elsevier, *Organometallics* **2004**, *23*, 4550–4563; e) S. H. Oakley, M. P. Coogan, R. J. Arthur, *Organometallics* **2007**, *26*, 2285–2290; f) W. Gao, D. Cui, *J. Am. Chem. Soc.* **2008**, *130*, 4984–4991.

[18] For the hybrid B3LYP density functional, see: a) A. D. Becke, *Phys. Rev. A* **1988**, *34*, 3098–3100; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789. DZP refers to the standard DZP basis sets for C, N, and H atoms and the pseudopotential-including basis set Lanl2dz for Cu. Geometric optimizations were performed without any constraints. A scaling factor of 0.9804 was used for computing thermal energy corrections within B3LYP/6-31G*. The relative electron energy [ΔG = G(**1b**) – G(**1a**)] and entropy [ΔS = S(**1b**) – S(**1a**)] at different temperatures were calculated at the B3LYP/DZP level of theory: T = 100, 150, 195, 200, 300 K, ΔG = 0.53, 0.25, 0.00, –0.04, –0.61 kcal/mol, and ΔS = 5.63, 5.70, 5.73, 5.74, 5.77 cal/mol K, respectively. By extrapolation, **1a** was computed to be ca. 1.15 kcal/mol lower in energy than **1b** at 0 K. All computations were performed with the Gaussian 03 package of programs: c) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N, Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O, Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, revision C.02, Gaussian, Inc., Wallingford, CT, **2004**.

[19] D. R. Lide, *Handbook of Chemistry and Physics*, CRC Press, Norman, OK, USA, **2003–2004**, *84*(9), pp. 16–17.

[20] L. Johnson, A. M. Willcocks, S. P. Richards, *Inorg. Chem.* **2009**, *48*, 8613–8622.

[21] The synthesis of [(IPr)CuPh] and [(SIPr)CuPh] by the reaction of [(IPr)CuCl] {or [(SIPr)CuCl]} with Ph_2Mg, has been reported.[3f] We treated [(IPM)CuCl] with PhLi and obtained [(IPM)CuPh] as an off-white solid in 84% yield. The ^{1}H and ^{13}C NMR spectroscopic data are as follows. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ = 1.41 (s, 6 H, C*Me*), 1.49 (d, $^3J_{HH}$ = 6.4 Hz, 12 H, CH*Me*$_2$), 3.88 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 7.39 (m, 1 H), 7.57 (m, 2 H), 8.37 (m, 2 H, *Ph*) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ = 8.6 (C*Me*), 24.7 (CH*Me*$_2$), 49.8 (*C*HMe$_2$), 122.7, 124.5, 127.8, 128.8, 141.6 (*Ph*, *C*Me), 166.8 (Cu-C_{Ph}), 174.8 (Cu-C_{IPM}) ppm.

[22] N. Kuhn, T. Kratz, *Synthesis* **1992**, 561–562.

[23] a) E. E. While, D. S. Stephenson, P. Capriel, G. Binsch, *J. Am. Chem. Soc.* **1982**, *104*, 405–415; b) M. H. Klingele, B. Kersting, *Z. Naturforsch., Teil B* **2001**, *56*, 437–439.

[24] *SHELXS-90, Program for Structure Solution*: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

[25] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, **1997**.

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