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Synthesis and Characterization of Copper(I) Complexes with a Fairly Bulky Tris(pyrazolyl)hydroborate Ligand. Probing the Flexibility of the Metal-Containing Pocket Formed by the Ligand

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Four copper(I) tris(pyrazolyl)hydroborate complexes are reported with the fairly bulky tris[3-(*p*-*tert*-butylphenyl)-5-methylpyrazol-1-yl]hydroborate ligand ($\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}$). $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}\mathrm{Cu(CH_3CN)}$ (**1**) was synthesized from CuCl and $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}\mathrm{Li(CH_3CN)}$. The acetonitrile ligand in **1** was easily replaced by CO, $\mathrm{PPh_3}$, and $\mathrm{P}^t\mathrm{Bu_3}$, forming $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}\mathrm{Cu(CO)}$ (**2**), $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}\mathrm{Cu(PPh_3)}$ (**3**), and $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}\mathrm{Cu(P}^t\mathrm{Bu_3)}$ (**4**), respectively. Complexes **1**−**4** have been crystallographically characterized. **1**·4$\mathrm{CH_3CN}$, 173 K: $\mathrm{C_{52}H_{67}BCuN_{11}}$, triclinic, $P\bar{1}$, $a = 13.4201(10)$ Å, $b = 15.132(2)$ Å, $c = 15.2125(13)$ Å, $\alpha = 60.743(6)°$, $\beta = 73.211(4)°$, $\gamma = 74.839(5)°$, $Z = 2$, R1 = 6.81% (wR2 = 18.91%). **2**, 296 K: $\mathrm{C_{43}H_{52}BCuN_6O}$, monoclinic, $C2/c$, $a = 25.592(4)$ Å, $b = 12.434(2)$ Å, $c = 28.044(3)$ Å, $\beta = 104.073(9)°$, $Z = 8$, R1 = 7.47% (wR2 = 22.08%). **3**·$\mathrm{CH_2Cl_2}$, 173 K: $\mathrm{C_{61}H_{69}BCl_2CuN_6P}$, triclinic, $P\bar{1}$, $a = 12.5080(13)$ Å, $b = 15.159(3)$ Å, $c = 17.151(2)$ Å, $\alpha = 64.271(10)°$, $\beta = 79.073(7)°$, $\gamma = 86.572(8)°$, $Z = 2$, R1 = 5.13% (wR2 = 13.28%). **4**·0.5 hexane, 298 K: $\mathrm{C_{57}H_{86}BCuN_6P}$, triclinic, $\mathrm{P}\bar{1}$, $a = 13.337(2)$ Å, $b = 13.435(2)$ Å, $c = 17.386(2)$ Å, $\alpha = 88.371(7)°$, $\beta = 71.863(8)°$, $\gamma = 80.223(9)°$, $Z = 2$, R1 = 6.96% (wR2 = 18.62%). The $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}$ ligands in **1**, **2**, and **3** bind in a tridentate fashion; the $\mathrm{CH_3CN}$ and CO ligands fit comfortably within the pocket formed by the *tert*-butylphenyl substituents and the $\mathrm{PPh_3}$ ligand interleaves between the pyrazole arms. The flexibility of the pocket was probed by calculating the area of the triangle created by connecting the midpoints of the 3-phenyl groups; this parameter increases by 15% for **3** (the largest) over **1** (the smallest). Thus, the pocket exhibits some flexibility, found to be due to both steric and electronic factors. Complex **4** features a bidentate $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}$ ligand as the $\mathrm{P}^t\mathrm{Bu_3}$ apparently exceeds the pocket's flexibility.

Introduction

The tris(pyrazolyl)hydroborate family of ligands (Tp) has been found to be quite versatile, forming complexes of p block, d block, as well as f block metal ions.[1] Many different uses have been proposed or discovered for Tp complexes, including their utility as synthetic reagents, catalysts and bioinorganic model complexes.[1,2] The synthesis of pyrazole rings with alkyl and aryl substituents at the 3- and 5-positions is often relatively trivial. The properties of the resulting Tp ligands and complexes can be dramatically different depending on the steric and electronic requirements of the Tp ligand and the nature of the metal center.[2]

A number of Tp copper(I) and copper(II) complexes are known, including several historically important contributions to copper chemistry. For example, Tp-ligation enabled the first crystallographic characterization of copper−carbonyl,[3] copper−ethylene,[4] and mononuclear−nitrosyl[5] complexes and the successful prediction of the dioxygen-binding mode in oxyhemocyanin.[6,7] Although many sterically bulky Tp ligands are now known,[2] the number of their reported copper complexes is limited.[2]

We are particularly interested in the tris[3-(*p*-*tert*-butylphenyl)-5-methylpyrazol-1-yl]hydroborate ligand ($\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}$)[8] because of the fairly deep pocket that this ligand should form at the metal center. Here we report[9] the first copper(I) complexes of $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}$ and make initial observations on the flexibility of the pocket. The latter is an important property to understand in order to more effectively utilize these ligands/complexes in various applications.

Experimental Section

All reagents were purchased from commercial sources. Cuprous chloride was purified by published procedures[10] and stored in a continuously purified nitrogen-atmosphere glovebox. Dichloromethane,

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(4) Thompson, J. S.; Harlow, R. L.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3522−3527.

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(7) Kitajima, N.; Moro-oka, Y. *Chem. Rev.* **1994**, *94*, 737−757.

(8) Specific Tp ligands are abbreviated such that Tp pyrazole substituents are superscripted after the Tp abbreviation; the 3-position group is listed first and the 5-position last when different (the position numbers are shown in eq 1).

(9) Adapted in part from Ji, G. M.S. Thesis, University of Nevada, Reno, NV, 1998.

(10) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.

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hexane, and acetonitrile were distilled from CaH$_2$. All syntheses were performed under nitrogen at ambient temperatures using standard Schlenk techniques.

^{1}H NMR spectra were obtained using a General Electric QE 300 MHz FT-NMR spectrometer; chemical shifts were referenced to the residual proton resonance of deuterated chloroform (7.26 ppm). ^{13}C NMR and ^{31}P NMR spectra were obtained using a Varian Unity Plus 500 MHz FT-NMR Spectrometer. ^{13}C NMR chemical shifts were referenced to CDCl$_3$ (77.23 ppm). The ^{31}P NMR spectra were referenced to an external triphenylphosphine resonance (−6.0 ppm) or to 85% aqueous phosphoric acid (0.0 ppm). Infrared spectra were recorded either on a Nicolet Protege, 460 FT-IR, or Perkin-Elmer 283 spectrometer as Nujol mulls unless otherwise stated and are reported in cm^{-1}. Melting points were obtained on a 6406-H Thomas-Hoover melting point apparatus and are uncorrected. FAB/MS were performed by the University of California, Riverside, Mass Spectrometry Facility and are reported as masses for the two largest peaks within each cluster (due to the copper isotopes) followed by assignments and relative intensities for each cluster. Elemental analyses were performed by Desert Analytics (Tucson, AZ) or NuMega Resonance Labs, Inc. (San Diego, CA).

Crystals of **1** (block) and **3** (plate) were coated with Paratone-N oil mixed with the crystallization solvents, maneuvered onto the tip of a glass fiber and placed in a −100 °C cold stream for data collection. Suitable crystals of **2** (plate) and **4** (plate) were mounted with silicone caulk to a glass fiber on the benchtop and the data collected at ambient temperatures. All data were collected with a Siemens P4 diffractometer with a graphite monochromator from 3.8° to 45° in 2θ for all four structures and octants $\pm h$, $\pm k$, $+l$ for **1**, **3**, and **4** and $\pm h$, $+k$, $+l$ for **2**. The structures were solved by Patterson techniques followed by subsequent cycles of least-squares refinement and calculation of difference Fourier maps. The data were refined (full-matrix least-squares on F^2) with the Siemens SHELXTL Version 5.0.3 PC software package,[11] including its semiempirical absorption correction from psi scans. None of the structures required an extinction correction. All non-hydrogen atoms were modeled anisotropically except for some solvent atoms in **1** that were modeled isotropically. Hydrogens were placed at calculated distances and use a riding model, where the positional and thermal parameters are derived from the carbon atom to which each hydrogen is bound to, while maintaining equivalent distances and optimal angles within a group. No peaks or holes of greater than 0.65 e$^-$/Å^3 remained in the final difference maps for the structures of **1**−**4**.

The structure of **1** contains four acetonitrile molecules in the lattice (not shown in the figure), two of which were well-behaved during refinement. One lattice acetonitrile is disordered, pivoting about the C$_{\mathrm{nitrile}}$ with 0.25 and 0.75 occupancies; hydrogen atoms on the C$_{\mathrm{methyl}}$ in the 0.75 fragment were not modeled. A second lattice acetonitrile molecule (although the identity cannot be assigned unequivocally from the crystallography, it at least looks more like an acetonitrile molecule than any other starting material or solvent used in the preparation) sits near a special position and is ill-behaved and refines to a crude model of a three-membered ring; no hydrogens were added to this fragment. For **1**, 10 283 reflections were collected; 6425 independent reflections ($R_{\mathrm{int}} = 0.0580$) were used in the refinement for 584 parameters, and the range of transmission factors was 0.5862−0.5756.

There were no lattice solvent molecules in the structure of **2**. Disorder in one *tert*-butyl group was modeled in two positions, which refined to 55% and 45% occupancies; however, only the major position is shown in the figure. For **2**, 6814 reflections were collected; 5666 independent reflections ($R_{\mathrm{int}} = 0.0295$) were used in the refinement for 498 parameters, and the range of transmission factors was 0.3305−0.2868.

The structure of **3** contains one methylene chloride molecule in the lattice that is not shown in the figure. This solvent molecule is somewhat disordered (pivoting about the central carbon atom); in addition, one of the *tert*-butyl groups has some apparent disorder. However, neither minor disorder was modeled in the final structure. For **3**, 8200 reflections were collected; 7260 independent reflections ($R_{\mathrm{int}} = 0.0396$) were used in the refinement for 651 parameters, and the range of transmission factors was 0.5225−0.4483.

One hexane molecule sitting on a special position in the structure of **4** is not shown in the figure. One *tert*-butyl group is disordered and refined to 60% and 40% occupancies; only the major position is shown in the figure. For **4**, 6399 reflections were collected; 5898 independent reflections ($R_{\mathrm{int}} = 0.0226$) were used in the refinement for 624 parameters, and the range of transmission factors was 0.3770−0.3612.

Tp$^{t\mathrm{Bu-Ph,Me}}$Cu(CH$_3$CN) (1). To a suspension of CuCl (56.6 mg, 0.572 mmol) in 5 mL of CH$_2$Cl$_2$ was added a solution of LiTp$^{t\mathrm{Bu-Ph,Me}}$(CH$_3$CN) (400 mg, 0.572 mmol) in 50 mL of (1:1) CH$_2$Cl$_2$/CH$_3$CN. A white precipitate formed immediately and was removed by filtration after stirring 2 h. Tp$^{t\mathrm{Bu-Ph,Me}}$Cu(CH$_3$CN) was isolated as a white solid by removing the solvent from the filtrate in vacuo (390 mg, 0.510 mmol, 89%). Large colorless crystals were obtained by recrystallization from CH$_2$Cl$_2$/CH$_3$CN. ^{1}H NMR (CDCl$_3$): δ 1.33 (s, 27 H, 3 × C(C*H*$_3$)$_3$), 1.87 (s, br, 3 H, C*H*$_3$CN), 2.47 (s, 9 H, 3 × Pz-C*H*$_3$), 6.11 (s, 3 H, 3 × *cyclo*-[C(Me)-N$_2$-C(C$_6$H$_4$-^{t}Bu)-C*H*]), 7.34, 7.77 (d, $J = 8.3$ Hz, 6 H each, 3 × Pz-C(C*H*)$_2$(C′*H*′)$_2$C-^{t}Bu). ^{13}C{^{1}H} (CDCl$_3$): δ 2.4 (s, br, *C*H$_3$CN), 13.0 (s, 3 × Pz-*C*H$_3$), 31.4 (s, 3 × C(*C*H$_3$)$_3$), 34.5 (s, 3 × *C*(CH$_3$)$_3$), 103.1 (s, 3 × *cyclo*-[C(Me)-N$_2$-C(C$_6$H$_4$-^{t}Bu)-*C*H]), 124.4, 127.1 (s, 3 × Pz-C(*C*H)$_2$(*C*′H′)$_2$C-^{t}Bu), 131.8 (s, 3 × Pz-C(CH)$_2$(C′H′)$_2$*C*-^{t}Bu), 143.6 (s, 3 × Pz-*C*(CH)$_2$(C′H′)$_2$C-^{t}Bu), 149.5, 150.3 (s, 3 × *cyclo*-[*C*(Me)-N$_2$-*C*(C$_6$H$_4$-^{t}Bu)-CH]). The nitrile carbon was not observed under the experimental conditions. IR: 2498 m ν(B−H), 2268 w ν(C≡N), 2236 w, 1568 w, 1547 w, 1520 m, 1366 m, 1337 w, 1186 s, 1120 w, 1059 s, 1019 w, 974 w, 846 ms, 783 s, 700 w. Anal. Calcd for C$_{44}$H$_{55}$N$_7$BCu: C, 69.87; H, 7.33; N, 12.96. Found: C, 70.05; H, 7.40; N, 12.92. MS *m*/*z*: 715/717 (MH$^+$ − CH$_3$CN, 23), 501/503 (M$^+$ − (Pz$^{t\mathrm{Bu-Ph,Me}}$ + CH$_3$CN), 100). Mp: 178−179 °C.

Tp$^{t\mathrm{Bu-Ph,Me}}$Cu(CO) (2). Complex **1** (74.8 mg, 0.099 mmol) was dissolved in 10 mL of CH$_2$Cl$_2$ to form a colorless solution. After this solution had been stirred for several minutes, 400 Torr of CO gas was added. The resulting solution was stirred overnight and the solvent removed in vacuo to give a white solid. Recrystallization from CH$_2$Cl$_2$/hexane afforded large light yellow single crystals of Tp$^{t\mathrm{Bu-Ph,Me}}$Cu(CO) (48.0 mg, 0.0646 mmol, 65%). ^{1}H NMR (CDCl$_3$): δ 1.34 (s, 27 H, 3 × C(C*H*$_3$)$_3$), 2.48 (s, 9 H, 3 × Pz-C*H*$_3$), 6.12 (s, 3 H, 3 × *cyclo*-[C(Me)-N$_2$-C(C$_6$H$_4$-^{t}Bu)-C*H*]), 7.41, 7.60 (d, $J = 8.3$ Hz, 6 H each, 3 × Pz-C(C*H*)$_2$(C′*H*′)$_2$C-^{t}Bu). ^{13}C{^{1}H} (CDCl$_3$): δ 12.8 (s, 3 × Pz-*C*H$_3$), 31.4 (s, 3 × C(*C*H$_3$)$_3$), 34.6 (s, 3 × *C*(CH$_3$)$_3$), 104.0 (s, 3 × *cyclo*-[C(Me)-N$_2$-C(C$_6$H$_4$-^{t}Bu)-*C*H]), 125.1, 127.3 (s, 3 × Pz-C(*C*H)$_2$(*C*′H′)$_2$C-^{t}Bu), 131.4 (s, 3 × Pz-C(CH)$_2$(C′H′)$_2$*C*-^{t}Bu), 144.1 (s, 3 × Pz-*C*(CH)$_2$(C′H′)$_2$C-^{t}Bu), 150.7, 151.7 (s, 3 × *cyclo*-[*C*(Me)-N$_2$-*C*(C$_6$H$_4$-^{t}Bu)-CH]). The carbonyl carbon was not observed under the experimental conditions. IR: 2504 w ν(B−H), 2078 s ν(C≡O), 1614 w, 1548 m, 1520 ms, 1338 w, 1306 m, 1182 s, 1110 m, 1058 s, 1018 w, 980 m, 842 s, 780 s, 723 s, 704 m. Anal. Calcd for C$_{43}$H$_{52}$N$_6$OBCu: C, 69.49; H, 7.05; N, 11.31. Found: C, 69.80; H, 7.46; N, 11.48. MS *m*/*z*: 715/717 (MH$^+$ − CO, 39), 501/503 (M$^+$ − (Pz$^{t\mathrm{Bu-Ph,Me}}$ + CO), 100). Mp: 222−223 °C (dec).

Tp$^{t\mathrm{Bu-Ph,Me}}$Cu(PPh$_3$) (3). To a mixture of **1** (38.2 mg, 0.050 mmol) and triphenylphosphine (13.5 mg, 0.0515 mmol) was added 10 mL CH$_2$Cl$_2$. After the solution had stirred overnight, the solvent was removed in vacuo to give a white solid. Recrystallization from CH$_2$Cl$_2$/hexane gave colorless single crystals of Tp$^{t\mathrm{Bu-Ph,Me}}$Cu(PPh$_3$) (24.1 mg, 0.0241 mmol, 48%). ^{1}H NMR (CDCl$_3$): δ 0.87 (s, 27 H 3 × C(C*H*$_3$)$_3$), 2.57 (s, 9 H, 3 × Pz-C*H*$_3$), 6.14 (s, 3 H, 3 × *cyclo*-[C(Me)-N$_2$-C(C$_6$H$_4$-^{t}Bu)-C*H*]), 6.28, 7.12 (d, $J = 8.3$ Hz, 6 H each, 3 × Pz-C(C*H*)$_2$(C′*H*′)$_2$C-^{t}Bu), 6.84 (m, 6 H, 3 × P−C(C*H*)$_2$(C′H′)$_2$CH), 7.00 (m, 6 H, 3 × P−C(CH)$_2$(C′*H*′)$_2$CH), 7.18 (m, 3 H, 3 × P−C(CH)$_2$(C′H′)$_2$C*H*). ^{13}C{^{1}H} (CDCl$_3$): δ 13.3 (s, 3 × Pz-*C*H$_3$), 31.0 (s, 3 × C(*C*H$_3$)$_3$), 34.0 (s, 3 × *C*(CH$_3$)$_3$), 104.8 (s, 3 × *cyclo*-[C(Me)-N$_2$-C(C$_6$H$_4$-^{t}Bu)-*C*H]), 124.9, 127.8 (s, 3 × Pz-C(*C*H)$_2$(*C*′H′)$_2$C-^{t}Bu), 127.7 (d, $^3J_{\mathrm{P-C}} = 9.3$ Hz, 3 × P-C_{meta}, 128.5 (d, $^4J_{\mathrm{P-C}} = 1.3$ Hz, 3 × P-C_{para}, 132.0 (s, 3 × Pz-C(CH)$_2$(C′H′)$_2$*C*-^{t}Bu), 133.4 (d, $^1J_{\mathrm{P-C}} = 32.9$ Hz, 3 × P-C_{ipso}, 134.6 (d, $^2J_{\mathrm{P-C}} = 15.6$ Hz, 3 × P-C_{ortho}, 143.8 (s, 3 × Pz-*C*(CH)$_2$(C′H′)$_2$C-^{t}Bu), 149.5, 152.8 (s, 3 × *cyclo*-[*C*(Me)-N$_2$-*C*(C$_6$H$_4$-^{t}Bu)-CH]). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −1.20. IR: 3055 w, 2518 w ν(B−H), 2387 w, 1567 w, 1549 m, 1524 ms, 1365 s, 1337 m, 1306 w,

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(11) Scattering factors from *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

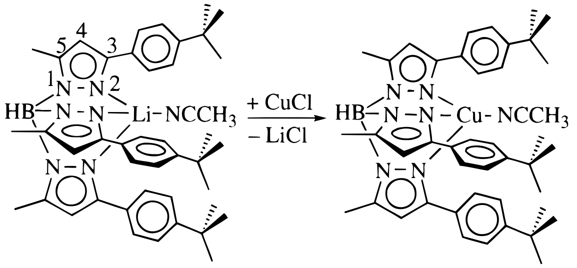
1202 s, 1112 m, 1091 m, 1062 s, 1020 m, 999 w, 985 w, 972 m, 920 w, 890 w, 843 vs, 829 ms, 788 s, 747 s. Anal. Calcd for $C_{60}H_{67}N_6BPCu$: C, 73.72; H, 6.91; N, 8.60. Found: C, 73.68; H, 7.10; N, 8.71. MS *m*/*z*: 977/979 (MH^+, 29), 763/765 (M^+ − Pz$^{t\mathrm{Bu-Ph,Me}}$, 92), 714/716 (M^+ - PPh_3, 43), 501/503 (M^+ − (Pz$^{t\mathrm{Bu-Ph,Me}}$ + PPh_3), 100). Mp: 252−253 °C.

Tp$^{t\mathrm{Bu-Ph,Me}}$Cu[P(^{t}Bu)$_3$] (4). To **1** (245 mg, 0.320 mmol) and P(^{t}-Bu)$_3$ (64.8 mg, 0.320 mmol) was added 10 mL CH_2Cl_2. After stirring 25 min, the solvent was removed in vacuo to give a white solid, 220 mg (0.240 mmol, 75%). Recrystallization from CH_2Cl_2/hexane gave colorless single crystals of Tp$^{t\mathrm{Bu-Ph,Me}}$Cu[P(*t*-Bu)$_3$]. ^{1}H NMR ($CDCl_3$): δ 0.68 (d, $J = 12.1$ Hz, 27 H, P−C(C*H*$_3$)$_3$), 1.38 (s, 27 H, 3 × C(C*H*$_3$)$_3$), 2.26 (s, 9 H, 3 × Pz-C*H*$_3$), 6.22 (s, 3 H, 3 × *cyclo*-[C(Me)-N_2-C(C_6H_4-^{t}Bu)-C*H*), 7.41, 7.59 (d, $J = 8.4$ Hz, 4 H each, 3 × Pz-C(C*H*)$_2$(C′*H*′)$_2$C-^{t}Bu). ^{13}C{^{1}H} ($CDCl_3$): δ 13.2 (s, 3 × Pz-*C*H$_3$), 31.6 (d, $J = 7.3$ Hz, P-C(*C*H$_3$)$_3$), 31.7 (s, 3 × C(*C*H$_3$)$_3$), 35.5 (d, $J = 112$ Hz, P-*C*(CH$_3$)$_3$), 36.2 (s, 3 × *C*(CH$_3$)$_3$), 105.1 (s, 3 × *cyclo*-[C(Me)-N_2-C(C_6H_4-^{t}Bu)-*C*H]), 125.5, 127.5 (s, 3 × Pz-C(*C*H)$_2$(*C*′H′)$_2$C-^{t}Bu), 133.4 (s, 3 × Pz-C(CH)$_2$(C′H′)$_2$*C*-^{t}Bu), 146.4 (s, 3 × Pz-*C*(CH)$_2$(C′H′)$_2$C-^{t}Bu), 150.1, 152.1 (s, 3 × *cyclo*-[*C*(Me)-N_2-*C*(C_6H_4-^{t}Bu)-CH]). ^{31}P NMR ($CDCl_3$): δ 62.8. ^{31}P NMR (C_6D_6): δ 62.3. IR (neat): 3062 m ν(C−H$_{\mathrm{arom}}$), 2962 vs ν(C−H$_{\mathrm{aliph}}$), 2472 m ν(B−H), 2392 w, 1549 m, 1522 s, 1471 s, 1435 s, 1393 m, 1362 s 1340 s, 1266 s, 1176 s, 1112 m, 1077 s, 1062 s, 1022 s, 980 s, 958 m, 840 vs, 808 vs, 784 vs, 739 s, 705 s, 649 w, 631 s. Anal. Calcd for $C_{54}H_{79}N_6BPCu$: C, 70.67; H, 8.68; N, 9.17. Found: C, 70.57; H, 8.81; N, 9.29. MS *m*/*z*: 715/717 (MH^+ − P(^{t}-Bu)$_3$, 39), 501/503 (M^+ − (Pz$^{t\mathrm{Bu-Ph,Me}}$ + P(^{t}Bu)$_3$, 100). Mp: 198−199 °C (dec).

Results and Discussion

Ligand Synthesis. The synthesis of TlTp$^{t\mathrm{Bu-Ph,Me}}$ was reported by Ghosh and Parkin[12,13] while this work was in progress, along with a Tp$^{t\mathrm{Bu-Ph,Me}}$ magnesium hydroxide complex.[12] In addition, two copper(II) complexes with a similar Tp ligand, Tp$^{\mathrm{Cum,Me}}$ (Cum = 4-^{i}Pr-Ph), and hydroxide and semiquinone co-ligands have been reported.[14] We synthesized LiTp$^{t\mathrm{Bu-Ph,Me}}$ in a manner similar to that described by Ghosh and Parkin.[12] However, instead of converting LiTp$^{t\mathrm{Bu-Ph,Me}}$ to TlTp$^{t\mathrm{Bu-Ph,Me}}$, we avoided use of toxic thallium salts by purifying LiTp$^{t\mathrm{Bu-Ph,Me}}$. Thus, the crude LiTp$^{t\mathrm{Bu-Ph,Me}}$ in THF was filtered through Celite, the solvent was removed and the resulting solid was washed extensively with acetonitrile to remove excess pyrazole. From the acetonitrile wash Tp$^{t\mathrm{Bu-Ph,Me}}$Li(CH_3CN)[15] was obtained in almost 70% isolated yield, based on $LiBH_4$, as reasonably stable white powder. For instance, CH_3CN is not lost after at least a day under vacuum at ambient temperature. Tp$^{t\mathrm{Bu-Ph,Me}}$Li(CH_3CN) is soluble in moderately polar to fairly nonpolar solvents such as THF, CH_2Cl_2, benzene, and toluene and is insoluble in more polar solvents, including CH_3CN and acetone. The IR spectrum of Tp$^{t\mathrm{Bu-Ph,Me}}$Li(CH_3CN) exhibited a B−H stretch at 2510 cm^{-1}, which is essentially the same as that observed for TlTp$^{t\mathrm{Bu-Ph,Me}}$ (2508 cm^{-1}).[12] The data are consistent with a lithium-bound CH_3CN, including the resistance to CH_3CN loss and the observation that the CH_3CN-derived IR bands at 2274 cm^{-1} [ν(C≡N)], and 2305 cm^{-1} [ν(C−C) + δ-(CH_3)] are shifted from those of free CH_3CN (2255 and 2293 cm^{-1}).[16]

Synthesis and Characterization of Tp$^{t\mathrm{Bu-Ph,Me}}$Cu(CH_3CN) (1). The stoichiometric reaction of Tp$^{t\mathrm{Bu-Ph,Me}}$Li(CH_3CN) and CuCl in a mixture of CH_2Cl_2/CH_3CN produces Tp$^{t\mathrm{Bu-Ph,Me}}$Cu-(CH_3CN) (**1**) in excellent yield (eq 1). Complex **1** is a white solid that is soluble in CH_2Cl_2, $CHCl_3$, and Et_2O and is insoluble in CH_3CN and saturated hydrocarbon solvents. Complex **1** is stable to the air for at least a month as a solid but is sensitive to air oxidation in nonacetonitrile containing solvents, for instance turning green within an hour in a chloroform solution open to the air. In addition, **1** is subject to acetonitrile loss under vacuum at ambient temperatures, forming more than one product, as indicated by ^{1}H NMR spectroscopy. No attempts were made to isolate and purify these products.



(1)

Tp$^{t\mathrm{Bu-Ph,Me}}$Li(CH_3CN) **1**

Complex **1** and the other three copper complexes reported here have been fully characterized, by IR and NMR spectroscopies, FAB/MS, elemental analysis and X-ray crystallography. Copper(I) ligation is indicated by the shifting of significant ^{1}H NMR and IR peaks for **1** versus Tp$^{t\mathrm{Bu-Ph,Me}}$Li-(CH_3CN),[15] such as ν(B−H) to 2498 cm^{-1}. The nitrile stretch for **1** was observed at 2268 cm^{-1}, which is just outside the range given for most typical metal-acetonitrile complexes (2270−2300 cm^{-1}).[16] However, it compares favorably with other Cu$^{\mathrm{I}}$-$NCCH_3$ complexes, which most frequently exhibit ν(C≡N) in the 2260−2280 cm^{-1} range.[17−24] There is a second weak peak in the IR spectrum of **1** at 2236 cm^{-1} that could be the combination band seen for acetonitrile complexes; however, it is well outside of the typical range (2290−2320 cm^{-1}),[16] making such an assignment tentative.

Colorless single crystals were grown by diffusion of CH_3CN into a CH_2Cl_2 solution of **1**. As these crystals desolvated at room temperature over several hours, the X-ray data were collected at low temperature (Table 1). The solid-state structure of **1** (Figure 1) shows that the copper ion is four-coordinate, bound to the three pyrazole nitrogen atoms as well as the nitrogen from the acetonitrile ligand. A few other TpCu$^{\mathrm{I}}$(CH_3-

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Table 1. Crystallographic Data for 1−4

parameter	**1**·4CH$_3$CN	**2**	**3**·CH$_2$Cl$_2$	**4**·0.5hexane
empirical formula	C$_{52}$H$_{67}$N$_{11}$BCu	C$_{43}$H$_{52}$N$_6$BCuO	C$_{61}$H$_{69}$N$_6$BCl$_2$CuP	C$_{57}$H$_{86}$N$_6$BCuP
fw	920.52	743.26	1062.44	960.64
temperature (K)	173	296	173	298
λ	0.710 73 Å (Mo Kα)	0.710 73 Å (Mo Kα)	0.710 73 Å (Mo Kα)	0.710 73 Å (Mo Kα)
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	13.4201(10)	25.592(4)	12.5080(13)	13.337(2)
b (Å)	15.132(2)	12.434(2)	15.159(3)	13.435(2)
c (Å)	15.2125(13)	28.044(3)	17.151(2)	17.386(2)
α (deg)	60.743(6)	90	64.271(10)	88.371(7)
β (deg)	73.211(4)	104.073(9)	79.073(7)	71.863(8)
γ (deg)	74.839(5)	90	86.572(8)	80.223(9)
V (Å$^{3)}$	2553.3(4)	8656(2)	2875.6(7)	2916.5(6)
Z	2	8	2	2
calculated ρ (g/cm$^{3)}$	1.197	1.141	1.227	1.094
cryst dimens (mm)	0.48 × 0.42 × 0.31	0.62 × 0.40 × 0.21	0.96 × 0.51 × 0.18	0.60 × 0.35 × 0.08
μ (mm$^{-1)}$	0.473	0.542	0.544	0.440
R1[a]	0.0681	0.0747	0.0513	0.0696
wR2[b]	0.1891	0.2208	0.1328	0.1862

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ (observed data, $I > 2\sigma(I)$). [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ (all data).

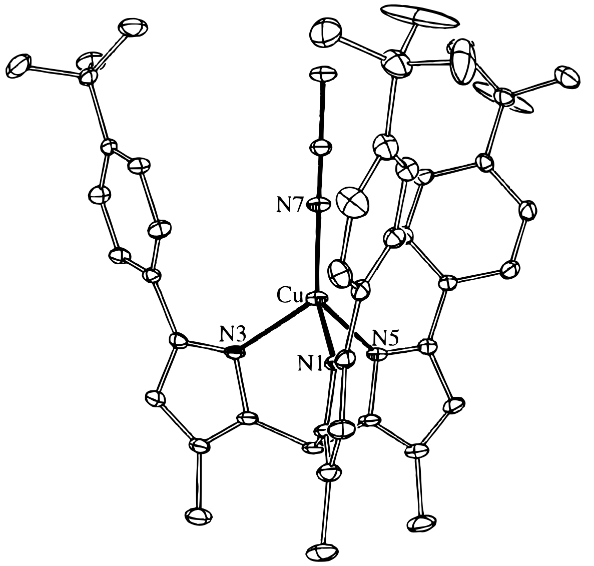

Figure 1. Thermal ellipsoid depiction of Tp$^{t\text{Bu}-\text{Ph},\text{Me}}$Cu(CH$_3$CN) (**1**) at the 20% probability level; hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Cu−N1, 2.089(5); Cu−N3, 2.083(5); Cu−N5, 2.092(5); Cu−N7, 1.891(5); C≡N7, 1.140(7); N1−Cu−N7, 124.8(2); N3−Cu−N7, 123.8(2); N5−Cu−N7, 124.7(2); N1−Cu−N3, 91.2(2); N1−Cu−N5, 90.9(2); N3−Cu−N5, 91.4(2); Cu−N7≡C, 178.4(5); N7≡C−C, 179.4(7).

CN) complexes are known[5,19,25−28] although apparently only two have been recently crystallographically characterized.[25,29−31] The geometry about the copper center in **1** is distorted tetrahedral, with angles ranging from 90.9 to 124.8°. As is typical for Tp four-coordinate structures, there are clearly two sets of angles, ones averaging near 90° for the angles between the pyrazole groups and larger angles, closer to 125°, between the Tp ligand and the fourth ligand. The three copper−pyrazole nitrogen distances are equal within error and are slightly longer (averaging 2.088 Å) than the Cu−N$_{\text{acetonitrile}}$ distance (1.891(5) Å). The Cu−N$_{\text{acetonitrile}}$ distance falls within the 1.86−2.16 Å range seen for some other four-coordinate copper(I)−acetonitrile complexes.[18,20−25,29−34]

The nitrile C−N distance in **1**, 1.140(7) Å, falls within the typical range found for transition metal acetonitrile complexes, 1.11−1.15 Å.[16] The acetonitrile ligand is essentially linear (∠N≡C−C, 179.4(7) Å), which is typical for copper−acetonitrile complexes.[18,20−25,30−32] The copper−nitrile angle for **1** is within the usual range for transition metal complexes (∠M−N≡C of 175 ± 5°)[16] and is clearly near that of other Cu−NCCH$_3$ complexes (157−180°).[18,20−25,29−33,35] The acetonitrile ligand in complex **1** can be readily replaced by other ligands, such as CO, PPh$_3$, and P^{t}Bu$_3$ in CH$_2$Cl$_2$ to form **2** through **4** (Scheme 1), as discussed below.

Synthesis and Characterization of Tp$^{t\text{Bu}-\text{Ph},\text{Me}}$Cu(CO) (2). The addition of excess CO gas to a CH$_2$Cl$_2$ solution of **1** forms Tp$^{t\text{Bu}-\text{Ph},\text{Me}}$Cu(CO) (**2**), which is isolated by the removal of the solvent in vacuo. Complex **2** has a similar solubility and air stability as **1**, however, it is significantly more stable toward ligand loss as a solid. In fact, the ^{1}H NMR and IR spectra are unchanged even after heating the complex to temperatures slightly higher than 100 °C under a vacuum for 10 h. This is a remarkably inert Cu−CO complex, as many Cu−CO complexes easily lose the CO ligand.[36] In fact, TpCu(CO) complexes are among the most robust Cu−CO complexes known.

The IR spectrum no longer contains the CH$_3$CN-derived vibrations and ν(B−H) has moved to 2504 cm^{-1}. The carbonyl stretch for **2**, at 2078 cm^{-1}, is clearly within the range of 2056−2086 cm^{-1} seen for the other known nonfluorinated tris(pyrazolyl)hydroborate copper(I) carbonyl complexes.[5,27,29,37−45]

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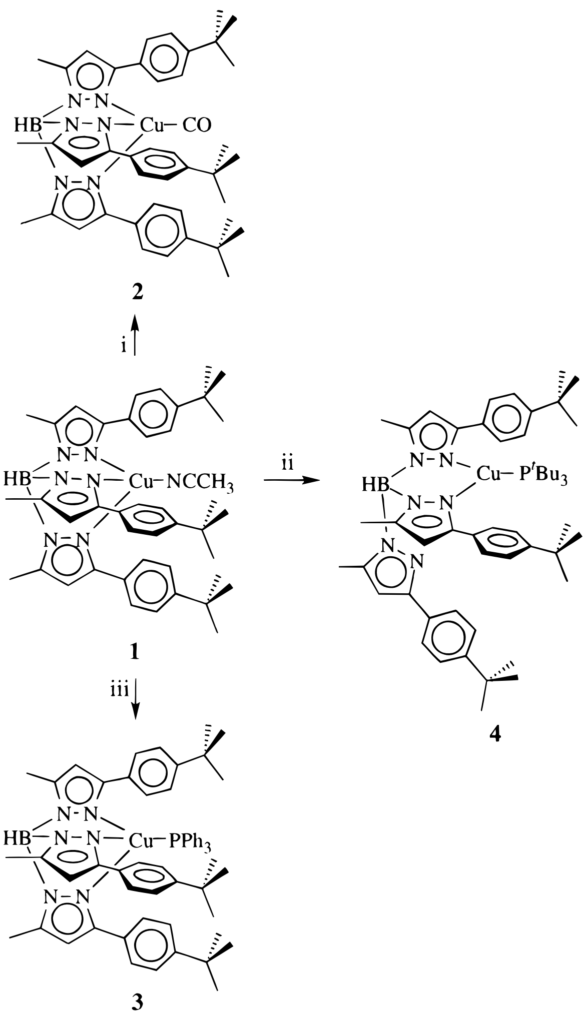
Scheme 1. Ligand Substitution Reactions of Complex **1** That Form **2**−**4**[a]



[a] Reaction conditions: (i) + CO; (ii) + P^{t}Bu$_3$; (iii) + PPh$_3$.

Consistent with the stability of TpCu(CO) complexes, the carbonyl stretches for these complexes occur at the low end of the range for terminal Cu−CO complexes reported through 1987 (2055−2180 cm^{-1}).[36]

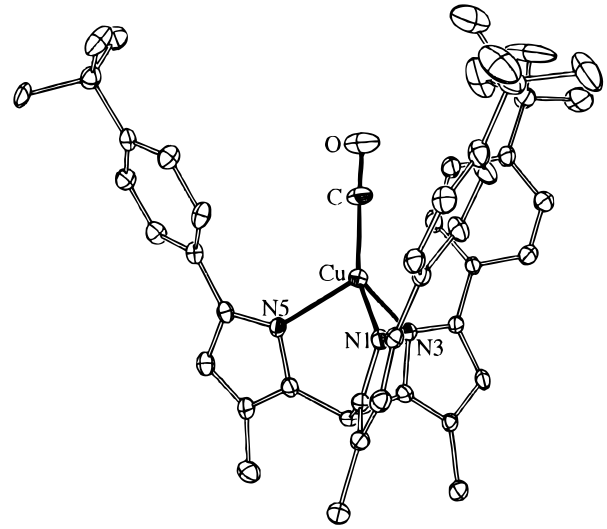


Figure 2. Thermal ellipsoid depiction of Tp$^{t\text{Bu}-\text{Ph,Me}}$Cu(CO) (**2**) at the 10% probability level; hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Cu−N1, 2.045(6); Cu−N3, 2.065(6); Cu−N5, 2.073(6); Cu−C, 1.752(10); C≡O, 1.120(10); N1−Cu−C, 124.9(4); N3−Cu−C, 125.9(4); N5−Cu−C, 122.7(4); N1−Cu−N3, 90.2(3); N1−Cu−N5, 91.5(2); N3−Cu−N5, 91.5(2); Cu−C≡O, 178.1(12).

Single crystals were grown by the slow diffusion of hexane into a CH$_2$Cl$_2$ solution of **2**. The X-ray crystal structure (Figure 2) shows that the geometry about the copper ion is similar to that found for **1**. The average pyrazole Cu−N distance in **2** (2.061 Å), is comparable to that for **1** and is at the long end of the range (2.018−2.078 Å) seen for all TpCu(CO) complexes that have been structurally characterized,[3,26,43−47] as well as for the 23 Tp−Cu(I) complexes surveyed through 1985, which average at 2.001(75) Å.[48] The Cu−C distance in **2** [1.752(10) Å] is at the low end of the range reported for all TpCu(CO) complexes (1.752(10)−1.808(4) Å).[3,26,43−47] The 18 Cu−CO structures in the Cambridge Crystallographic Database through 1985 also have similar Cu−C distances, with a 1.787(19) Å average.[48] The C≡O distance in **2**, 1.120(10) Å, at first appearance appears to be on the long side when compared to all TpCu(CO) structures (1.08(1)−1.126(5) Å), however, the errors make these values similar. In general, Cu−CO complexes exhibit relatively short C−O distances compared to all transition metal carbonyl complexes, which, for over 10 000 structures averaged at 1.145(20) Å.[48] The Cu−C−O angle in **2** is nearly linear, which is typical, for instance, for TpCu(CO) complexes, which range from 176.6(5)−180.0°.

Synthesis and Characterization of Tp$^{t\text{Bu}-\text{Ph,Me}}$Cu(PPh$_3$) (3). The addition of one equivalent of PPh$_3$ to **1** in CH$_2$Cl$_2$ causes substitution of the acetonitrile ligand by PPh$_3$, forming Tp$^{t\text{Bu}-\text{Ph,Me}}$Cu(PPh$_3$) (**3**). Complex **3** is soluble in moderately polar solvents such as CH$_2$Cl$_2$ and Et$_2$O and is insoluble in saturated hydrocarbon solvents and is air stable, both as a solid and in chloroform solution, for at least three weeks. No CH$_3$CN-derived vibrations are observed in the IR spectrum and ν(B−H) is now at 2518 cm^{-1}. The ^{31}P{^{1}H} resonance, at −1.20 ppm, is typical for Cu$^{\text{I}}$−PPh$_3$ complexes, which usually shift the PPh$_3$ signal downfield (from −6.0 ppm) by less than 15 ppm.[49−52] A few other TpCu$^{\text{I}}$(PPh$_3$)[38,42,43,50−54] complexes

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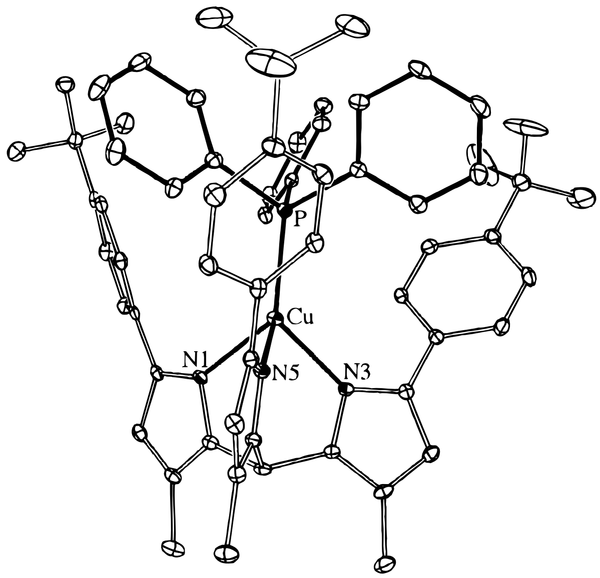

Figure 3. Thermal ellipsoid depiction of Tp$^{t\mathrm{Bu-Ph,Me}}$Cu(PPh$_3$) (**3**) at the 20% probability level; hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Cu−P, 2.2189(13); Cu−N1, 2.161(3); Cu−N3, 2.173(3); Cu−N5, 2.131(3); P−Cu−N1, 126.11(10); P−Cu−N3, 125.72(10); P−Cu−N5, 124.22(10); N1−Cu−N3, 87.90(13); N1−Cu−N5, 89.84(13); N3−Cu−N5, 91.90(13).

are known, three of these have been structurally characterized.[50−52]

Single crystals were grown by diffusion of hexane into a CH$_2$Cl$_2$ solution of **3**. The solid-state structure (Figure 3) contains a distorted tetrahedral copper(I) center. Whereas the CO and CH$_3$CN ligands clearly fit comfortably within the pocket, to bind the triphenylphosphine ligand, the PPh$_3$ phenyl rings had to interleave between the pyrazole arms of Tp$^{t\mathrm{Bu-Ph,Me}}$ ligand. A lengthening of the pyrazole Cu−N distances in **3** results, as the average (2.155 Å) is longer than those for **1** and **2**, as well as for Tp$^{\mathrm{Me}_2}$Cu(PPh$_3$)[50] and Tp$^{\mathrm{H}_2}$Cu(PPh$_3$)[51] which average 2.098 and 2.076 Å, respectively. However, the Cu−N$_{\mathrm{pz}}$ average in **3** is much more comparable to that in Tp$^{(\mathrm{CF}_3)_2}$Cu(PPh$_3$)[52] at 2.173 Å, suggesting steric hindrance may be contributing to the lengthening in both structures. The Cu−P distance in **3** of 2.2189(13) Å falls well within the range of 2.126−2.330 Å seen for some other four-coordinate, copper(I), mono-PPh$_3$ structures.[35,55−66] A similar lengthening is seen for the Cu−P bond as was observed for the Cu−N$_{\mathrm{pz}}$ bonds among TpCu(PPh$_3$) structures; Tp$^{\mathrm{Me}_2}$Cu(PPh$_3$)[50] and Tp$^{\mathrm{H}_2}$Cu(PPh$_3$)[51] exhibit 2.166(6) and 2.153(2) Å Cu−P lengths, while for Tp$^{(\mathrm{CF}_3)_2}$Cu(PPh$_3$) the Cu−P bond length is longer, at 2.219(1) Å and is more similar to that observed for **3**.

Synthesis and Characterization of Tp$^{t\mathrm{Bu-Ph,Me}}$Cu(P^{t}Bu$_3$) (4). The addition of one equivalent of P^{t}Bu$_3$ to **1** in CH$_2$Cl$_2$ causes substitution of the acetonitrile ligand by P^{t}Bu$_3$, forming Tp$^{t\mathrm{Bu-Ph,Me}}$Cu(P^{t}Bu$_3$) (**4**). Complex **4** is soluble in most organic solvents and is air sensitive in solution; the solid is more air stable but will also slowly acquire a green color. No CH$_3$CN-derived vibrations are observed in the IR spectrum and ν(B−H) is observed at 2472 cm^{-1}. The ^{31}P{^{1}H} resonance, at 62.3 ppm, is only slightly shifted downfield from that for free P^{t}Bu$_3$ ($\Delta\delta$ = 0.5 ppm in benzene). The resonance is clearly much broader than that of free P^{t}Bu$_3$, consistent with P^{t}Bu$_3$ binding to the quadrupolar copper(I) center.

A couple other TpCu$^{\mathrm{I}}$(Palkyl$_3$)[38,42] complexes are known, although, to our knowledge, none have been structurally characterized. The ^{1}H and ^{13}C NMR solution spectra of **4** at room temperature are consistent with coordination of all three pyrazole arms or, more likely, with rapid exchange of the coordinated and uncoordinated pyrazole groups. ^{1}H NMR spectra consistent with the solid-state structure of **4** were not observed down to −50 °C in CDCl$_3$ solution.

Single crystals of **4** were grown by the partial evaporation of an hexane/CH$_2$Cl$_2$ solution containing **4**. The P^{t}Bu$_3$ ligand is apparently too large to be contained within the pocket, which is not able to accommodate the bulky *tert*-butyl groups between the pyrazole arms. Thus, at least in the solid state, one of the pyrazole rings from the Tp$^{t\mathrm{Bu-Ph,Me}}$ ligand is not coordinated, resulting in a distorted trigonal planar geometry about the copper(I) ion (Figure 4). Although the angles about the copper center average to 119.4°, the two P−Cu−N$_{\mathrm{pyrazole}}$ angles are much larger [132.1(2)° and 137.3(2)°] than the N$_{\mathrm{pyrazole}}$−Cu−N$_{\mathrm{pyrazole}}$ angle [88.8(3)°]. The copper ion is displaced 0.152 Å from the N$_2$P plane, away from the third, uncoordinated pyrazole arm. The Cu−P distance of 2.220(2) Å is similar to that (2.228(4) Å) found for [CuBr(P^{t}Bu$_3$)]$_4$,[67] although the copper ion in the latter structure is four-coordinate. The average Cu−N distance for **4** is 2.027 Å, which is shorter than those found for **1**−**3**. This follows the general trend that three-coordinate copper structures have shorter bond distances than four coordinate structures.[36] This is the first example, to the authors' knowledge, of a TpCu(L) complex (where L is a single monodentate ligand) whose crystal structure features a dangling Tp-pyrazole arm.

Structural Comparisons. To probe for ligand-induced changes to the pocket formed by the Tp$^{t\mathrm{Bu-Ph,Me}}$ ligand about the copper(I) center, we calculated the area of the triangle (area$_{\mathrm{tri}}$) formed by connecting the midpoints of the phenyl rings in the structures of **1**, **2** and **3** (illustrated for **3** in Figure 5). In addition, the same calculations were made for other TpCu$^{\mathrm{I}}$(L) complexes with 3-phenyl substituents whose structures have been reported, Tp$^{(\mathrm{Ph})_2}$Cu(CO),[45] Tp$^{(\mathrm{Ph})_2}$Cu(Hpz$^{(\mathrm{Ph})_2}$),[19] and Tp$^{\mathrm{Ms,H}}$Cu(THF)[29] (Ms = mesityl) for comparison (Table 2). There are also two TpCu$^{\mathrm{II}}$(L) with 3-phenyl substituents whose structures have been reported[14,68] that were excluded to compare only copper(I) complexes. This type of measurement is a useful

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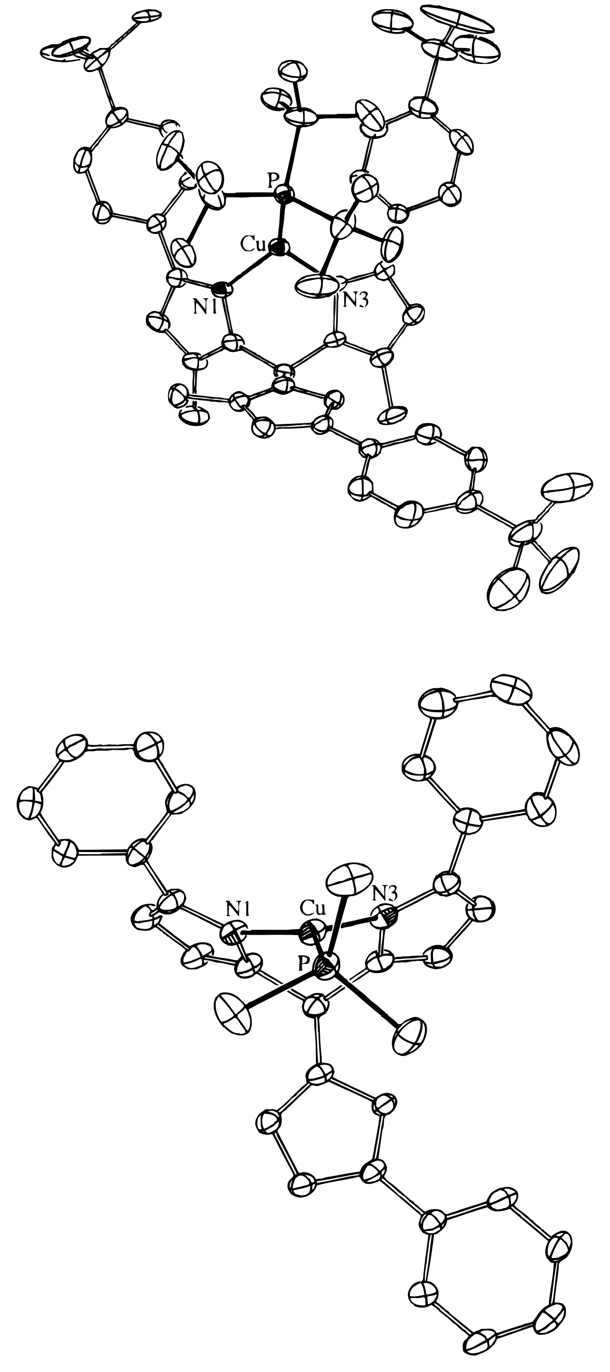

Figure 4. Thermal ellipsoid depictions of $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}\mathrm{Cu}(\mathrm{P}^t\mathrm{Bu}_3)$ (**4**) at the 20% probability level. (Above) All nonhydrogen atoms shown. (Below) Slightly different view with all hydrogen atoms, *tert*-butyl, and methyl groups omitted for clarity. Selected bond distances (Å) and angles (deg): Cu−P, 2.220(2); Cu−N1, 2.025(7); Cu−N3, 2.028(6); P−Cu−N1, 132.1(2); P−Cu−N3, 137.3(2); N1−Cu−N3, 88.8(3).

supplement to the more commonly used cone angle[69−71] as it is less dependent upon the orientation of the phenyl rings. It has been noted that Tp ligands with planar 3-substituents yield the least meaningful cone angles.[72] Wedge angles [2,73] were then introduced to describe the open space between pyrazole arms with planar groups, but, unfortunately, also have similar problems with ring orientation.[2] Although we have found the analysis using $\mathrm{area}_{\mathrm{tri}}$ to be useful here, it obviously has limited application, i.e., applying only to a set of similar tripodal ligands with phenyl groups in the proper positions.

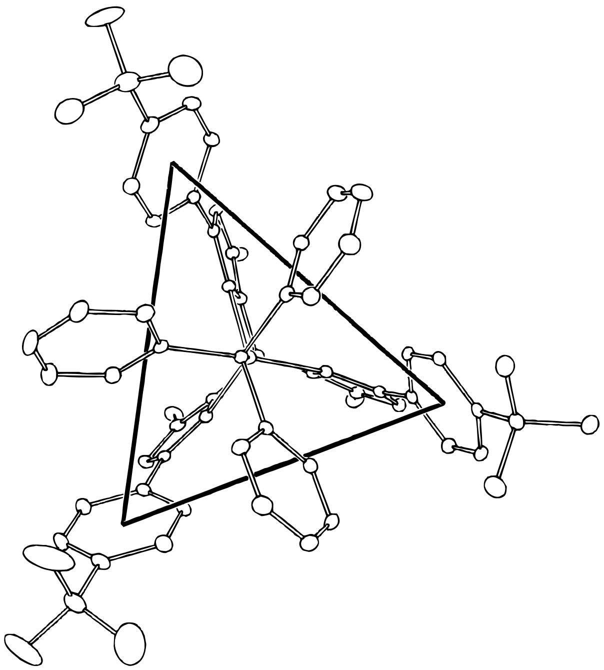

Figure 5. View of **3** illustrating the interleaving of the phenyl rings and the triangle used to calculate $\mathrm{area}_{\mathrm{tri}}$.

The size of the $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}$ pocket appears to depend on the nature of the enclosed ligand, as the more sterically demanding PPh_3 and 3,5-diphenylpyrazole ($\mathrm{Hpz}^{\mathrm{Ph}_2}$) ligands give the largest values of $\mathrm{area}_{\mathrm{tri}}$ (Table 2). Notably, even though the PPh_3 phenyl groups can interleave between the pyrazolyl groups of $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}$, there is still some opening of the pocket upon binding the PPh_3 ligand. Thus, there is a 15% increase in $\mathrm{area}_{\mathrm{tri}}$ for **3** (26.9 Å^2) versus **1** (22.8 Å^2). Some of the flexibility of the pocket can probably be attributed to a scissors-like motion of the $\mathrm{Tp}^{t\mathrm{Bu-Ph,Me}}$ ligand, because a concomitant decrease was also observed in the area of the triangle formed by connecting the 5-position methyl-carbon atoms ($\mathrm{area}_{5'-\mathrm{C}}$, 9.5 and 9.0 Å^2 for **1** and **2**, respectively, a 5% difference in area). The smaller decrease in this parameter is reasonable, as the methyls are closer to the pivot point and will experience a smaller magnitude change. However, larger values of $\mathrm{area}_{\mathrm{tri}}$ are not totally caused by this pivoting motion. For instance, the next to largest value of $\mathrm{area}_{\mathrm{tri}}$, for $\mathrm{Tp}^{\mathrm{Ph}_2}\mathrm{Cu}(\mathrm{Hpz}^{\mathrm{Ph}_2})$, exhibits the same area for the triangle formed by connecting the 5-position *ipso*-phenyl carbon atoms ($\mathrm{area}_{5'-\mathrm{C}}$) as that for **1**, which has the smallest $\mathrm{area}_{\mathrm{tri}}$. The numerical comparison of $\mathrm{area}_{5'-\mathrm{C}}$ between these two complexes suffers because they also have a significant difference between the pyrazole and carbon (methyl or phenyl-*ipso*) distances used in the calculation. This difference, however, is in accord with the conclusion that pivoting is not the only mechanism to increase $\mathrm{area}_{\mathrm{tri}}$. The pyr−$\mathrm{C}_{ipso}$ distances in $\mathrm{Tp}^{\mathrm{Ph}_2}\mathrm{Cu}(\mathrm{Hpz}^{\mathrm{Ph}_2})$ are shorter than the pyr−C_{Me} distances in **1**. This shorter distance for $\mathrm{Tp}^{\mathrm{Ph}_2}\mathrm{Cu}(\mathrm{Hpz}^{\mathrm{Ph}_2})$ causes its $\mathrm{area}_{5'-\mathrm{C}}$ to be smaller than if measured at the same distance as **1**. Thus, the comparative value of $\mathrm{area}_{5'-\mathrm{C}}$ for $\mathrm{Tp}^{\mathrm{Ph}_2}\mathrm{Cu}(\mathrm{Hpz}^{\mathrm{Ph}_2})$ should be larger than that

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Table 2. Comparative Structural Data for Tp−Cu^I−L Complexes with 3-Phenyl Substituents

complex	$area_{tri}$	$area_{5'-C}$	average Cu−N_{pyr}	*D*(Cu−center of tri)	average ∠N_{pyr}−Cu−N_{pyr}	average ∠N_{pyr}−Cu−L	reference
1	22.8 $Å^2$	9.5 $Å^2$	2.088 Å	1.62 Å	91.2°	124.4°	this work
2	24.7 $Å^2$	10.0 $Å^2$	2.061 Å	1.52 Å	91.1°	125.8°	this work
3	26.9 $Å^2$	9.0 $Å^2$	2.155 Å	1.31 Å	89.9°	125.4°	this work
$Tp^{Ph_2}Cu(CO)$	23.7 $Å^2$	10.1 $Å^2$	2.059 Å	1.55 Å	90.4°	125.0°	45
$Tp^{Ph_2}Cu(Hpz^{Ph_2})$	25.8 $Å^2$	9.5 $Å^2$	2.128 Å	1.38 Å	90.7°	123.1°	19
$Tp^{Ms,H}Cu(THF)$	21.9 $Å^2$	n/a	2.061 Å	1.69 Å	92.9°	122.8°	29

observed, which is consistent with a smaller $area_{tri}$ instead of the larger one seen for that complex.

There is also clearly an electronic component to the pocket size, as seen by comparing the structures of **1** and **2**. The larger $area_{tri}$ for **2** cannot be explained using a steric argument as CO is the smaller of the two ligands, neither of which is expected to have much of a steric influence anyway. The carbonyl complexes **2** and $Tp^{Ph_2}Cu(CO)$ have the most similar parameters, differences in which are probably attributable to steric differences in the Tp ligands, as the electronic environments about the metal center are predicted to be similar, based on the fact that the carbonyl stretches are essentially the same, 2078 cm^{-1} for **2** and 2080 cm^{-1} for $Tp^{Ph_2}Cu(CO)$.[45] Although we cannot totally discount the possibility of packing forces causing some of the differences seen in these solid-state structures, the similarities between the two carbonyl structures and the reasonable trends among the others suggest at least the larger differences are significant.

The $Tp^{{}^tBu-Ph,Me}$ pocket flexibility appears then to be caused by both steric and electronic influences imparted by the ancillary ligands, which are also reflected in the bond angles and distances about the copper(I) ions. The average Cu−N_{pyr} distances are longer for **3** (2.155 Å) than for **1** (2.088 Å). Thus, the Cu ion in **3** sits closer to the pocket opening, which can also be seen as a decrease in the distance from Cu to the center of the triangular plane used to calculate $area_{tri}$ (1.31 Å for **3**, 1.62 Å for **1**). In addition, the N_{pyr}−Cu−P angles in **3** (125.4° av) are larger than the N_{pyr}−Cu−N_{acet} angles in **1** (124.4° av) and the N_{pyr}−Cu−N_{pyr} angles in **3** (89.9° av) are smaller than in **1** (91.2° av). Interestingly, the smallest value of $area_{tri}$ is found for $Tp^{Ms,H}$-Cu(THF); the copper ion in this complex sits deeper in the pocket than in the other structures, which causes larger N_{pyr}−Cu−N_{pyr} angles and smaller N_{pyr}−Cu−L angles. Thus, at least in the structures and structural parameters examined here, there is no influence attributable to steric repulsion of the substituents in the 5-position (which would cause the pocket and $area_{tri}$ to be smaller).

Conclusions

Four new copper complexes of the fairly bulky $Tp^{{}^tBu-Ph,Me}$ ligand have been synthesized and completely characterized. Using the crystal structures, it was found that there is at least some flexibility to the pocket, as the pocket opened to accommodate the bulkier PPh_3 ligand compared to the smaller CH_3CN and CO ligands. However, changes in the pocket size appear to be due to both steric and electronic factors imparted by the ancillary ligands. The Tp ligand has some flexing capabilities. The coordination parameters about the copper(I) ion, due to both steric and electronic factors, cause these variations to the pocket width and depth. When the pocket size, flexibility and interleaving capacities are exceeded, such as by binding the bulky phosphine P^tBu_3, the ligation mode of the tris(pyrazolyl)hydroborate ligand to the copper center changed from tridentate to bidentate.

We are continuing to study additional Cu(I) and Cu(II) complexes with $Tp^{{}^tBu-Ph,Me}$ and related ligands to further probe not only the pocket dynamics, but how $Tp^{{}^tBu-Ph,Me}$ influences the chemistry and/or allows the synthesis of unusual types of copper complexes.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available free of charge via the Internet at http://pubs.acs.org. Ordering information is given on any current masthead page.

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