

**Diazoalkanes react with a bis(phosphino)borate copper(I) source to generate  $[\text{Ph}_2\text{BP}^{\text{tBu}}_2]\text{Cu}(\eta^1\text{-N}_2\text{CR}_2)$ ,  $[\text{Ph}_2\text{BP}^{\text{tBu}}_2]\text{Cu}(\text{CR}_2)$ , and  $[\text{Ph}_2\text{BP}^{\text{tBu}}_2]\text{Cu-N}(\text{CPh}_2)(\text{NCPh}_2)$**

Neal P. Mankad and Jonas C. Peters\*

Supporting Information

**General.** All manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thoroughly sparging with  $\text{N}_2$  gas followed by passage through an activated alumina column. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. Lithium 2,4,6-trimethylanilide was prepared by deprotonation of 2,4,6-trimethylaniline with *n*-butyllithium.  $[\text{Ph}_2\text{BP}^{\text{tBu}}_2]\text{Li}(\text{OEt}_2)$ ,<sup>1</sup> diphenyldiazomethane,<sup>2</sup> bis(2,4,6-trimethylphenyl)diazomethane,<sup>3</sup> and bis(trimethylsilyl)diazomethane<sup>4</sup> were prepared according to literature procedures.  $\text{N}_2^{13}\text{CPh}_2$  was prepared from benzophenone-(carbonyl- $^{13}\text{C}$ ) (Cambridge Isotopes) according to literature procedures.<sup>2</sup> Elemental analyses were performed by Desert Analytics, Tucson, AZ. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 3-Å molecular sieves prior to use. X-ray diffraction studies were carried out at the Beckman Institute Crystallography Facility on a Brüker Smart 1000 CCD diffractometer and solved using SHELX v. 6.14.

**Spectroscopic measurements.** A Varian Mercury-300 spectrometer was used to record  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  NMR spectra at ambient temperature.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were referenced to the residual solvent peaks.  $^{19}\text{F}$  and  $^{31}\text{P}$  chemical shifts were referenced to external hexafluorobenzene ( $\delta = -165$  ppm) and phosphoric acid ( $\delta = 0$  ppm) respectively. Optical spectroscopy measurements were taken on a Cary 50 UV/Vis Spectrophotometer using a 1-cm quartz cell.

**Computational Methods.** All calculations were performed using the Jaguar 5.0 program package (Jaguar 5.0, Schrodinger, LLC, Portland, OR). The calculations employed the hybrid DFT functional B3LYP. The LACVP\*\* basis set<sup>5</sup> was used for the Cu atom. The 6-31G\*\* basis set was used for the P atoms, as well as the carbene C atom. The MIDI! basis set<sup>6</sup> was used for all other C atoms, as well as B and H atoms. Input coordinates for the geometry optimizations were derived as described in the text. The calculations were spin-restricted, and no symmetry

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<sup>2</sup> J. B. Miller, *J. Org. Chem.* **1959**, *24*, 560.

<sup>3</sup> H. E. Zimmerman, D. H. Paskovich, *J. Am. Chem. Soc.*, **1964**, *86*, 2149.

<sup>4</sup> E. Glozbach, J. Lorberth, *J. Organomet. Chem.* **1980**, *191*, 371.

<sup>5</sup> P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, 299.

<sup>6</sup> R. E. Easton, D. J. Giesen, A. Welch, C. J. Cramer, D. G. Truhlar, *Theo. Chim. Acta* **1996**, 281.

constraints were used. The default values for geometry and SCF iteration cutoffs were used, and all structures converged under these criteria.

**X-ray Crystallography Procedures.** X-ray diffraction studies were carried out at the Beckman Institute Crystallography Facility on a Bruker Smart 1000 CCD diffractometer and solved using SHELX v. 6.14. X-ray quality crystals were grown as indicated in the experimental procedures per individual complex. The crystals were mounted on a glass fiber with Paratone N oil. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. **Spatial refinement details:** Refinement of  $F^2$  against ALL reflections. The weighted R-factor ( $wR$ ) and goodness of fit ( $S$ ) are based on  $F^2$ , conventional R-factors ( $R$ ) are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and R-factors based on ALL data will be even larger. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles, and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Synthesis of  $[\text{Ph}_2\text{BP}^{\text{tBu}}_2]\text{Cu}(\text{pyr})$  (1).**  $[\text{Ph}_2\text{BP}^{\text{tBu}}_2]\text{Li}(\text{OEt}_2)$  (1.83 g, 3.25 mmol) and  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$  (1.02 g, 3.25 mmol) were combined in a 250-mL flask equipped with a stirbar and dissolved in diethyl ether (100 mL). The initially cloudy purple mixture was stirred for 3.5 h, yielding a cloudy white suspension. The solvent was removed *in vacuo*, and the residues were suspended in minimal acetonitrile. A white powder was collected on a sintered glass frit, dissolved in minimal THF, and filtered through Celite. Pyridine (2 mL) was added to the colorless filtrate, giving a clear, bright yellow solution that gradually became cloudy. After stirring for 1 h, the solvent was removed *in vacuo* to yield analytically pure **1** (1.48 g, 73%). X-ray quality crystals were obtained by slow diffusion of petroleum ether vapors into a concentrated THF solution of **1**.  $^1\text{H}$  (THF- $d_8$ ,  $\delta$ ): 8.74 (dt,  $J = 2.2$  and 4.4 Hz, 2H, pyridine *ortho*-CH), 7.80 (tt,  $J = 1.4$  and 7.7 Hz, 1H, pyridine *para*-CH), 7.55 (tq,  $J = 1.4$  and 6.9 Hz, 2H, pyridine *meta*-CH), 7.37 (br, 4H, phenyl *ortho*-CH), 6.88 (t,  $J = 7.3$  Hz, 4H, phenyl *meta*-CH), 6.67 (t,  $J = 7.2$  Hz, 2H, phenyl *para*-CH), 1.58 (br, 4H,  $\text{BCl}_2\text{P}$ ), 1.09 (d,  $^3J_{\text{PH}} = 6.3$  Hz, 18H,  $\text{P}[\text{C}(\text{CH}_3)_3]_2$ ), 1.07 (d,  $^3J_{\text{PH}} = 6.1$  Hz, 18H,  $\text{P}[\text{C}(\text{CH}_3)_3]_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  (THF- $d_8$ ,  $\delta$ ): 152.5 (m, *ipso*-C), 150.6 (s, pyridine C2), 136.7 (s, pyridine C4), 134.8, 133.7, 126.8, 122.5 (s, pyridine C3), 35.8 (br,  $\text{P}[\text{C}(\text{CH}_3)_3]_2$ ), 34.5 (br,  $\text{P}[\text{C}(\text{CH}_3)_3]_2$ ), 31.0 (d,  $^2J_{\text{PC}} = 4.2$  Hz,  $\text{P}[\text{C}(\text{CH}_3)_3]_2$ ), 30.9 (d,  $^2J_{\text{PC}} = 4.1$  Hz,  $\text{P}[\text{C}(\text{CH}_3)_3]_2$ ), 28.0 (m,  $\text{BCl}_2\text{P}$ ).  $^{31}\text{P}\{^1\text{H}\}$  (THF- $d_8$ ,  $\delta$ ): 35.7 (s). IR (KBr,  $\text{cm}^{-1}$ ): 3055, 3030, 2976, 2941, 1595, 1470, 1444, 1383, 1362, 1155, 1103, 1067, 1016, 934, 861, 810. Anal. Calcd for  $\text{C}_{35}\text{H}_{55}\text{BCuNP}_2$ : C, 67.14; H, 8.85; N, 2.24. Found: C, 66.75; H, 8.62; N, 2.34.

**Synthesis of  $\{[\text{Ph}_2\text{BP}^{\text{tBu}}_2]\text{Cu}(\text{NHMe}_s)\}\{\text{Li}(12\text{-C-4})_2\}$  (2).** **1** (1.07 g, 1.71 mmol) and  $\text{LiNHMe}_s$  (0.242 g, 1.71 mmol) were combined in THF (50 mL), giving a cloudy brown solution. After stirring for 5 min, 12-crown-4 (0.690 mL, 4.26 mmol) was added. The resulting clear yellow-brown solution was stirred for 0.5 h, and then the solvent was removed *in vacuo*. The residues were triturated with petroleum ether (50 mL), and a tan powder was collected on a sintered glass frit. Subsequent washes with petroleum ether (5 x 10 mL) gave spectroscopically pure **2** (1.71 g,

96%). X-ray quality crystals were obtained by slow diffusion of petroleum ether vapors into a concentrated THF solution of **2**.  $^1\text{H}$  (THF- $d_8$ ,  $\delta$ ): 7.37 (br, 4H, *ortho*-CH), 6.82 (t,  $J = 7.3$  Hz, 4H, phenyl *meta*-CH), 6.61 (t,  $J = 7.0$  Hz, 2H, *para*-CH), 6.38 (s, 2H, mesityl *meta*-CH), 3.60 (s, 32H, O(CH $_2$ ) $_2$ O), 2.80 (br, 1H, CuNHMes), 2.19 (s, 6H, *ortho*-CH $_3$ ), 2.01 (s, 3H, *para*-CH $_3$ ), 1.41 (br, 4H, BCH $_2$ P), 1.06 (d,  $^3J_{\text{PH}} = 5.5$  Hz, 18H, P[C(CH $_3$ ) $_3$ ] $_2$ ), 1.05 (d,  $^3J_{\text{PH}} = 5.5$  Hz, 18H, P[C(CH $_3$ ) $_3$ ] $_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  (THF- $d_8$ ,  $\delta$ ): 160.0 (s, mesityl *ipso*-C), 155.4 (br, phenyl *ipso*-C), 134.1, 129.1, 126.4, 121.9, 120.7, 114.0, 69.4 (s, O(CH $_2$ ) $_2$ O), 34.0 (br, P[C(CH $_3$ ) $_3$ ] $_2$ ), 31.1 (d,  $^2J_{\text{PC}} = 7.2$  Hz, P[C(CH $_3$ ) $_3$ ] $_2$ ), 31.0 (d,  $^2J_{\text{PC}} = 7.2$  Hz, P[C(CH $_3$ ) $_3$ ] $_2$ ), 21.4 (s, *ortho*-CH $_3$ ), 21.2 (s, *para*-CH $_3$ ), 14.6 (br, BCH $_2$ P).  $^{31}\text{P}\{^1\text{H}\}$  (THF- $d_8$ ,  $\delta$ ): 29.0 (s). IR (KBr,  $\text{cm}^{-1}$ ): 3374 (N-H st), 2909, 2864, 1629 (N-H  $\delta$ ), 1603, 1475, 1445, 1362, 1289, 1248, 1136, 1098, 1024, 916, 853, 812. Anal. Calcd for  $\text{C}_{55}\text{H}_{94}\text{BCuLiNO}_8\text{P}_2$ : C, 63.48; H, 9.11; N, 1.35. Found: C, 62.12; H, 8.73; N, 1.24. Note: Satisfactory combustion analysis results could not be obtained, even when doubly recrystallized material was submitted for analysis. For evidence of purity,  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra are reproduced below (Figures S10 and S11).

**Synthesis of [Ph $_2$ BP $^{\text{tBu}}$ ] $_2$ Cu(NH $_2$ Mes) (**3**).** **2** (1.66 g, 1.60 mmol) was dissolved in toluene (50 mL) and cooled to  $-90$   $^\circ\text{C}$ . Separately, tetrafluoroboric acid (0.219 mL of a 48 wt% solution in diethyl ether, 1.60 mmol) was diluted with toluene (10 mL) and cooled to  $-30$   $^\circ\text{C}$ . The acid solution was then added slowly at  $-90$   $^\circ\text{C}$ , giving a cloudy brown mixture that was allowed to warm gradually to room temperature. After stirring for 2 h at room temperature, the mixture was filtered through Celite. Concentration of the gold-yellow filtrate gave a tacky yellow residue, which was triturated with petroleum ether (20 mL) and collected by filtration. Subsequent washes with petroleum ether (3 x 10 mL) gave analytically pure **3** (0.813 g, 74%). X-ray quality crystals were obtained by slow diffusion of petroleum ether vapors into a concentrated dichloromethane solution of **3**.  $^1\text{H}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 7.92 (br d,  $J = 5.4$  Hz, 4H, *ortho*-CH), 7.39 (t,  $J = 7.5$  Hz, 4H, phenyl *meta*-CH), 7.13 (t,  $J = 7.2$  Hz, 2H, *para*-CH), 6.56 (s, mesityl *meta*-CH), 3.43 (br, 2H, CuNH $_2$ Mes), 2.05 (s, 3H, *para*-CH $_3$ ), 1.9 (br, 4H, BCH $_2$ P), 1.87 (s, 6H, *ortho*-CH $_3$ ), 1.01 (d,  $^3J_{\text{PH}} = 6.0$  Hz, 18H, P[C(CH $_3$ ) $_3$ ] $_2$ ), 0.99 (d,  $^3J_{\text{PH}} = 6.0$  Hz, 18H, P[C(CH $_3$ ) $_3$ ] $_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 150.9, 144.2, 136.7, 134.4, 133.7, 127.3, 124.5, 123.3, 36.1 (br, P[C(CH $_3$ ) $_3$ ] $_2$ ), 33.9 (br, P[C(CH $_3$ ) $_3$ ] $_2$ ), 31.1 (d,  $^2J_{\text{PC}} = 7.2$  Hz, P[C(CH $_3$ ) $_3$ ] $_2$ ), 31.0 (d,  $^2J_{\text{PC}} = 7.2$  Hz, P[C(CH $_3$ ) $_3$ ] $_2$ ), 28.1 (s, *ortho*-CH $_3$ ), 27.7 (s, *para*-CH $_3$ ), 17.9 (br, BCH $_2$ P).  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 37.1 (s). IR (KBr,  $\text{cm}^{-1}$ ): 3353 (N-H st), 3292 (N-H st), 3053, 2938, 1580, 1480, 1428, 1381, 1364, 1305, 1260, 1219, 1156, 1105, 1015, 940, 860, 808. Anal. Calcd for  $\text{C}_{39}\text{H}_{63}\text{BCuNP}_2$ : C, 68.66; H, 9.31; N, 2.05. Found: C, 68.51; H, 9.28; N, 1.79.

**Preparation of [Ph $_2$ BP $^{\text{tBu}}$ ] $_2$ Cu(THF) (**4**).** Petroleum ether vapors were diffused slowly into a saturated THF solution of **3** to provide a quantitative yield of **4**.  $^1\text{H}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 7.90 (d,  $J = 5.8$  Hz, 4H, phenyl *ortho*-CH), 7.39 (t,  $J = 7.7$  Hz, 4H, phenyl *meta*-CH), 7.13 (t,  $J = 8.3$  Hz, 2H, phenyl *para*-CH), 3.55 (m, 4H, O-(CH $_2$ -CH $_2$ ) $_2$ ), 1.84 (br, 4H, BCH $_2$ P), 1.38 (m, 4H, O-(CH $_2$ -CH $_2$ ) $_2$ ), 1.02 (d,  $^3J_{\text{PH}} = 6.0$  Hz, 18H, P[C(CH $_3$ ) $_3$ ] $_2$ ), 1.00 (d,  $^3J_{\text{PH}} = 6.3$  Hz, 18H, P[C(CH $_3$ ) $_3$ ] $_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 136.4, 135.9, 133.6, 123.3, 68.7 (br, O-(CH $_2$ -CH $_2$ ) $_2$ ), 34.8 (br, P[C(CH $_3$ ) $_3$ ] $_2$ ), 34.1 (br, P[C(CH $_3$ ) $_3$ ] $_2$ ), 31.4 (P[C(CH $_3$ ) $_3$ ] $_2$ ), 30.7 (P[C(CH $_3$ ) $_3$ ] $_2$ ), 27.7 (m, BCH $_2$ P), 26.1 (O-(CH $_2$ -CH $_2$ ) $_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 37.5 (s). IR (KBr,  $\text{cm}^{-1}$ ): 3054, 2941, 1474, 1364, 1103, 860, 815. Anal. Calcd for  $\text{C}_{34}\text{H}_{58}\text{BCuOP}_2$ : C, 65.96; H, 9.44. Found: C, 66.21; H, 9.22.

**Synthesis of [Ph<sub>2</sub>BP<sup>tBu</sup>]<sub>2</sub>Cu(N<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>) (5).** Bis(trimethylsilyl)diazomethane (0.0598 mL of a 1.87 M stock solution in hexanes, 0.112 mmol) was added to a stirring solution of **3** (63.6 mg, 0.0932 mmol) in benzene (5 mL). The resulting yellow solution was heated to 60 °C for 24 h, and then concentrated *in vacuo* to a solid yellow-orange residue. Recrystallization from petroleum ether (1.5 mL, -30 °C) gave **5** as faint yellow crystals (7.3 mg, 11%). X-ray quality crystals were obtained by slow evaporation of a petroleum ether solution of **5**. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, δ): 8.01 (br d, *J* = 5.4 Hz, 4H, *ortho*-CH), 7.42 (t, *J* = 7.3 Hz, 4H, *meta*-CH), 7.16 (t, *J* = 7.2 Hz, 2H, *para*-CH), 1.91 (br, 4H, B<sub>CH</sub><sub>2</sub>P), 1.22 (d, <sup>3</sup>*J*<sub>PH</sub> = 6.3 Hz, 18H, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 1.20 (d, <sup>3</sup>*J*<sub>PH</sub> = 5.8 Hz, 18H, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), -0.03 (s, 12H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, δ): 166.1 (m, *ipso*-C), 133.6, 127.4, 132.2, 34.1 (d, <sup>1</sup>*J*<sub>PC</sub> = 5.8 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 34.0 (d, <sup>1</sup>*J*<sub>PC</sub> = 5.8 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 30.8 (d, <sup>2</sup>*J*<sub>PC</sub> = 4.1 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 30.7 (d, <sup>2</sup>*J*<sub>PC</sub> = 4.1 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 29.5 (br m, N<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>), 12.5 (br q, <sup>1</sup>*J*<sub>BC</sub> = 42.0 Hz, B<sub>CH</sub><sub>2</sub>P), -0.4 (s, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, δ): 39.2 (s). IR (C<sub>6</sub>H<sub>6</sub>, cm<sup>-1</sup>): 2932, 2865, 2108 (CN<sub>2</sub> st), 1477, 1425, 1364, 1260, 1102, 1071, 899, 867, 817. Anal. Calcd for C<sub>37</sub>H<sub>68</sub>BCuN<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>: C, 60.59; H, 9.35; N, 3.82. Found: C, 60.47; H, 9.43; N, 3.59.

**Synthesis of [Ph<sub>2</sub>BP<sup>tBu</sup>]<sub>2</sub>Cu(N<sub>2</sub>CMes<sub>2</sub>) (6).** **3** (0.200 g, 0.293 mmol) and bis(2,4,6-trimethylphenyl)diazomethane (0.0816 g, 0.293 mmol) were combined in benzene (10 mL), giving a clear red-orange solution which was stirred for 40 min and then concentrated *in vacuo*. Petroleum ether (20 mL) was added, and the solution was cooled to -78 °C. A pre-cooled solution of tetrafluoroboric acid (0.0402 mL of a 48 wt% solution in diethyl ether, 0.293 mmol) was added in one portion, and the solution was allowed to warm gradually to room temperature with stirring. After 25 min at room temperature, a white precipitate was filtered off, and the filtrate was concentrated to a red-orange powder (0.130 g, 54%). X-ray quality crystals were obtained by slow evaporation of a petroleum ether solution of **6**. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, δ): 7.95 (br d, *J* = 6.9 Hz, 4H, *ortho*-CH), 7.40 (t, *J* = 7.4 Hz, 4H, phenyl *meta*-CH), 7.14 (t, 2H, *para*-CH), 6.70 (s, 4H, mesityl *meta*-CH), 2.09 (s, 6H, *para*-CH<sub>3</sub>), 2.06 (s, 12H, *ortho*-CH<sub>3</sub>), 1.91 (br, 4H, B<sub>CH</sub><sub>2</sub>P), 1.07 (d, <sup>3</sup>*J*<sub>PH</sub> = 6.3 Hz, 18H, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 1.05 (d, <sup>3</sup>*J*<sub>PH</sub> = 6.0 Hz, 18H, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, δ): 137.8 (br, phenyl *ipso*-C), 137.6, 133.6, 130.6, 129.7, 127.4, 126.6, 123.4, 99.3 (N<sub>2</sub>CMes<sub>2</sub>), 34.0 (d, <sup>1</sup>*J*<sub>PC</sub> = 6.7 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 33.9 (d, <sup>1</sup>*J*<sub>PC</sub> = 6.7 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 30.7 (d, <sup>2</sup>*J*<sub>PC</sub> = 3.7 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 30.6 (d, <sup>2</sup>*J*<sub>PC</sub> = 3.7 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 21.3 (s, *para*-CH<sub>3</sub>), 21.1 (s, *ortho*-CH<sub>3</sub>), 14.3 (br, B<sub>CH</sub><sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, δ): 45.9 (s). IR (C<sub>6</sub>H<sub>6</sub>, cm<sup>-1</sup>): 2921, 2868, 2041 (CN<sub>2</sub> st), 1444, 1366, 1099, 812. Anal. Calcd for C<sub>49</sub>H<sub>72</sub>BCuN<sub>2</sub>P<sub>2</sub>: C, 71.30; H, 8.79; N, 3.39. Found: C, 71.41; H, 8.43; N, 5.42. Note: High levels of N were found consistently by elemental analysis. For evidence of purity, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra are reproduced below (Figure S12 and S13). In addition, the IR spectrum reproduced below (Figure S14) precludes the presence of residual free N<sub>2</sub>CMes<sub>2</sub>.

**Synthesis of [Ph<sub>2</sub>BP<sup>tBu</sup>]<sub>2</sub>Cu(N(=CPh<sub>2</sub>)(NCPPh<sub>2</sub>)) (7).** Diphenyldiazomethane (32.0 mg, 0.165 mmol) was dissolved in benzene (5 mL) and added to solid **3** (56.3 mg, 0.0825 mmol), giving a deep inky-blue solution. Over several hours, the solution turned orange-brown. After 24 h, a crude reaction aliquot showed >90% conversion to the desired product (by <sup>31</sup>P NMR). The solution was concentrated *in vacuo* to a solid brown residue, which was recrystallized from diethyl ether (1.5 mL, -30 °C) to give **7** as dark orange crystals (23.8 mg, 32%). X-ray quality crystals were obtained by slow diffusion of hexamethyldisiloxane vapors into a diethyl ether solution of **7** at -30 °C. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, δ): 9.10 (br, 2H), 8.05 (br d, *J* = 6.3 Hz, 4H, *ortho*-BPh<sub>2</sub>), 7.67 (m, 8H), 7.42 (t, *J* = 7.3 Hz, 4H, *meta*-BPh<sub>2</sub>), 7.33 (m, 8H), 7.13-6.89 (m, 34H), 1.91 (br, 4H,

BCH<sub>2</sub>P), 1.09 (d, <sup>3</sup>J<sub>PH</sub> = 5.8 Hz, 18H, P[C(CH<sub>3</sub>)<sub>2</sub>]), 1.07 (d, <sup>3</sup>J<sub>PH</sub> = 5.5 Hz, 18H, P[C(CH<sub>3</sub>)<sub>2</sub>]).  
<sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, δ): 176.5 (m, Cu-N=CPh<sub>2</sub>), 166.3 (br m, *ortho*-BPh<sub>2</sub>), 160.4 (s, Cu-N-N=CPh<sub>2</sub>),  
139.1, 136.7, 132.5, 131.5, 130.2, 130.1, 129.6, 129.1, 128.7, 128.4, 127.3, 123.3, 33.9 (d, <sup>1</sup>J<sub>PC</sub> =  
5.8 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 33.8 (d, <sup>1</sup>J<sub>PC</sub> = 5.8 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 30.8 (d, <sup>2</sup>J<sub>PC</sub> = 3.8 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>),  
30.7 (d, <sup>2</sup>J<sub>PC</sub> = 3.8 Hz, P[C(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>), 14.0 (br q, <sup>1</sup>J<sub>BC</sub> = 41.7 Hz, BCH<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, δ):  
39.9 (s). IR (KBr, cm<sup>-1</sup>): 3055, 2940, 2866, 1584 (C=N st), 1561 (C=N st), 1487, 1445, 1393,  
1362, 1319, 1178, 1157, 1103, 1074, 955, 865. Anal. Calcd for C<sub>56</sub>H<sub>70</sub>BCuN<sub>2</sub>P<sub>2</sub>: C, 74.12; H,  
7.77; N, 3.09. Found: C, 74.10; H, 7.48; N, 3.21.

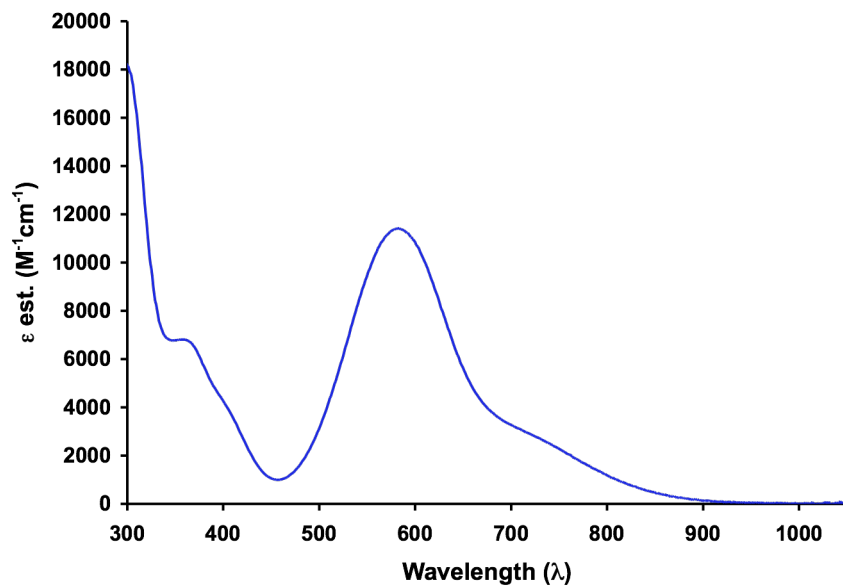
**Observation of the optical spectrum for [Ph<sub>2</sub>BP<sup>tBu</sup>]<sub>2</sub>Cu=CPh<sub>2</sub> (**8**).** Diphenyldiazomethane (0.5 mg, 0.0026 mmol) was dissolved in benzene (3 mL) and added to solid **3** (1.8 mg, 0.0026 mmol) in a volumetric flask, resulting in an immediate color change to an intense inky blue. The volume was brought up to 20.0 mL, and an aliquot was removed for observation by UV-Vis. A intense feature at 583 nm was observed. In a separate experiment under identical conditions, **8** was present in ca. 70 mol% by <sup>31</sup>P{<sup>1</sup>H} spectroscopy. On this basis, an ε value of ca. 12 000 was estimated.

**Observation of <sup>13</sup>C-labelled **8**.** N<sub>2</sub><sup>13</sup>CPh<sub>2</sub> (13.1 mg, 0.0671 mmol) was dissolved in benzene-*d*<sub>6</sub> (1 mL) and added to solid **3** (49.8 mg, 0.730 mmol), resulting in an immediate color change to an intense inky blue. The reaction was monitored by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR. In the initial reaction mixture, the salient features attributed to **8**-<sup>13</sup>C were as follows. <sup>13</sup>C{<sup>1</sup>H} (δ): 331.5 (t, <sup>2</sup>J<sub>PC</sub> = 40.4 Hz, Cu=CPh<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} (δ): 64.8 (d, <sup>2</sup>J<sub>PC</sub> = 41.2 Hz).

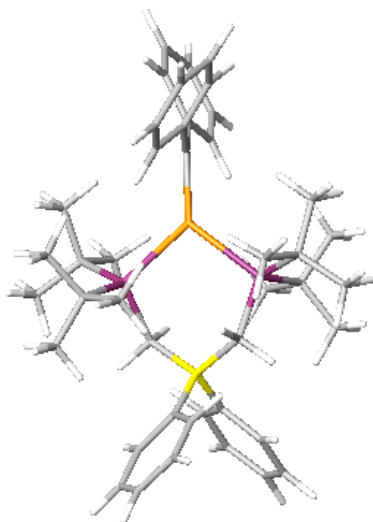
**Carbene transfer to CO.** Using the reaction conditions described above, **8** was generated in situ and transferred to a J. Young NMR tube. The solution was frozen, and then the dinitrogen atmosphere was evacuated and replaced with carbon monoxide (1 atm). The reaction mixture was examined by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR, showing quantitative conversion of **8** to the previously characterized [Ph<sub>2</sub>BP<sup>tBu</sup>]<sub>2</sub>Cu(CO).<sup>7</sup> The solution was then transferred to a solution IR cell and examined by IR spectroscopy, revealing diagnostic CO stretching vibrations for both [Ph<sub>2</sub>BP<sup>tBu</sup>]<sub>2</sub>Cu(CO) and Ph<sub>2</sub>C=C=O, 2082 cm<sup>-1</sup>.<sup>8</sup> In a separate experiment, the copper-containing components of the product mixture were precipitated with petroleum ether, and analysis of the supernatant by ESI-MS revealed the presence of Ph<sub>2</sub>C=C=O.

<sup>7</sup> J. C. Thomas, J. C. Peters, *Polyhedron* **2004**, *23*, 2901.

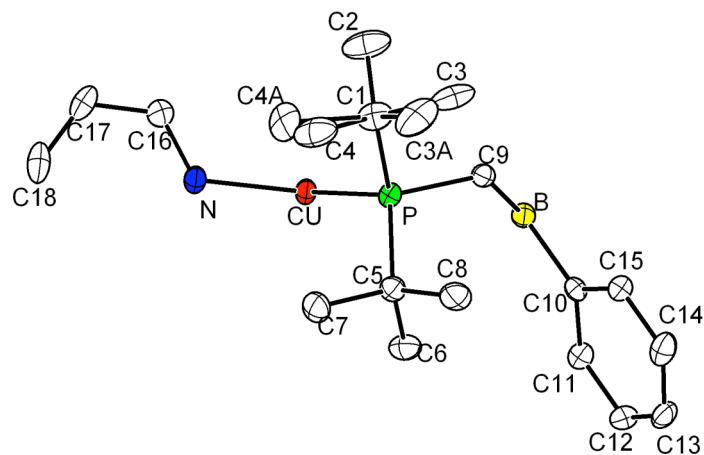
<sup>8</sup> A. E. Taggi, A. M. Ahmed, H. Wack, B. Young, D. Ferraris, T. Leckta, *J. Am. Chem. Soc.* **2002**, *23*, 6626.



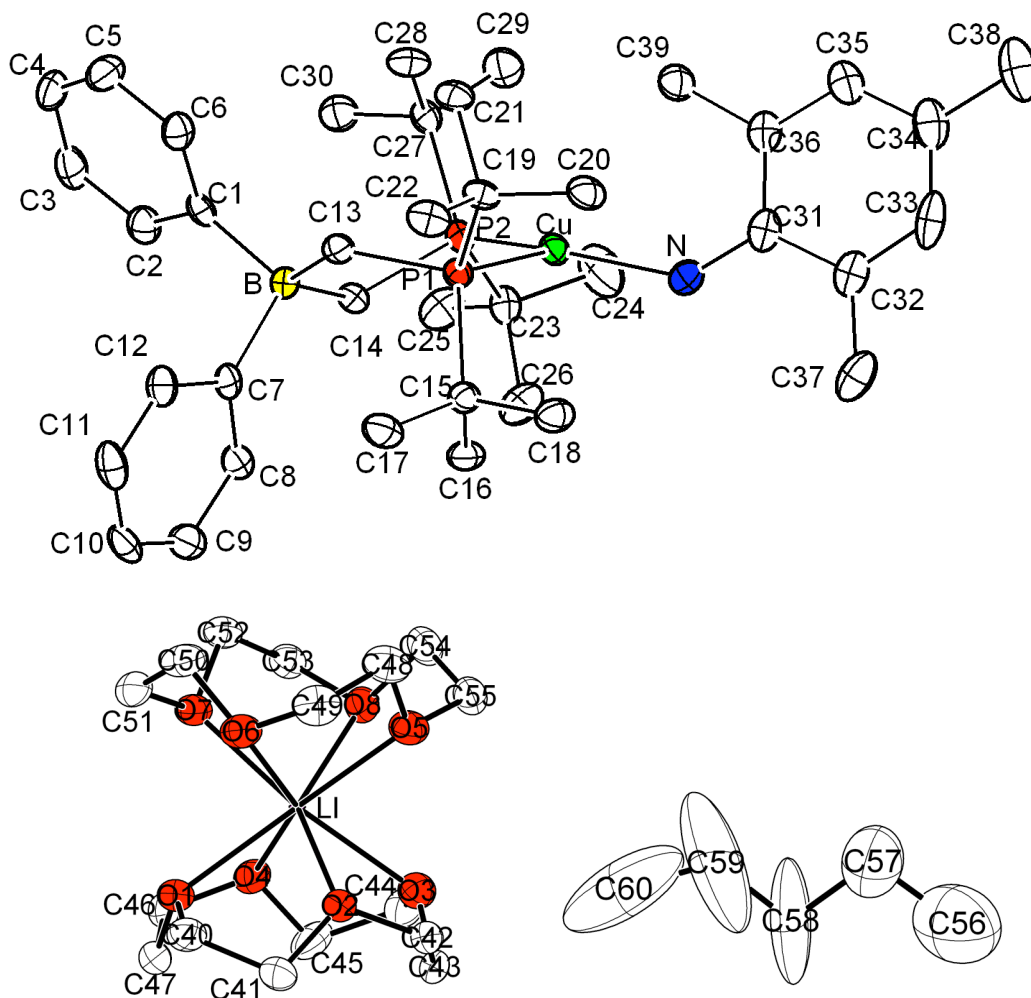
**Figure S1.** Optical spectrum of **8**.



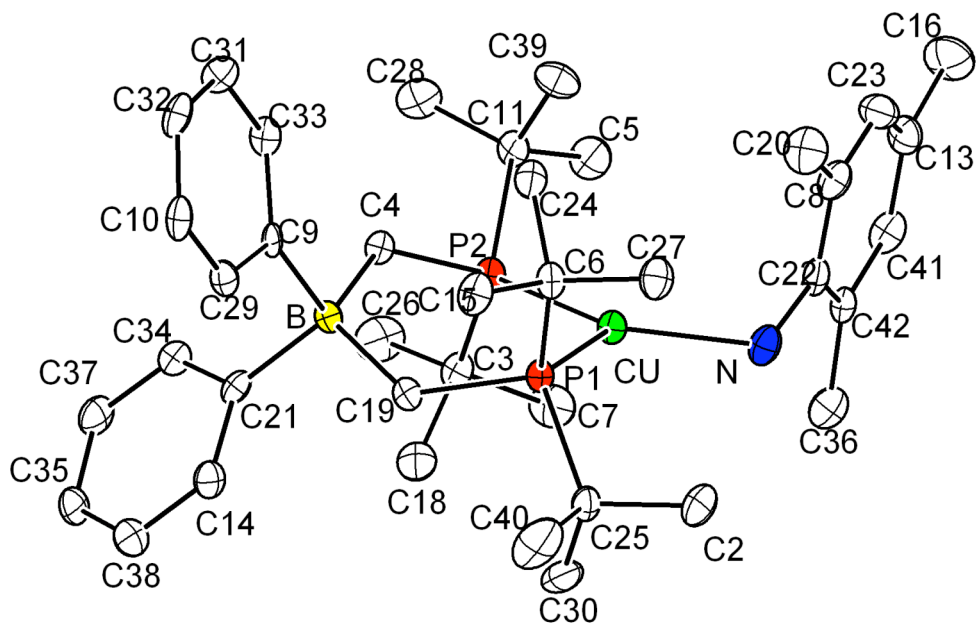
**Figure S2.** Optimized structure of **8**, as determined by DFT.



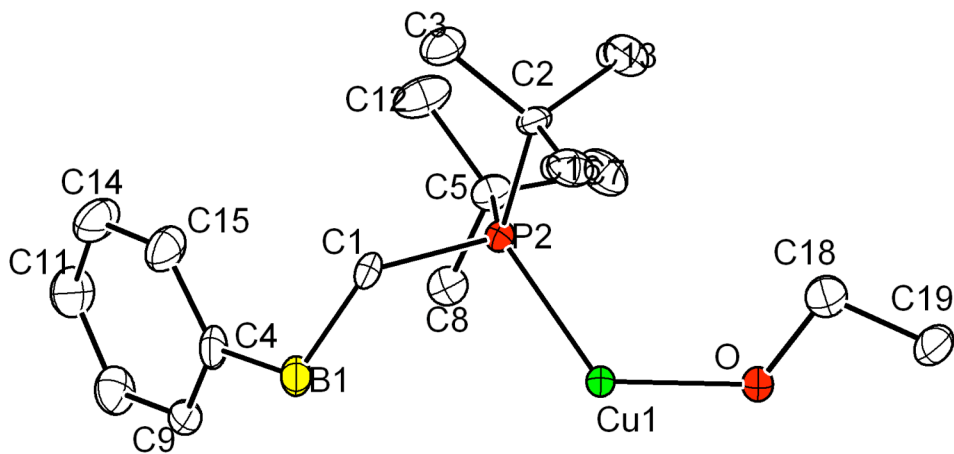
**Figure S3.** Fully-labelled diagram of **1**. Half of the molecule (not shown) was generated by symmetry operations. Disorder in the *tert*-butyl group was modeled as shown.



**Figure S4.** Fully-labelled diagrams of **2** and a co-crystallized pentane molecule.

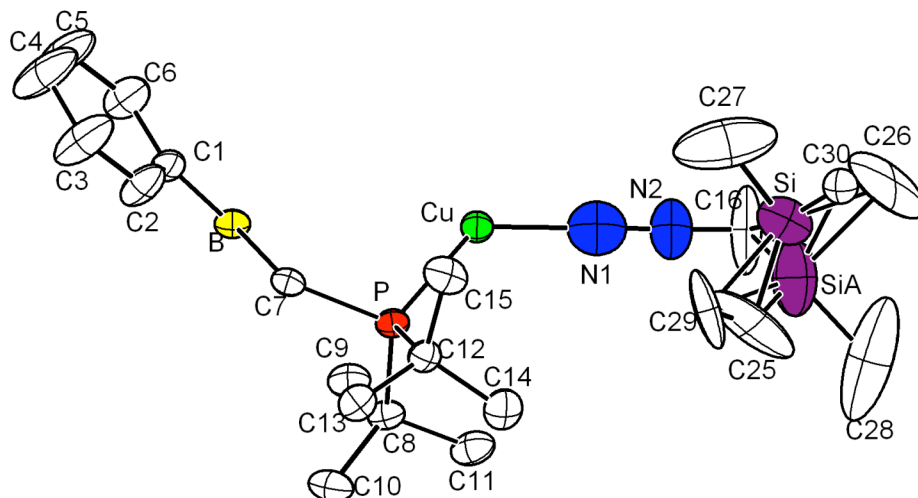


**Figure S5.** Fully-labelled diagram of 3.

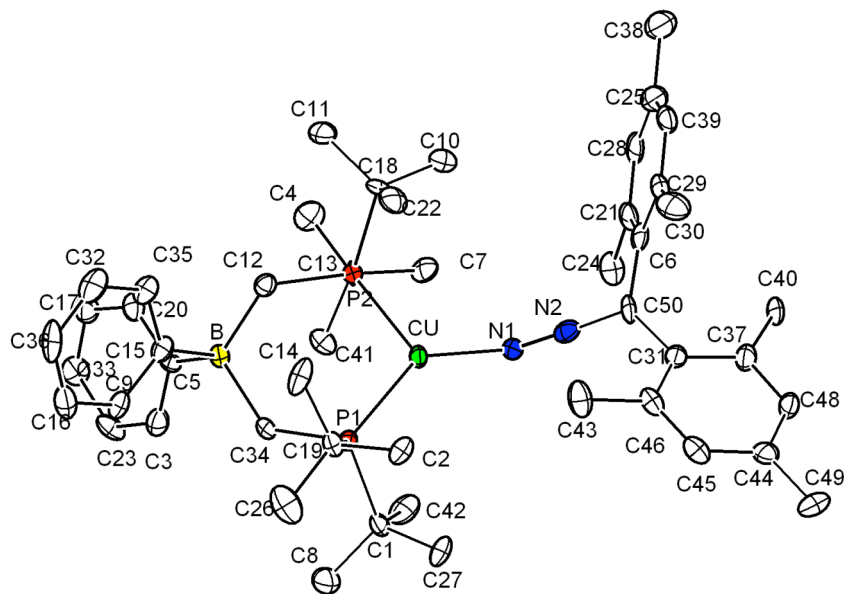


**Figure S6.** Fully-labelled diagram of 4. Half of the molecule (not shown) was generated by symmetry operations.

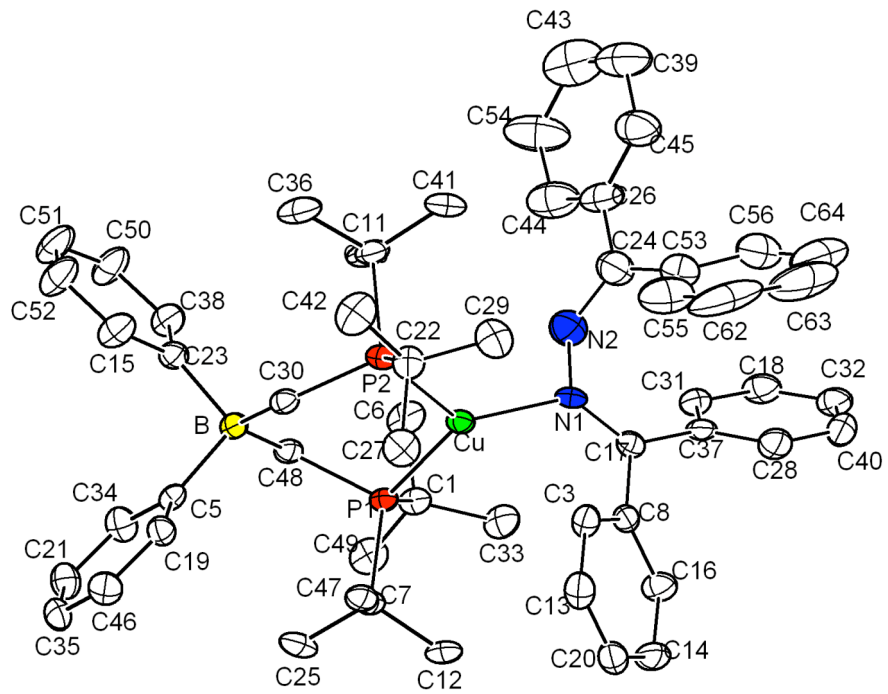




**Figure S7.** Fully-labelled diagram of **5**. Half of the molecule (not shown) was generated by symmetry operations. Disorder in the SiMe<sub>3</sub> group was modeled as indicated in the diagram.



**Figure S8.** Fully-labelled diagram of **6**.



**Figure S9.** Fully-labelled diagram of 7.

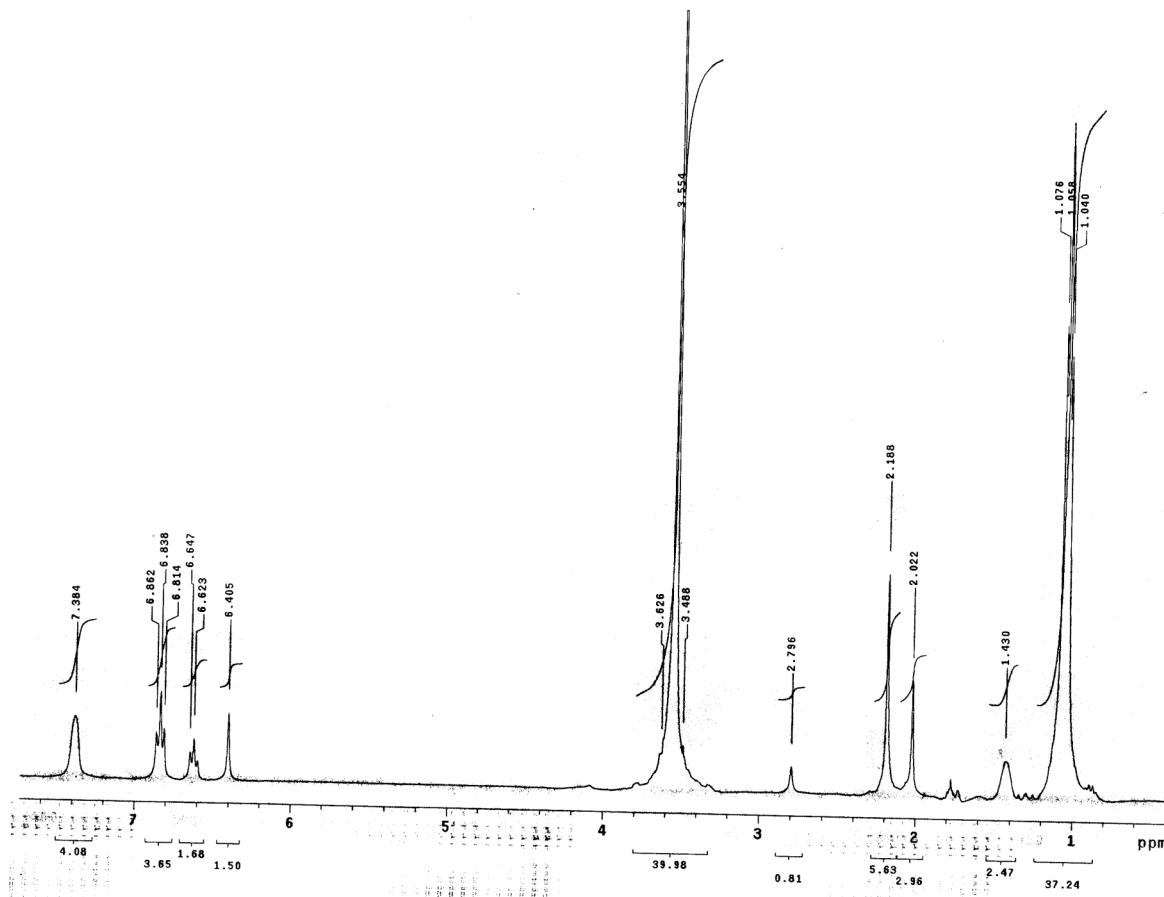
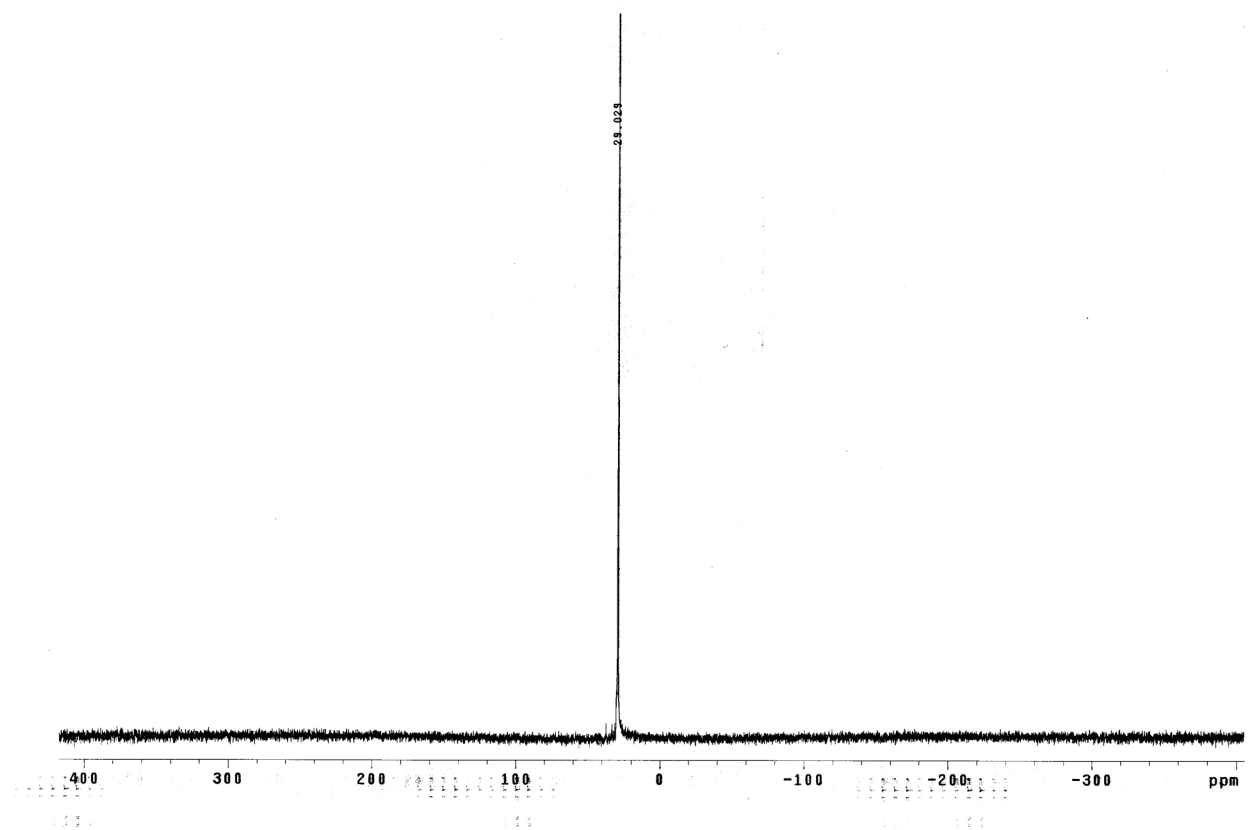


Figure S10.  $^1\text{H}$  NMR spectrum of **2**.



**Figure S11.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2**.

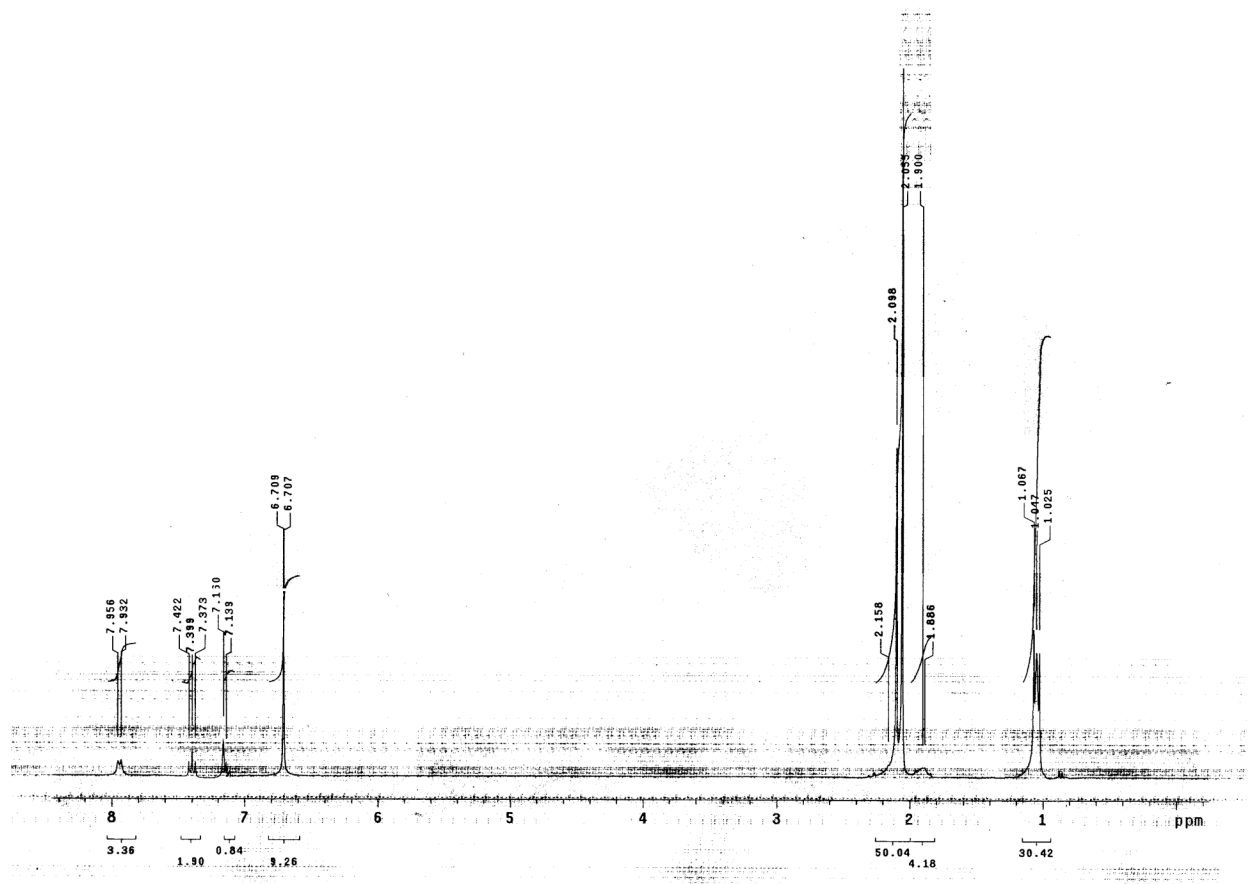
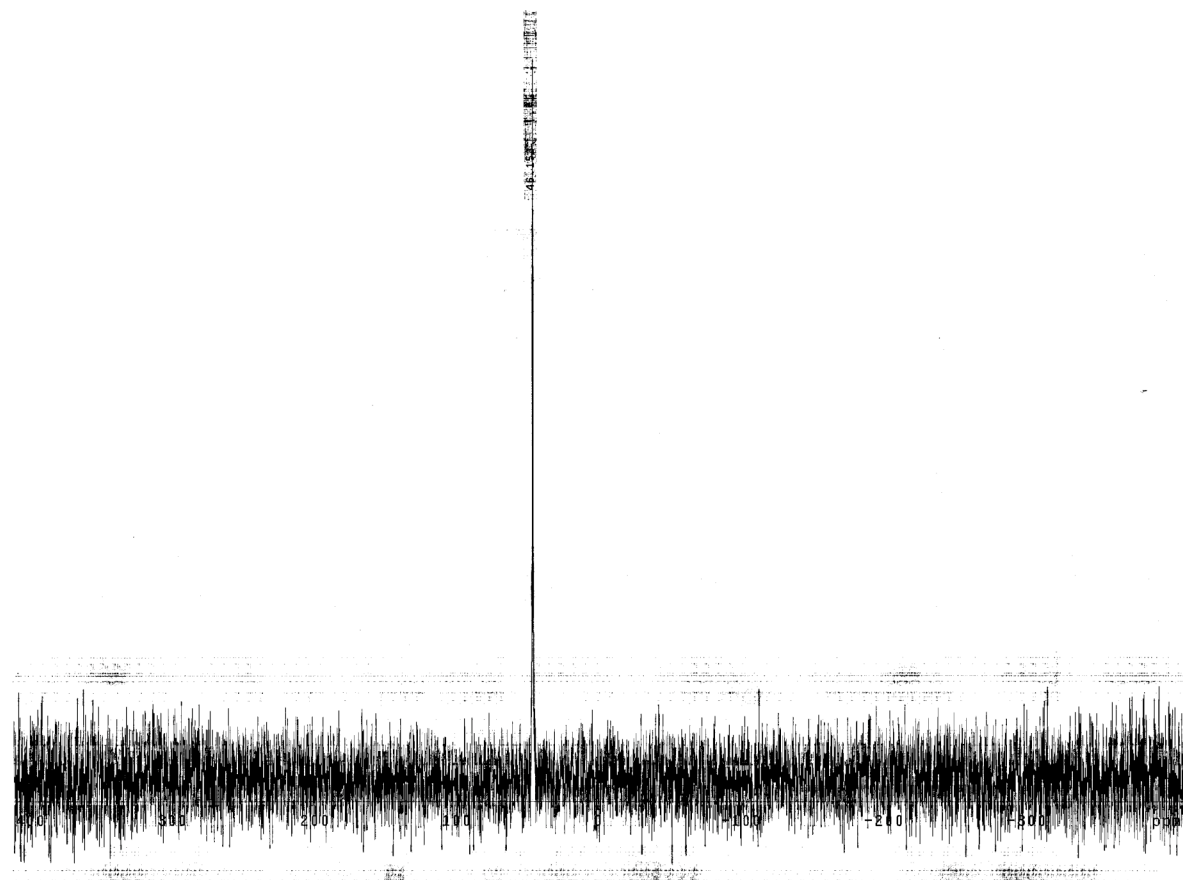
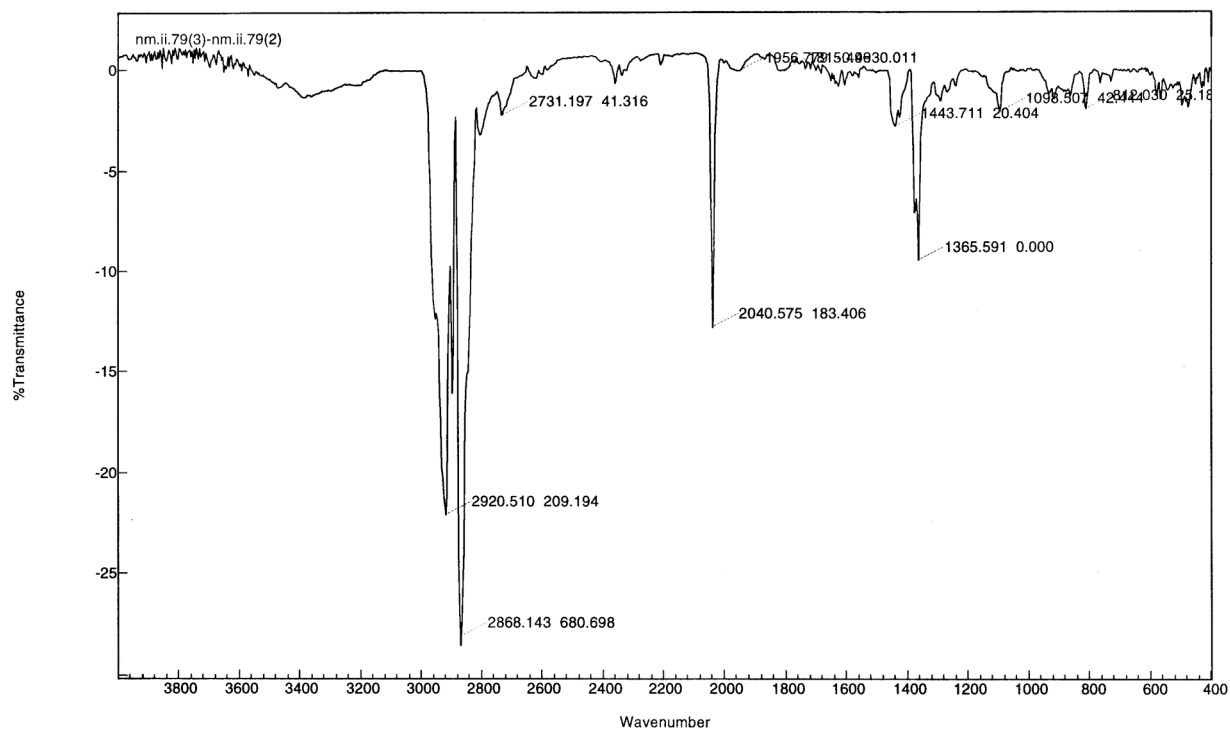


Figure S12.  $^1\text{H}$  NMR spectrum of 6.



**Figure S13.**  $^{31}\text{P}$  NMR spectrum of **6**.



**Figure S14.** Solution IR spectrum ( $C_6H_6$ ) of **6**. The diazoalkane  $CN_2$  stretching region features a single peak ( $2041\text{ cm}^{-1}$ ), indicating the presence of only one diazoalkane-containing species in solution.