

## Synthesis of Bis(phosphine) and N-Heterocyclic Carbene Supported α- Diazoalkyl Complexes of Copper(I)

Vlad M. Iluc, Carl A. Laskowski, and Gregory L. Hillhouse\*

Department of Chemistry, Gordon Center for Integrative Science, The University of Chicago, 929 E. 57th Street, Chicago, Illinois 60637

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Summary: (2,6-Dimesitylphenyl)diazomethane,  $N_2CH(dmp)$ (1;  $dmp = 2,6-(2,4,6-Me_3C_6H_2)_2C_6H_3$ ), undergoes deprotonation by  $LiN(i-Pr)_2$  to give  $[N_2C(dmp)][Li]$  (2), which reacts with diethyl ether solutions of { $(dtbpe)Cu(\mu-Cl)_2$  (3; dtbpe = 1,2bis(di-tert-butylphosphino)ethane) or (IPr)Cu(Cl) (4; IPr = 1,3bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) to generate the metathesis products (L)Cu-C(N\_2)dmp (5, L = dtbpe; 6, L = IPr) as diamagnetic yellow crystalline solids in 80% and 82% yields, respectively. Reaction of 1 with n-BuLi results in addition of n-Bu<sup>-</sup> to the terminal nitrogen of 1 to generate a hydrazonyl anion that reacts with 3 to afford the hydrazonyl complex (dtbpe)Cu-N(n-Bu)N=CH(dmp) (7) in 75% yield. Complexes 5-7 have been characterized by spectroscopic (NMR, IR) and X-ray diffraction methods.

Interest in the coordination chemistry of diazoalkanes (N<sub>2</sub>CRR') has been fueled by their use as synthons for carbene complexes (L<sub>n</sub>M=CR<sub>2</sub>) upon N<sub>2</sub> loss, in stoichiometric and catalytic carbene-transfer processes.<sup>1</sup> Often, however, these energy-rich molecules form stable coordination complexes that are impervious to dinitrogen elimination.<sup>2</sup> While no comparable reagents of general utility for the direct installation of carbyne ligands (L<sub>n</sub>M=CR) have been developed, it is noteworthy that monosubstituted diazoalkanes (N<sub>2</sub>CHR) can be deprotonated to give the lithiated anionic derivatives [N<sub>2</sub>CR][Li], which in turn have been used in salt metathesis reactions to prepare  $\alpha$ -diazoalkyl complexes of Co, Rh, Os, Ni, Pd, and Pt (i.e., L<sub>n</sub>M-C(N<sub>2</sub>)R).<sup>3</sup> These complexes have not yet been successfully converted to stable carbyne species, but N<sub>2</sub> elimination with subsequent

carbyne trapping or rearrangement has been observed.<sup>3</sup> Herein we report the synthesis and structural characterization of Cu(I) diazoalkyls containing trialkylphosphine and N-heterocyclic carbene ancillary ligands and a bulky terphenyl substituent on the diazenyl carbon.

## **Results and Discussion**

For these studies we sought a crystalline, bulky monosubstituted diazoalkane to facilitate synthetic manipulations and offer steric stabilization. (2,6-Dimesitylphenyl)diazomethane,  $N_2$ CH(dmp) (1; dmp = 2,6-(2,4,6-Me\_3C\_6H\_2)\_2C\_6H\_3), was prepared in three steps from 2,6-dimesitylphenyl iodide, (dmp)I,<sup>4</sup> in 54% overall yield. The preparation followed standard synthetic protocols, except that longer reaction times and higher temperatures were required compared with the reaction conditions for smaller aryl derivatives (e.g., N<sub>2</sub>CHPh).<sup>5</sup> Following a procedure for a related compound,<sup>6</sup> monolithiation of (dmp)I in cyclohexane<sup>4b</sup> followed by addition of N,N-dimethylformamide allowed for the isolation of (dmp)CH=O in 70% yield. Hydrazine condensation with the aldehyde gave (dmp)-CH= $N_2H_2$  (93% yield), and oxidation of the hydrazone with an excess of HgO gave 1 as a light salmon colored solid in 82% yield. The IR spectrum of 1 shows  $v_{\rm NN}$  2052 cm<sup>-1</sup> and  $v_{\rm CN}$  1374 cm<sup>-1</sup>. No photosensitivity was observed on prolonged exposure of a  $C_6D_6$  solution of 1 (NMR tube) to ambient light, and this is likely correlated to its weak absorption in the visible region.

Reaction of 1 with 1 equiv of LiN(*i*-Pr)<sub>2</sub> (LDA) results in deprotonation to form  $[N_2C(dmp)][Li]$  (2; Scheme 1), which was not isolated but was used in situ. Addition of solutions of 2 to ether solutions of {(dtbpe)Cu( $\mu$ -Cl)}<sub>2</sub> (3; dtbpe = 1,2-bis-(di-*tert*-butylphosphino)ethane)<sup>7</sup> or (IPr)Cu(Cl) (4; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene)<sup>8</sup> generates the diazoalkyls (L)Cu-C(N<sub>2</sub>)dmp (5, L = dtbpe; 6, L = IPr) as diamagnetic yellow crystalline solids in 80% and 82% yields, respectively (Scheme 1; Figures 1 and 2). The NMR spectra of 5 and 6 exhibit  $C_{2\nu}$  pseudosymmetric environments, indicating free rotation around the Cu-C bonds in both complexes. Attempts to induce N<sub>2</sub> elimination, either thermally or photochemically, led to decomposition and intractable products.

<sup>\*</sup>To whom correspondence should be addressed. E-mail: g-hillhouse@ uchicago.edu.

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Figure 1. Molecular structure of 5 drawn with 35% probability ellipsoids. H atoms are omitted for clarity. Selected metrical parameters: Cu-C = 1.963(2), C-N(1) = 1.286(2), N(1)-N(2) = 1.151(2), C-C(31) = 1.494(2) Å; Cu-C-C(31) = 134.75(12), Cu-C-N(1) = 112.98(12), C(31)-C-N(1) = 111.88(14), C-N(1)-N(2) = 177.41(2), P(1)-Cu-P(2) = 91.76(2), P(1)-Cu-C = 151.40(5),  $P(2)-Cu-C = 116.43(5)^{\circ}$ .

Scheme 1. Synthesis of dtbpe (5) and IPr (6) Supported Cu(I)  $\alpha$ -Diazoalkyl and Hydrazonyl (7) Complexes (Mes = 2,4,6-Trimethylphenyl)



Initial attempts to generate **2** utilized *n*-BuLi as a "deprotonating" agent, but interestingly *n*-BuLi acts rather as a nucleophile, adding to the terminal nitrogen of N<sub>2</sub>CH(dmp) to generate a hydrazonyl anion that on reaction with **3** gives the diamagnetic hydrazonyl complex (dtbpe)Cu-N(n-Bu)N=CH-(dmp) (7) in 75% isolated yield (Scheme 1; Figure 3).

Single-crystal X-ray diffraction studies of **5** and **6** reveal structures with similar metrical parameters for the  $\alpha$ -diazoalkyl ligands, including short N–N (1.151(2) and 1.155(2) Å, respectively) and C–N bond distances (1.286(2) and 1.305(3) Å, respectively) consistent with the preservation of



Figure 2. Molecular structure of 6 drawn with 35% probability ellipsoids. H atoms are omitted for clarity. Selected metrical parameters: Cu(1)-C(4) = 1.896(2), C(4)-N(4) = 1.305(3), N(4)-N(5) = 1.155(2), C(4)-C(31) = 1.476(3) Å; C(4)-N(4)-N(5) = 175.0(2), C(1)-Cu(1)-C(4) = 163.47(9), Cu(1)-C(4)-C(31) = 129.3(2), Cu(1)-C(4)-N(4) = 114.1(2),  $C(31)-C(4)-N(4) = 116.4(2)^{\circ}$ .



**Figure 3.** Molecular structure of one of two conformers of 7 drawn with 35% probability ellipsoids. H atoms (except on C(1)) are omitted for clarity. Selected metrical parameters: Cu(1)-N(1) = 1.918(3), N(1)-N(2) = 1.337(4), N(2)-C(2) = 1.292(5), N(1)-C(1) = 1.465(5) Å; Cu(1)-N(1)-C(1) = 120.5(2), C(1)-N(1)-N(2) = 110.8(3),  $Cu(1)-N(1)-N(2) = 128.7(2)^{\circ}$ .

the diazoalkane functionality (Figures 1 and 2). Structures of previously reported transition-metal diazoalkyls show similar N–N (~1.14 Å) and C–N (~1.29 Å) values.<sup>3</sup> The Cu–C bond distances (1.963(2), 1.896(2) Å) are typical of those found for other Cu(I) alkyls,<sup>9</sup> with that in **5** being slightly elongated with respect to **6** probably for steric reasons. Copper exhibits planar coordination in **5**, with steric interactions leading to a distinct distortion from a Y-shaped geometry (P–Cu–C = 151.40(5),  $116.43(5)^{\circ}$ ) in the solid state.

Structural characterization of 7 reveals two independent molecules within the unit cell differing in the conformation of the n-Bu substituent (Figure 3; only one conformation

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shown). The hydrazonyl ligand is planar. Although it is not crystallographically required, C(1), N(11), N(12), C(151), and the central aryl ring are coplanar due to extended conjugation. The Cu(1)–N(11) bond, at 1.918(3) Å, is somewhat longer than in previously characterized copper amides.<sup>7,10</sup> The geometry of the metal center is trigonal planar, and with the steric pressure of the terphenyl moiety ameliorated in 7 relative to **5**, the complex adopts a traditional Y-shaped structure.

## **Experimental Section**

Unless stated otherwise, all operations were performed in an MBraun LabMaster drybox under an atmosphere of purified nitrogen. Anhydrous diethyl ether was purchased from Fisher, stirred over sodium metal, and filtered through activated alumina. n-Pentane was purchased from Sigma Aldrich and dried by passage through activated alumina and Q-5 columns.  $C_6D_6$ was purchased from Cambridge Isotope Laboratories, degassed by freeze-pump-thaw cycles, and dried over CaH2 or activated 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated by evacuation overnight at 180 °C. (dmp)I,<sup>4</sup>  $\{(dtbpe)Cu(\mu-Cl)\}_2$  (3),<sup>7</sup> and (IPr)Cu(Cl) (4)<sup>8</sup> were prepared according to the literature methods. All other chemicals were used as received. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN). <sup>1</sup>H NMR spectra were recorded on Bruker 500 MHz NMR spectrometers and reported with reference to residual  $C_6D_5H$  in  $C_6D_6$  (7.16 ppm) and CHCl<sub>3</sub> in CDCl<sub>3</sub> (7.24 ppm). X-ray diffraction data were collected on a Siemens Platform goniometer with a charged coupled device (CCD) detector. Structures were solved by direct methods using the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

**Preparation of (dmp)CH=O.** A cold solution of 4 mL of 1.6 M *n*-BuLi in hexanes was added to a solution of 2.2 g (5 mmol) of (dmp)I in 25 mL of cyclohexane.<sup>4b</sup> After the mixture was stirred at room temperature for 12 h, 0.4 mL (0.377 g, 5.2 mmol) of dry dimethylformamide was added to the reaction mixture. The reaction mixture was heated to reflux for 2 h and then quenched with 50 mL of H<sub>2</sub>O at 0 °C. The organic layer was separated and the aqueous layer extracted with 3 × 10 mL of diethyl ether. The combined organic layers were dried over MgSO<sub>4</sub> and filtered, and the solvent was removed under reduced pressure to yield a white crystalline solid. Further purification on a silica column using hexanes as an eluent yielded 1.2 g (3.5 mmol, 70%) of pure product. <sup>1</sup>H NMR (22 °C, 500.13 MHz, CDCl<sub>3</sub>):  $\delta$  9.66 (s, CHO, 1H), 7.67 (t, C<sub>6</sub>H<sub>3</sub>, 1H, J<sub>HH</sub> = 7.6 Hz), 7.18 (d, C<sub>6</sub>H<sub>3</sub>, 2H, J<sub>HH</sub> = 7.6 Hz), 6.96 (s, C<sub>6</sub>H<sub>2</sub>, 4H), 2.35 (s, CH<sub>3</sub>, 6H), 1.97 (s, CH<sub>3</sub>, 12H). GC MS (*m*/*z*): 324 (M<sup>+</sup>), 310.

**Preparation of (dmp)CH=N<sub>2</sub>H<sub>2</sub>.** A 100 mL round-bottom flask was charged with 1.028 g (3 mmol) of (dmp)CH=O, 50 mL of ethanol, and 5 mL (100 mmol) of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O. The mixture was heated at reflux for 12 h. After the mixture was cooled in an ice bath for 30 min, a crystalline precipitate was filtered and dried under reduced pressure to give 1.00 g (2.8 mmol, 93%) of the hydrazone (dmp)CH=N<sub>2</sub>H<sub>2</sub>. <sup>1</sup>H NMR (20 °C, 500.13 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.20 (s, CHN, 1H), 7.13 (t, C<sub>6</sub>H<sub>3</sub>, 1H, J<sub>HH</sub> = 7.5 Hz), 6.96 (d, C<sub>6</sub>H<sub>3</sub>, 2H, J<sub>HH</sub> = 7.5 Hz), 6.89 (s, C<sub>6</sub>H<sub>2</sub>, 4H), 4.21 (s, NH<sub>2</sub>, 2H), 2.22 (s, CH<sub>3</sub>, 6H), 2.12 (s, CH<sub>3</sub>, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C, 125.77 MHz, C<sub>6</sub>D<sub>6</sub>): δ 140.79 (s, C<sub>Ar</sub>), 139.24 (s, C<sub>Ar</sub>), 138.32 (s, C<sub>Ar</sub>), 136.19 (s, C<sub>Ar</sub>), 135.75 (s, C<sub>Ar</sub>), 132.65 (s, CHN), 129.34 (s, C<sub>Ar</sub>), 128.36 (s, C<sub>Ar</sub>), 127.98 (s, C<sub>Ar</sub>), 21.24 (s, CH<sub>3</sub>), 20.95 (s, CH<sub>3</sub>). GC MS (m/z): 356 (M<sup>+</sup>), 341.

**Preparation of N<sub>2</sub>CH(dmp)** (1). To a mixture of (dmp)-CH=N<sub>2</sub>H<sub>2</sub> (1.00 g, 2.8 mmol), 0.94 g (4.24 mmol) of HgO, and 0.5 g (3.52 mmol) of Na<sub>2</sub>SO<sub>4</sub> in 10 mL of diethyl ether was added a 0.5 mL saturated KOH solution in ethanol with vigorous stirring. The orange suspension turned dark green,

and the mixture was stirred at room temperature for another 2 h. The solvent was removed under reduced pressure, the solids were extracted with 20 mL of *n*-pentane, and the filtrate was cooled to -35 °C followed by filtration to give orangepink crystals of **1** (0.82 g, 2.31 mmol, 82%). <sup>1</sup>H NMR (20 °C, 500.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.96 (t, C<sub>6</sub>H<sub>3</sub>, 1H, J<sub>HH</sub> = 7.5 Hz), 6.88 (d, C<sub>6</sub>H<sub>3</sub>, 2H, J<sub>HH</sub> = 7.5 Hz), 6.84 (s, C<sub>6</sub>H<sub>2</sub>, 4H), 4.04 (s, CH=N, 1H), 2.20 (s, CH<sub>3</sub>, 6H), 2.07 (s, CH<sub>3</sub>, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C, 125.77 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  137.41 (s, C<sub>Ar</sub>), 137.36 (s, C<sub>Ar</sub>), 136.64 (s, C<sub>Ar</sub>), 135.56 (s, C<sub>Ar</sub>), 129.16 (s, C<sub>Ar</sub>), 128.43 (s, C<sub>Ar</sub>), 127.57 (s, C<sub>Ar</sub>), 124.49 (s, C<sub>Ar</sub>), 44.08 (s, CH=N), 21.24 (s, CH<sub>3</sub>), 20.95 (s, CH<sub>3</sub>). IR (CaF<sub>2</sub>, Fluorolube): 3065 (w), 2969 (w), 2914 (w), 2854 (w), 2052 (s,  $\nu_{N=N}$ ), 1611 (w), 1437 (m,  $\nu_{C=N}$ ), 1374 (w) cm<sup>-1</sup>. GC MS (*m*/*z*): 354 (M<sup>+</sup>), 326.

**Preparation of (dtbpe)** $Cu-C(N_2)$ dmp (5). To a cold (-35 °C) ether solution of 1 (70.9 mg, 0.2 mmol in 5 mL of Et<sub>2</sub>O) was added a 2 mL cold ether solution of LiN(*i*-Pr)<sub>2</sub> (21.4 mg, 0.2 mmol, -35 °C) at once. After the mixture was stirred for 30 min at room temperature, the bright red solution was added to a cold suspension of [(dtbpe)CuCl]<sub>2</sub> (3; 133.1 mg, 0.1 mmol, 5 mL of  $Et_2O$ , -35 °C). The mixture turned bright yellow and was stirred for additional 30 min at room temperature. The volatiles were removed under reduced pressure, and the residual vellow solids were extracted with pentanes. Analytically pure 5 was isolated by crystallization from a concentrated pentane solution at -35 °C (110 mg, 0.15 mmol, 75%). <sup>1</sup>H NMR (20 °C, 500.13 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.572 (m, C<sub>6</sub>H<sub>3</sub>, 3H), 7.09 (s, CH, 1H), 6.95 (s, C<sub>6</sub>H<sub>2</sub>, 4H), 2.43 (s, CH<sub>3</sub>, 6H), 2.36 (s, CH<sub>3</sub>, 12H), 1.21 (m, C<sub>2</sub>H<sub>4</sub>, 4H), 1.03 (m,  $-C(CH_3)_3$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (20 °C, 202.47 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  44.22 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C, 125.75 MHz,  $C_6D_6$ ):  $\delta$  198.31 (s,  $-C(=N_2)$ dmp), 152.15 (s), 148.62 (s), 140.13 (s), 135.18 (d,  $J_{CP} = 6$  Hz), 131.33 (s), 129.46 (s), 120.48 (s), 118.11 (s), 34.18 (t,  $-C_2H_4-$ ,  $J_{CP} = 5$  Hz), 31.81 (t,  $-C(CH_3)_3$ ,  $J_{\rm CP} = 8$  Hz), 20.32 (s, o-C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 20.01 (s, p-C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 19.01 (t,  $-C(CH_3)_3$ ,  $J_{HP} = 15$  Hz). IR (CaF<sub>2</sub>, Fluorolube): 2042 (m,  $\nu_{C=N}$ ), 1412 (s,  $\nu_{N=N}$ ) cm<sup>-1</sup>. Anal. Calcd for C<sub>43</sub>H<sub>65</sub>N<sub>2</sub>CuP<sub>2</sub>: C, 70.2; H, 8.91; N, 3.81. Found C, 70.2; H, 8.84; N, 3.57.

(IPr)Cu–CN<sub>2</sub>(dmp) (6). This complex was prepared and isolated in a manner analogous to that described above for **5**, except that (IPr)Cu(Cl) (**4**; 98 mg, 0.2 mmol) was used instead of **3**. **6** was isolated in 82% yield (132 mg) as a bright yellow solid. <sup>1</sup>H NMR (20 °C, 500.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.23 (t, IPr<sub>Ar</sub>, 2H,  $J_{\rm HH} = 8$  Hz), 7.07 (d, IPr<sub>Ar</sub>, 4H,  $J_{\rm HH} = 8$  Hz), 6.98 (t, C<sub>6</sub>H<sub>3</sub>, 1H,  $J_{\rm HH} = 7$  Hz), 6.89 (d, C<sub>6</sub>H<sub>3</sub>, 2H,  $J_{\rm HH} = 7$  Hz), 6.79 (s, C<sub>6</sub>H<sub>2</sub>, 4H), 6.18 (s, CH=CH, 2H), 2.55 (sept, -CH(CH<sub>3</sub>)<sub>3</sub>, 4H,  $J_{\rm HH} = 7$  Hz), 2.33 (s, *p*-CH<sub>3</sub>, 6H), 2.08 (s, *o*-CH<sub>3</sub>, 12H), 1.15 (d, -CH(CH<sub>3</sub>)<sub>3</sub>, 12H,  $J_{\rm HH} = 7$  Hz), 1.00 (d, -CH(CH<sub>3</sub>)<sub>3</sub>, 12H,  $J_{\rm HH} = 7$  Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C, 125.75 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  183.4, 145.3, 140.8, 140.2, 135.9, 135.2, 134.2, 130.5, 128.9, 128.3, 124.4, 123.2, 122.6, 28.9, 24.0, 23.9, 21.1. IR (CaF<sub>2</sub>, Fluorolube): 1975 (s,  $\nu_{\rm N=N}$ ), 1459 (m,  $\nu_{\rm C=N}$ ) cm<sup>-1</sup>. Anal. Calcd for C<sub>52</sub>H<sub>61</sub>N<sub>4</sub>Cu: C, 77.5; H, 7.63, N 6.95. Found C, 77.3; H, 7.54; N, 7.09.

Preparation of (dtbpe)Cu-N(n-Bu)N=CH(dmp) (7). To a cold (-35 °C) solution of 1 (70.9 mg, 0.2 mmol in 5 mL of Et<sub>2</sub>O) was added 0.1 mL of n-BuLi (2 M in cyclohexane). After the mixture was stirred for 30 min at room temperature, the solution turned bright red and was added to a cold suspension of {(dtbpe)Cu(µ-Cl)}<sub>2</sub> (3; 133 mg, 0.1 mmol, 5 mL of Et<sub>2</sub>O, -35 °C). The mixture turned bright yellow and was stirred for an additional 30 min at room temperature. The volatiles were removed under reduced pressure and the residual yellow solids extracted with pentanes. 4 was isolated by crystallization from a concentrated pentane solution at -35 °C (75%). <sup>1</sup>H NMR (20 °C, 500.13 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.07 (m, C<sub>6</sub>H<sub>3</sub>, 3H), 6.99 (s, CH, 1H), 6.91 (s,  $C_6H_2$ , 4H), 3.0 (t,  $\alpha$ -CH<sub>2</sub>, 2H,  $J_{HH} = 7$  Hz), 2.37 (s, CH<sub>3</sub>, 12H), 2.31 (s, CH<sub>3</sub>, 6H), 1.41 (m, β-CH<sub>2</sub>, γ-CH<sub>2</sub> 4H), 1.21  $(t, C_2H_4, 4H, J_{HP} = 3 Hz), 1.09 (t, \delta CH_3, 3H, J_{HH} = 7 Hz), 0.89$ (t, C(CH<sub>3</sub>)<sub>3</sub>, 18H,  $J_{HP} = 3$  Hz), <sup>31</sup>P{<sup>1</sup>H} NMR (20 °C, 202.47 MHz, C<sub>6</sub>D<sub>6</sub>): 29.04 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C, 125.75 MHz,

<sup>(10)</sup> Gunnoe, B. T. Eur. J. Inorg. Chem. 2007, 1185-1203.

C<sub>6</sub>D<sub>6</sub>): δ 142.75 (s), 138.51 (s), 136.26 (d,  $J_{CP} = 3$  Hz), 133.72 (s), 129.23 (s), 128.29 (s), 121.19 (s), 116.04 (s), 62.30 (s, =CH), 36.70 (s, α-CH<sub>2</sub>), 33.33 (t, C<sub>2</sub>H<sub>4</sub>,  $J_{CP} = 3$  Hz), 30.26 (t, C(CH<sub>3</sub>)<sub>3</sub>,  $J_{CP} = 5$  Hz), 21.57 (s, o-C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 21.39 (s, p-C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>), 21.14 (s,  $\beta$ -CH<sub>2</sub>), 20.18 (t, C(CH<sub>3</sub>)<sub>3</sub>,  $J_{HP} = 13$  Hz), 14.99 (s,  $\gamma$ -CH<sub>2</sub>), 14.23 (s,  $\delta$ -CH<sub>3</sub>). <sup>13</sup>C NMR (20 °C, 125.77 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  62.32 (t, N=CH,  $J_{CH} = 131$  Hz). IR (CaF<sub>2</sub>, Nujol): 1479 (m,  $\nu_{N=N}$ ) cm<sup>-1</sup>. Anal. Calcd for C<sub>47</sub>H<sub>75</sub>N<sub>2</sub>CuP<sub>2</sub>: C, 71.1; H, 9.53; N, 3.53. Found: C, 71.0; H, 9.62; N, 3.79. Acknowledgment. This work was supported by the National Science Foundation through Grant No. CHE-0615274 to G.L.H.

**Supporting Information Available:** Text, tables, figures, and CIF files giving complete crystallographic details for 5–7 characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.