Synthesis and structures of isopropyl-β-diketiminato copper(I) complexes

Paul O. Oguadinma and Frank Schaper

Abstract: The reaction of *N*,*N*′-diisopropyl-2-amino-4-iminopent-2-ene (nacnac$^{i\text{-Pr}}$H, **1**) either with CuO*t*-Bu or with a mixture of mesityl copper and 10% CuO*t*-Bu afforded, in the presence of PPh_3, $CN(C_6Me_2H_3)$, or MeCN, the Lewis base coordinated complexes nacnac$^{i\text{-Pr}}$CuPPh$_3$·0.5 C_6H_{14} (**2**), nacnac$^{i\text{-Pr}}$CuCN($C_6Me_2H_3$) (**3**), and nacnac$^{i\text{-Pr}}$Cu(NCMe) (**4**). Compounds **2**, **3**, and **4** were characterized by single-crystal X-ray diffraction studies. Compound **4** afforded two species in deuterated benzene in a 2:1 ratio, which were assigned to {nacnac$^{i\text{-Pr}}$Cu}$_2$(μ-NCMe) and nacnac$^{i\text{-Pr}}$CuNCMe (**4**). Upon addition of 5 equiv. of MeCN, the two sets collapsed into that of **4**. No copper complexes were formed in the presence of styrene, stilbene, or diphenylacetylene.

Key words: diketiminate, copper, coordination chemistry.

Résumé : La réaction du *N*,*N*′-diisopropyl-2-amino-4-iminopent-2-ène (nacnac$^{i\text{-Pr}}$H, **1**) avec le CuO*t*-Bu ou un mélange du mésityl-cuivre et du CuO*t*-Bu à 10 % a donné, en présence de PPh_3, de $CN(C_6Me_2H_3)$ ou de MeCN, les complexes nacnac$^{i\text{-Pr}}$CuPPh$_3$·0,5 C_6H_{14} (**2**), nacnac$^{i\text{-Pr}}$CuCN($C_6Me_2H_3$) (**3**), et nacnac$^{i\text{-Pr}}$Cu(NCMe) (**4**). Les composés **2**, **3** et **4** ont été caractérisés par diffraction des rayons-X sur monocristaux. Le spectre RMN de **4** dans C_6D_6 comporte deux séries de signaux selon un rapport 2:1, assignés à {nacnac$^{i\text{-Pr}}$Cu}$_2$(μ-NCMe) et à nacnac$^{i\text{-Pr}}$CuNCMe (**4**). Après l'addition de 5 equiv. de MeCN, seuls les signaux de **4** ont été observés. Aucun complexe de cuivre n'a été obtenu en présence de styrène, de stilbène ou de diphenylacétylène.

Mots-clés : dikétiminate, cuivre, chimie de coordination.

Introduction

Brookhart's demonstration in the mid 1990s that late transition-metal α-diimine complexes of Pd and Ni were effective as catalysts in olefin polymerization[1] paved the way for the synthesis of the corresponding anionic diketiminate versions of these ligand systems.[2] Since then, interest in diketiminates has continued unabatedly, and today β-diketiminates represent one of the most extensively employed nitrogen-based, bidentate ligands in coordination chemistry.[3] The acronym "nacnac" is often used to describe 2-amino-4-iminopent-2-ene, which is the N-analogue of the ubiquitous acetylacetonate (acac). The nacnac ligands are monoanionic spectator ligands, which have assisted in the isolation of metal complexes in unusual oxidation states and (or) coordination numbers.[4] For copper in particular, Tolman and co-workers used diketiminate complexes to model the active site of metalloproteins.[5] Warren and co-workers isolated a nacnac copper carbene complex, which they employed in catalytic cyclopropanation, and used copper diketiminates for amination reactions.[6–8] While most applications of diketiminate ligands revolve around N-aryl substituents, their N-alkyl derivatives have not been well-exploited. For copper(I), they are limited to applications in atomic layer deposition[9] or analyses of copper–ligand bonding.[10] In continuation of previous work on diketiminate copper complexes with N-alkyl substituents,[11,12] we report here the syntheses and characterization of *N*,*N*′-diisopropyl nacnac Cu^{I} complexes. Just prior to submission of this manuscript, Arii et al. reported nacnac$^{i\text{-Pr}}$Cu germylene complexes, using the same ligand.[13]

Results and discussion

Ligand and complex synthesis

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

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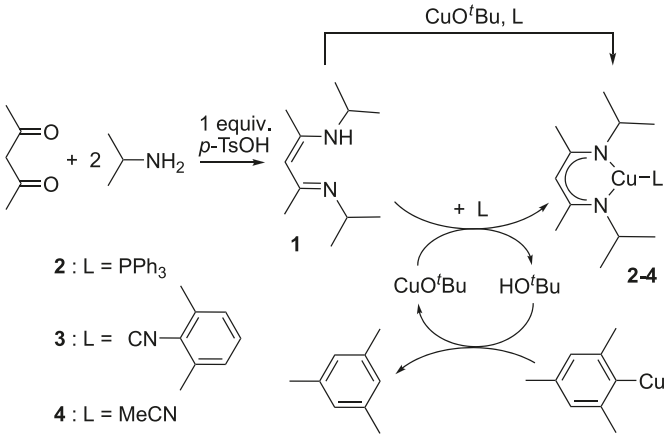
Scheme 1.



amounts of CuO*t*-Bu (Scheme 1). Mesityl copper in the absence of CuO*t*-Bu has been shown to be unreactive.[11] Though no major differences in terms of yields were observed between the use of CuO*t*-Bu or MesCu/CuO*t*-Bu, the complexes crystallized easier when MesCu/CuO*t*-Bu was used, probably due to the smaller amounts of *tert*-butanol present.

Compound **1** did not react with CuO*t*-Bu in the presence of styrene, stilbene, or diphenylacetylene. Identical observations were made with copper complexes carrying the chiral nacnac$^{CH(Me)Ph}$ ligand.[11] On the other hand, Cu–styrene complexes are readily obtained with nacnac^{Mes} (Mes = 2,4,6-$Me_3C_6H_3$)[18] or nacnac^{dipp} (dipp = 2,6-*i*-$Pr_2C_6H_3$, see Experimental section), one of the most sterically encumbered *N*-aryl diketiminates, as well as with nacnac^{Bn} or nacnac$^{i\text{-}Bu}$.[12,17] In-plane coordination of the two carbon atoms of an olefin is thus possible for diketiminate ligands with aryl or primary alkyl substituents, but not if secondary alkyls are present on the nitrogen. The implied increased steric demand of nacnac$^{i\text{-}Pr}$ compared with nacnac^{dipp} has to be set into contrast to observations for other systems. When compared with nacnac^{dipp}, diketiminate ligands with secondary alkyl substituents on the nitrogen allow additional intramolecular π-coordination in Ti complexes[19] or coordination of a second nacnac to Zr.[20] When considering steric congestion imposed by diketiminate ligands, it is thus important to differentiate between the first coordination sphere around the metal centre, where nacnac$^{i\text{-}Pr}$ imposes a congested environment, and general steric demand in the (outer) coordination sphere, where it does not.

Crystal structure studies

All three compounds are monomeric and crystallize in the $P2_1/c$ space group with copper in a distorted trigonal-planar geometry. Complex **2** (Fig. 1) co-crystallizes with half a molecule of hexane. The methine hydrogen atoms of the *i*-Pr substituent point towards the methyl groups in the ligand backbone, even in the sterically encumbered **2**. C–N and C–C bond lengths of the diketiminate ligand are in agreement with complete delocalization of the double bonds (Table 1). Cu–N bond distances in **3** and **4** are close to the average generally observed in nacnacCu complexes (1.94 ± 0.06 Å),[21] and the copper centre is found in the mean plan of the ligand. With the bulkier phosphine ligand in **2**, longer Cu–N distances and a displacement of C3 and the copper atom by 0.1 and 0.4 Å, respectively, out of the ligand mean plane are observed (plane defined by N1, N2, C2, and C4). While Cu–P and Cu–N bond distances (2.191(1) Å; 1.978(1) and 1.983(1) Å) are comparable to those in nacnac$^{CH(Me)Ph}$CuPPh$_3$ (2.195(1) Å; 1.972(1) and 1.983(1) Å),[11] they are longer than in nacnac^{Ar}Cu(PPh$_3$) complexes (2.16–2.18 Å and 1.94–1.97 Å)[7,22–24] in agreement with increased steric bulk introduced by a secondary alkyl substituent on the nitrogen atoms.

Spectroscopic properties

The PPh_3 resonance in the ^{31}P NMR spectrum of compound **2** in C_6D_6 was observed at δ 4.0. This value is intermediate between those of nacnac^{Ar}CuPPh$_3$ complexes (Ar = $Me_3C_6H_2$: 5.2 ppm,[7] Ar = $Me_2C_6H_3$: 5.4 ppm,[23] and Ar = *i*-$Pr_2C_6H_3$: 3.6 ppm[22]) and nacnac^{R}CuPPh$_3$ complexes (R = Bn: 3.5 ppm[12] and R = CH(Me)C_6H_5: 3.9 ppm[11]). While N-aryl-substituted diketiminate ligands tend to show ^{31}P resonances at lower field, differences are too small to be correlated to the ligand properties. Similar to the behaviour observed for nacnac$^{CH(Me)Ph}$Cu(NCMe),[11] which also carries a secondary alkyl substituent on N, pure crystals of **4** dissolved in C_6D_6 gave two sets of nacnac resonances in a ratio of 2:1 in its ^1H NMR spectrum; the resonances of the major species being slightly broadened. Only one resonance was observed for MeCN. Fast exchange of coordinated and free Lewis base was observed before in nacnacCuL complexes,[11,12,25] and the amount of coordinated MeCN in the two species thus cannot be derived from NMR. Only one peak for ν_{CN} was observed at 2259 cm^{-1} in the IR spectrum of **4** in toluene solution, 5 cm^{-1} higher than that of free MeCN.[26] Addition of excess MeCN (5 equiv.) caused the peaks to collapse to one set of resonances in its ^1H and ^{13}C spectra, belonging to the previously minor component. Changes in the overall concentration, on the other hand, did not affect the observed ratio, which rules out equilibrium [1] in Scheme 2. Complete MeCN redistribution (equilibrium [2] in Scheme 2) also seems unlikely, since bis(acetonitrile) complexes have not been reported for diketiminate copper complexes and nacnac$^{i\text{-}Pr}$Cu complexes could not be obtained in the absence of ancillary ligands. We thus assign the species favoured at higher acetonitrile concentrations to the MeCN complex nacnac$^{i\text{-}Pr}$CuNCMe (**4**), observed in the crystal structure, and the broadened peaks of the major species to the bridged complex {nacnac$^{i\text{-}Pr}$Cu}$_2$(μ-NCMe) (**4b**) (equilibrium [3] in Scheme 2). While bridging coordination of acetonitrile is rare, it is not unknown.[27] Monomer–dimer equilibria similar to equilibrium [3] in Scheme 2 have been observed for nacnac^{Bn}Cu, which forms a diphenylacetylene-bridged dimer in the solid state and a monomeric complex in solution when excess diphenylacetylene is present,[12] and for nacnac^{Ar}Cu complexes, which display an equilibrium between a monomeric and a dimeric benzene-coordinated complex in solution.[7,25] While single-crystal diffraction studies confirmed the formation of **4**, we were unable to obtain satisfactory elemental analyses, even from the crystalline material. Synthesis of **4** was reported at the time of submission of this article by Arii et al. from the reaction of [Cu(NCMe)$_4$][CF_3SO_3] with nacnac$^{i\text{-}Pr}$Li.[13] Although not discussed therein, they also observed a variable ratio of two products in NMR spectra of **4**.[28]

The stretching frequency ν_{CN} = 2105 cm^{-1} of the isocyanide

Fig. 1. Crystal structures of **2**–**4**. Hydrogen atoms and solvent are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

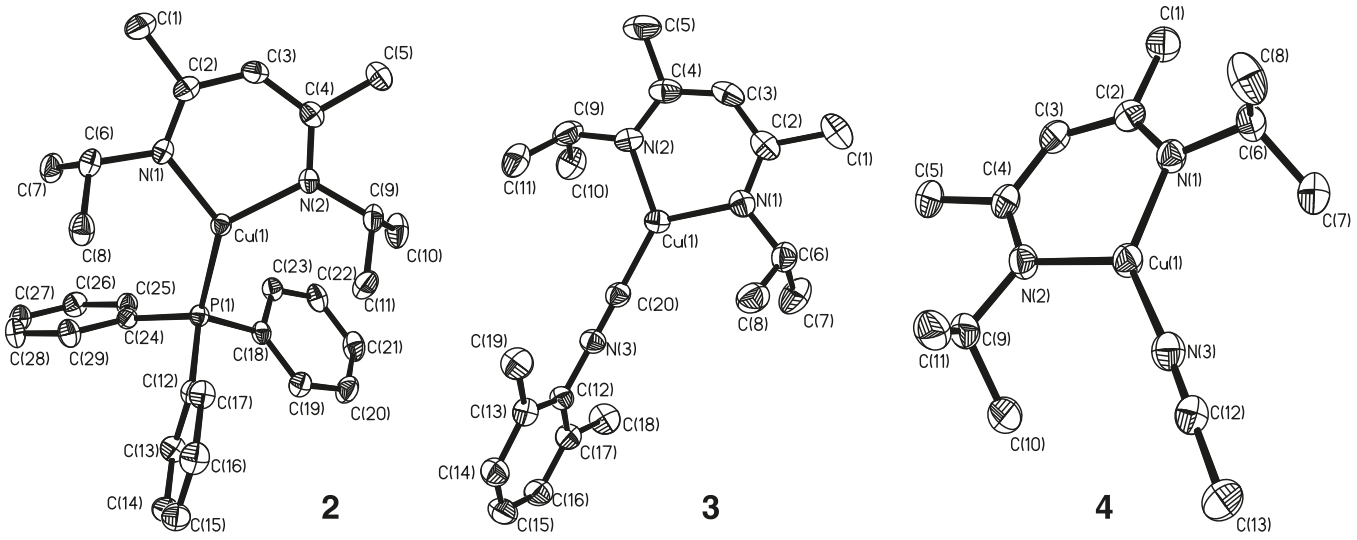


Table 1. Selected bond distances (Å) and bond angles (°) for **2**, **3**, and **4**.

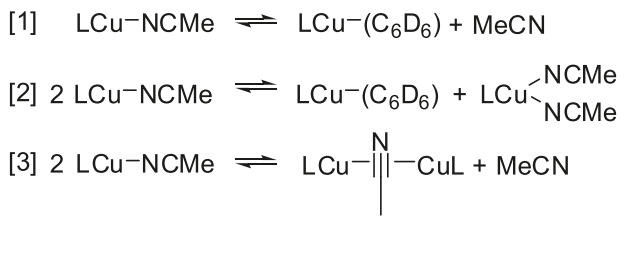
	2	3	4
Bond distances (Å)			
Cu1—N1	1.978(1)	1.939(2)	1.940(1)
Cu1—N2	1.987(1)	1.935(2)	1.961(2)
Cu1—X[a]	2.191(1)	1.822(2)	1.893(2)
N1—C2	1.323(2)	1.332(2)	1.326(3)
N2—C4	1.321(2)	1.331(2)	1.314(3)
C2—C3	1.408(2)	1.407(3)	1.413(3)
C3—C4	1.411(2)	1.407(3)	1.416(2)
X—Y[b]	1.839(2)	1.161(2)	1.148(3)
Bond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

[a]Cu1—P1 (**2**), Cu1—C20 (**3**), and Cu1—N3 (**4**).

[b]Average of P1—C12, P1—C18, and P1—C24 (**2**), N3—C20 (**3**), N3—C12 (**4**).

[c]N1,2–Cu1–P1 (**2**), N1,2–Cu1–C20 (**3**), N1,2–Cu1–N3 (**4**).

Scheme 2.



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

In the course of preparing compound **3**, a minor side product, **5**, was obtained. ^{1}H and ^{13}C NMR spectra of **5** showed resonances of the diketiminate ligand and isocyanide in a ratio of 1:2, which would suggest the formation of nacnac$^{i\text{-Pr}}$Cu(CNC$_6$Me$_2$H$_3$)$_2$. Satisfactory elemental analysis of **5**, however, could not be obtained and, more importantly, addition of 1 equiv. xylyl isocyanide did not transform **3** into **5**. Complex **5** showed the same stretching frequency in its IR spectrum as **3**. Taking also the low solubility of **5** in toluene into account, assignment as a bisisocyanide adduct seems improbable and the structure of **5** remains unclear.

Conclusions

Copper complexes of nacnac$^{i\text{-Pr}}$ were readily prepared if additional Lewis base was present to stabilize the complex. In agreement with observations made for nacnac$^{CH(Me)Ph}$,[11] diketiminate ligands with secondary alkyl substituents are slightly more Lewis-basic, but sterically more demanding in the first coordination sphere than diketiminates with aryl or primary alkyl substituents.

Experimental section

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

nacnac$^{i\text{-Pr}}$H (1)[14,15]

Acetylacetone (4.0 mL, 38 mmol), *para*-toluenesulfonic

Table 2. Details of X-ray diffraction studies.

Complex	**2**	**3**	**4**
CCDC No.	764335	764336	764337
Formula	$C_{29}H_{36}CuN_2P\cdot(C_6H_{14})_{0.5}$	$C_{20}H_{30}CuN_3$	$C_{13}H_{24}CuN_3$
M_r (g/mol); $d_{calcd.}$(g/cm^3)	550.19; 1.247	376.01; 1.239	285.89; 1.277
T (K); F(000)	150 ; 1172	150; 800	150; 608
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell			
a (Å)	13.9417(4)	8.9807(3)	6.8103(1)
b (Å)	12.4813(4)	13.3632(4)	11.4563(3)
c (Å)	17.8496(6)	16.9799(5)	19.1252(3)
β (°)	109.348(1)	98.320(1)	94.780(1)
V (Å^3); Z	2930.60(16); 4	2016.33(11); 4	1486.97(5); 4
θ range (°); completeness	3.36–73.61; 0.99	4.23–71.45; 0.99	4.50–67.82; 0.93
Reflections: collec./indep.; R_{int}	41989/5843; 0.037	24118/3879; 0.038	23408/2512; 0.034
μ (mm^{-1}); abs. corr.	1.72; SADABS	1.55; SADABS	1.93; SADABS
$R_1(F)$; $wR(F^2)$; GoF(F^2)[a]	0.0348; 0.0959; 1.052	0.0413; 0.1128; 1.00	0.0308; 0.0906; 1.067
Residual electron density	0.68; –0.38	0.32; –0.36	0.32; –0.51

[a] $R_1(F)$ based on observed reflections with $I > 2\sigma(I)$, $wR(F^2)$ and GoF(F^2) based on all data.

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

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 11.44 (bs, 1H, NH), 4.38 (s, 1H, *H*C(C=N)$_2$), 3.64 (sp, J = 6 Hz, 2H, C*H*(CH$_3$)$_2$), 1.89 (s, 6H, Me(C=N)$_2$), 1.16 (d, J = 6 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 158.5 (C=N), 93.5 (H*C*(C=N)$_2$), 46.7 (*C*H(CH$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 18.7 (*Me*(C=N)$_2$). ^{1}H NMR (C_6D_6, 400 MHz) δ: 11.63 (bs, 1H, NH), 4.46 (s, 1H, *H*C(C=N)$_2$), 3.46 (sp, J = 6 Hz, 2H, C*H*(CH$_3$)$_2$), 1.71 (s, 6H, Me(C=N)$_2$), 1.11 (d, J = 6 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 101 MHz) δ: 158.0 (C=N), 94.6 (H*C*(C=N)$_2$), 47.0 (*C*H(CH$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 18.8 (*Me*(C=N)$_2$).

nacnac$^{i\text{-Pr}}$CuPPh$_3$·0.5 C$_6$H$_{14}$ (2)

nacnac$^{i\text{-Pr}}$H (300 mg, 1.65 mmol), mesitylcopper (301 mg, 1.65 mmol), CuO*t*-Bu (22 mg, 0.165 mmol), and PPh_3 (437 mg, 1.65 mmol) were dissolved in toluene (12 mL) to give a yellow-brown solution. After stirring for 1 h, the solution was filtered, concentrated to 1/5 of its volume and layered with hexane (5 mL). It was then kept at –35 °C. Yellow crystals together with powder formed after 3 day (700 mg, 84%).

^{1}H NMR (C_6D_6, 400 MHz) δ: 7.66–7.02 (m, 15H, PPh_3), 4.67 (s, 1H, *H*C(C=N)$_2$), 3.86 (sp, J = 6 Hz, 2H C*H*(CH$_3$)$_2$), 2.10 (s, 6H, Me(C=N)$_2$), 0.98 (d, J = 6 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 101 MHz) δ: 161.3 (C=N), 135.1 (d, J = 30 Hz, *ipso* PPh_3), 134.7 (d, J = 14 Hz, *ortho* PPh_3), 129.7 (*para* PPh_3), 128.6 (d, J = 9 Hz, *ortho* PPh_3), 95.4 (H*C*(C=N)$_2$), 51.4 (*C*H(CH$_3$)$_2$), 26.7 (CH(*C*H$_3$)$_2$), 23.1 (*Me*(C=N)$_2$). ^{31}P NMR (C_6D_6, 75 MHz) δ: 4.0. Anal. Calcd. for $C_{29}H_{36}N_2PCu$: C, 68.68; H, 7.15; N, 5.52. Found: C, 67.85; H, 7.48; N, 4.97.

nacnac$^{i\text{-Pr}}$CuCN(C$_6$Me$_2$H$_3$) (3)

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

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

The solid obtained after filtration, **5,** gave the following data: IR (toluene) ν_{CN}: 2114 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz) δ: 6.69 (t, J = 8 Hz, *p*-CN(C$_6$Me$_2$*H*$_3$), 2H), 6.52 (d, J = 8 Hz, *m*-CN(C$_6$Me$_2$*H*$_3$), 4H), 4.61 (s, 1H, *H*C(C=N)$_2$), 4.02 (septet, J = 6 Hz, C*H*(CH$_3$)$_2$, 2H), 2.14 (s, 12H, CN(C$_6$*Me*$_2$H$_3$), 2.08 (s, 6H, Me(C=N)$_2$), 1.43 (d, 12H, J = 6 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 101 MHz) δ: 160.7 (C=N), 135.4, 128.6, 128.1, 127.8, 94.8 (H*C*(C=N)$_2$), 50.8 (*C*H(CH$_3$)$_2$), 27.5 (CH(*C*H$_3$)$_2$), 22.4 (*Me*(C=N)$_2$), 18.8. (CN(C$_6$*Me*$_2$H$_3$)). (*C*N(C$_6$Me$_2$H$_3$) elusive).

nacnac$^{i\text{-Pr}}$CuNCMe (4)

nacnac$^{i\text{-Pr}}$H (75 mg, 0.41 mmol) and MeCN (41 mg,

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

Two species were observed in C_6D_6 solutions of **4** (see text). IR (toluene) ν_{NC}: 2259 cm^{-1}. **4**: ^1H NMR (C_6D_6, 400 MHz) δ: 4.52 (s, 1H, *H*C(C=N)$_2$), 4.03 (septet, J = 6 Hz, C*H*(CH$_3$)$_2$, 2H), 2.11 (s, 6H, Me(C=N)$_2$), 1.38–1.52 (m, 12H, CH(C*H*$_3$)$_2$), 0.57 (NCMe). ^{13}C NMR (C_6D_6, 101 MHz) δ: 160.6 (C=N), 116.5 (N*C*Me), 65.9 (H*C*(C=N)$_2$), 50.7 (*C*H(CH$_3$)$_2$), 26.9 (CH(*C*H$_3$)$_2$), 22.3 (*Me*(C=N)$_2$) and 0.3 (NC*Me*). **4b**: ^1H NMR (C_6D_6, 400 MHz) δ: 5.29 (bs, 1H, *H*C(C=N)$_2$), 3.92–3.99 (featureless septet, C*H*(CH$_3$)$_2$, 2H), 2.56 (bs, 6H, Me(C=N)$_2$), 2.08 (s, 6H, CN(C$_6$*Me*$_2$H$_3$) and 1.38–1.52 (m, 12H, CH(C*H*$_3$)$_2$) overlapping with that of **4.** Elemental analysis was unsatisfactory with varying results (ΔC = 2%–3%), which might be related to acetonitrile dissociation and complex decomposition.

NMR-scale preparation of nacnac^{dipp}Cu(styrene)

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

^1H NMR (C_6D_6, 400 MHz) δ: 6.35–7.21 (m, 11H, 2,6-*i*-Pr$_2$C$_6$H$_3$ and styrene), 5.08 (dd, J = 9 Hz and 14 Hz, 1H, Ph*H*C=), 4.97 (s, 1H, HC(C=N)$_2$), 3.48–3.56 (m, 3H, C*H*(CH$_3$)$_2$ and *cis* H$_2$C=), 3.34 (d, J = 9 Hz, 1H, *trans* H$_2$C=), 3.07 (sp, J = 7 Hz, 2H, C*H*(CH$_3$)$_2$, 1.75 (s, 6H, Me(C=N)), 1.33 (d, J = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.15 (d, J = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.09 (d, J = 7 Hz, 6H, CH(C*H*$_3$)$_2$).

X-ray diffraction studies

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

Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5390. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDCs 764335–764337 contain the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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