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Synthesis and Characterization of Cationic [Tris(pyrazolyl)methane]copper(I) Carbonyl and Acetonitrile Complexes

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The reaction of [Cu(NCMe)$_4$]PF$_6$ with equimolar amounts of the tris(substituted-pyrazolyl)methane ligands HC(3,5-Me$_2$pz)$_3$, HC(3-Phpz)$_3$, and HC(3-Bu^{t}pz)$_3$ yields the respective salts {[HC(3,5-Me$_2$pz)$_3$]Cu(NCMe)}PF$_6$, {[HC(3-Phpz)$_3$]Cu(NCMe)}PF$_6$, and {[HC(3-Bu^{t}pz)$_3$]-Cu(NCMe)}PF$_6$. These complexes are unusually resistant toward reaction with dioxygen. These acetonitrile complexes react with carbon monoxide to yield the stable complexes {[HC(3,5-Me$_2$pz)$_3$]Cu(CO)}PF$_6$, {[HC(3-Phpz)$_3$]Cu(CO)}PF$_6$, and {[HC(3-Bu^{t}pz)$_3$]Cu(CO)}PF$_6$, respectively. The solid-state structures of {[HC(3-Bu^{t}pz)$_3$)]Cu(NCMe)}PF$_6$·CH$_2$Cl$_2$ and {[HC(3-Bu^{t}pz)$_3$]Cu(CO)}PF$_6$ have been determined by X-ray crystallography. The structures are very similar, with the Cu−N distances to the donor atoms of the HC(3-Bu^{t}pz)$_3$ ligand 0.03 Å shorter in the carbonyl complex.

Introduction

Since tris(pyrazolyl)borate ligands were used by Bruce and co-workers in the synthesis and structural characterization of the first copper(I) carbonyl complex, [HB(pz)$_3$]CuCO (pz = pyrazolyl ring),[1] numerous reports of [tris(pyrazolyl)borate]CuCO complexes have appeared.[2] The range of tris(pyrazolyl)borate ligands used in these complexes includes [HB(3,5-Pr^i)$_2$pz)$_3$]CuCO,[2b] with bulky substituents on the pyrazolyl ring, and a recently reported complex with a fluorinated ligand, [HB(3,5-(CF$_3$)$_2$pz)$_3$]CuCO.[2d] In addition, the analogous neutral tris(imidazolyl)phosphine ligands have been used to prepare analogous cationic monomeric copper(I) carbonyls.[3] A driving force for much of the chemistry in this area stems from its biological relevance as structural probes for oxygen-binding enzymes[4] and from recent advances in organometallic heterogeneous catalysis.[5]

We have initiated a study of the coordination chemistry of the neutral tris(pyrazolyl)methane ligand system with a variety of post-transition and transition metals.[6] In addition to the previously known ligand HC(3,5-Me$_2$pz)$_3$,[7] we are studying the chemistry of the bulkier HC(3-Phpz)$_3$[8] and HC(3-Bu^{t}pz)$_3$[9] ligands, "relatives" of the bulky second-generation poly(pyrazolyl)borate ligands.[10] We are interested in contrasting the chemistry of the neutral tris(pyrazolyl)methane ligands with that previously developed for anionic tris(pyrazolyl)borate ligands. Reported here are the syntheses of the cationic, four-coordinate copper(I) acetonitrile and carbonyl complexes derived from these three tris(pyrazolyl)methane ligands. The solid-state structures for the matched pair {[HC(3-Bu^{t}pz)$_3$]Cu(NCMe)}PF$_6$·CH$_2$Cl$_2$ and {[HC(3-Bu^{t}pz)$_3$]Cu(CO)}PF$_6$ have been determined by X-ray crystallography.

Experimental Section

All operations were carried out either under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm versus TMS. [Cu(NCMe)$_4$]PF$_6$,[11] HC(3,5-Me$_2$pz)$_3$,[7b] HC(3-Phpz)$_3$,[8] and HC(3-Bu^{t}pz)$_3$[9] were prepared according to literature procedures. Clusters assigned

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to specific ions in the mass spectra show appropriate isotopic patterns as calculated for the atoms present. Elemental analyses were performed by National Chemical Consulting, Inc.

{[HC(3,5-Me$_2$pz)$_3$]Cu(NCMe)}PF$_6$ (1). A solid mixture of [Cu(NCMe)$_4$]PF$_6$ (0.25 g, 0.67 mmol) and HC(3,5-Me$_2$pz)$_3$ (0.20 g, 0.67 mmol) was charged in a 100 mL flask and suspended in CH$_2$Cl$_2$ (5 mL). After it was stirred for 24 h, the reaction mixture was treated with hexanes (20 mL). The mixture was filtered, and the remaining pale yellow solid was washed with hexanes (3 × 5 mL) and dried under vacuum for several hours (0.278 g, 0.51 mmol; 76%); mp 238−243 °C. ^{1}H NMR (d_6-acetone; δ): 7.96 (s; 1; *H*C(3,5-Me$_2$pz)$_3$); 6.11 (s; 3; 4-*H* pz); 2.66, 2.29 (s, s; 9, 9; 3,5-Me pz); 2.52 (s; 3; C*H*$_3$CN). Mass spectrum (*m/z*): 361 {[HC(3,5-Me$_2$pz)$_3$]Cu}$^+$. Anal. Calcd for C$_{18}$H$_{25}$CuF$_6$N$_7$P: C, 39.46; H, 4.60. Found: C, 39.44; H, 4.30.

{[HC(3-Phpz)$_3$]Cu(NCMe)}PF$_6$ (2). This compound was prepared as above using HC(3-Phpz)$_3$ (0.30 g, 0.68 mmol) to yield a white solid (0.415 g, 0.60 mmol; 89%); mp 210−212 °C. ^{1}H NMR (CDCl$_3$; δ): 8.92 (s; 1; *H*C(3-Phpz)$_3$); 8.28 (br; 3; 5-*H* pz); 7.78, 7.40 (br, br; 6, 9; C$_6$*H*$_5$); 6.56 (br; 3; 4-*H* pz); 2.06 (s; 3; C*H*$_3$CN). Mass spectrum (*m/z*): 506 {[HC(3-Phpz)$_3$]Cu}$^+$. Anal. Calcd for C$_{30}$H$_{25}$CuF$_6$N$_7$P: C, 52.06; H, 3.64. Found: C, 51.75; H, 3.75.

{[HC(3-Bu^{t}pz)$_3$]Cu(NCMe)}PF$_6$ (3). This compound was prepared as above using HC(3-Bu^{t}pz)$_3$ (0.26 g; 0.68 mmol) to yield a white solid (0.385 g; 0.61 mmol; 91%); mp 246−248 °C. ^{1}H NMR (CDCl$_3$; δ): 8.59 (s; 1; *H*C(3-Bu^{t}pz)$_3$); 8.02 (d, J_{HH} = 3 Hz; 3; 5*H* pz); 6.12 (d, J_{HH} = 3 Hz; 3; 4*H* pz); 2.40 (s; 3; C*H*$_3$CN); 1.36 (s; 27; C(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$; δ): 163.9 (s; 3-*C* pz); 131.8, 103.5 (s, s; 4,5-*C*'s pz); 116.0 (s; *C*N); 76.3 (s; H*C*(3-Bu^{t}pz)$_3$); 32.1 (s; *C*(CH$_3$)$_3$); 29.9 (s; C(*C*H$_3$)$_3$); 2.6 (s; *C*H$_3$-CN). Mass spectrum (*m/z*): 445 {HC(3-Bu^{t}pz)$_3$]Cu}$^+$. Crystals suitable for an X-ray structure and the analytical sample were grown by slow diffusion of hexanes into a saturated CH$_2$Cl$_2$ solution. One equivalent of CH$_2$Cl$_2$ is retained in the crystal lattice. Anal. Calcd for C$_{24}$H$_{37}$CuF$_6$N$_7$P·CH$_2$Cl$_2$: C, 41.88; H, 5.48. Found: C, 42.16; H, 5.57.

{[HC(3,5-Me$_2$pz)$_3$]Cu(CO)}PF$_6$ (4). A solid mixture of [Cu(NCMe)$_4$]PF$_6$ (0.25 g, 0.67 mmol) and HC(3,5-Me$_2$pz)$_3$ (0.20 g, 0.67 mmol) was charged in a 100 mL flask and suspended in CH$_2$Cl$_2$ (5 mL). The mixture was degassed by the freeze−pump−thaw method (three cycles). On the last thaw cycle, the reaction mixture was placed under 1 atm of carbon monoxide. After it was warmed to room temperature, the reaction solution became homogeneous. The yellow solution was stirred for 16 h. Hexanes (25 mL) were added, and the yellow solid that precipitated was isolated by removing the mother liquor via cannula filtering and drying under vacuum (0.28 g, 0.53 mmol; 79%); mp 266−272 °C. ^{1}H NMR (CDCl$_3$; δ): 7.85 (s; 1; *H*C(Me$_2$pz)$_3$); 5.99 (s; 3; 4-*H* pz); 2.59, 2.31 (s, s; 9, 9; 3,5-Me$_2$pz). IR spectrum (Nujol mull; cm^{-1}): 2113 (CO). Low-resolution mass spectrum (*m/z*): 361 {[HC(3,5-Me$_2$pz)$_3$]-Cu}$^+$, 389 {[HC(3,5-Me$_2$pz)$_3$]Cu(CO)}$^+$. FAB high-resolution mass spectrum for {[HC(3,5-Me$_2$pz)$_3$]Cu(CO)}$^+$ (*m/e*): calcd for C$_{17}$H$_{22}$^{65}CuN$_6$O, 391.1133; found, 391.1123. Anal. Calcd for C$_{17}$H$_{22}$CuF$_6$N$_6$OP: C, 38.17; H, 4.15. Found: C, 38.14; H, 4.09.

{[HC(3-Phpz)$_3$]Cu(CO)}PF$_6$ (5). A CH$_2$Cl$_2$ (5 mL) solution of {[HC(3-Phpz)$_3$]Cu(NCMe)}PF$_6$ (0.40 g, 0.58 mmol) was degassed by the freeze−pump−thaw method (three cycles). Before the last thaw cycle, the solution was placed under an atmosphere of CO and the reaction mixture was slowly warmed to room temperature. After it was stirred for 18 h, the reaction mixture was treated with hexanes (20 mL). A white solid precipitated. The mother liquor was removed by cannula filtering, and the remaining white solid was dried under vacuum (0.32 g, 0.47 mmol; 81%); mp 175−176 °C. ^{1}H NMR (CDCl$_3$; δ): 9.10 (s; 1; *H*C(3-Phpz)$_3$); 8.36 (d; J_{HH} = 2.5 Hz; 3; 5*H* pz); 7.64, 7.47 (br; br; 6, 9; C$_6$*H*$_5$); 6.61 (d; J_{HH} = 2.5 Hz; 3; 4*H* pz). IR spectrum (Nujol mull; cm^{-1}): 2104 (CO). Anal. Calcd for C$_{29}$H$_{22}$CuF$_6$N$_6$OP: C, 51.30; H, 3.27. Found: C, 51.78; H, 3.34.

Table 1. Crystallographic Data for {[HC(3-Bu^{t}pz)$_3$]Cu(NCMe)}PF$_6$ (3) and {[HC(3-Bu^{t}pz)$_3$]Cu(CO)}PF$_6$ (6)

	3·CH$_2$Cl$_2$	**6**
formula	C$_{25}$H$_{39}$Cl$_2$CuF$_6$N$_7$P	C$_{23}$H$_{34}$CuF$_6$N$_6$OP
fw	717.04	619.07
cryst syst	orthorhombic	orthorhombic
space group	*Pna*2$_1$	*Pbca*
a, Å	20.587(7)	17.723(3)
b, Å	17.183(5)	18.059(3)
c, Å	9.650(2)	18.260(7)
V, Å^3	3414(2)	5844(3)
Z	4	8
D_{exptl}, g cm^{-3}	1.395	1.407
μ(Mo Kα), cm^{-1}	9.03	8.67
T, K	296	293
no. of rflns (collctd, indpdnt)	3067, 2674	4727, 3820
$R(F)$, $R(wF^2)$,[a] %	6.49, 16.36	5.57, 10.63

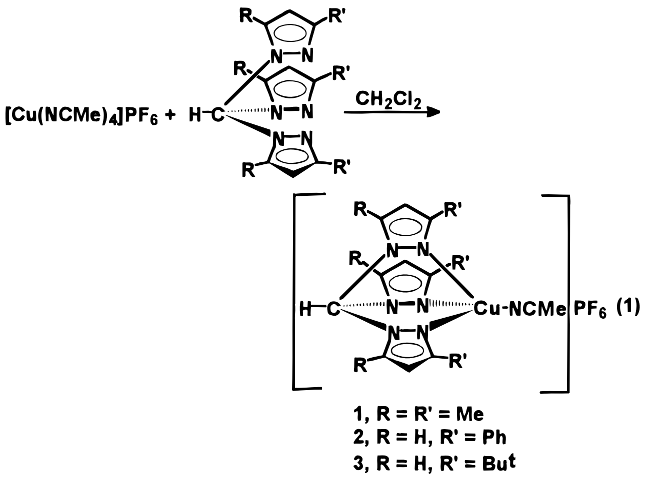
[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R(wF^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/\sigma^2(F)$.

{[HC(3-Bu^{t}pz)$_3$]Cu(CO)}PF$_6$ (6). This compound was prepared as for {[HC(3,5-Me$_2$pz)$_3$]Cu(CO)}PF$_6$ using HC-(3-Bu^{t}pz)$_3$ (0.26 g, 0.68 mmol) to yield a white solid (0.35 g, 0.55 mmol; 83%); mp 248−254 °C. ^{1}H NMR (CDCl$_3$; δ): 8.76 (s; 1; *H*C(3-Bu^{t}pz)$_3$); 8.10 (d, J_{HH} = 3 Hz; 3; 5*H* pz); 6.23 (d, J_{HH} = 3 Hz; 3; 4*H* pz); 1.42 (s; 27; C(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$; δ): 165.2 (3*C* pz); 133.4, 104.9 (4,5-*C*'s pz); 76.0 (H*C*(3-Bu^{t}pz)$_3$); 32.6 (*C*(CH$_3$)$_3$); 30.7 (C(*C*H$_3$)$_3$). The carbonyl carbon atom resonance was not located. IR spectrum (Nujol mull; cm^{-1}): 2100 (CO). Low-resolution mass spectrum (*m/z*): 445 {HC(3-Bu^{t}pz)$_3$]Cu}$^+$; 473 {Cu[HC(3-Bu^{t}pz)$_3$](CO)}$^+$. Accurate FAB high-resolution mass spectrum for {Cu[HC(3-Bu^{t}pz)$_3$]-(CO)}$^+$ (*m/e*): calcd for C$_{23}$H$_{34}$^{63}CuN$_6$O, 473.2090; found, 473.2089. Anal. Calcd for C$_{23}$H$_{34}$CuF$_6$N$_6$OP: C, 44.62; H, 5.54. Found: C, 44.63; H, 5.62.

Crystallographic Structure Determination. Crystals of **3** and **6** suitable for an X-ray structural analysis were grown by allowing hexanes to diffuse slowly into a saturated CH$_2$Cl$_2$ solution of each. Crystallographic data are collected in Table 1. Crystals of both samples were photographically characterized and determined to belong to the orthorhombic crystal system. Systematic absences in the diffraction data were consistent for either *Pna*2$_1$ or *Pnam* (nonstandard setting of *Pnma*) for **3** and uniquely consistent for *Pbca* for **6**. For **3**, the noncentrosymmetric space group was chosen based on *Z*, the distribution of *E* factors, and the failure of any of the potential molecular mirror planes to align with the crystal axes. This choice was substantiated by the results of refinement. Azimuthal scans indicated that no correction for absorption was required; $T_{max}/T_{min} < 1.1$. The structures were solved by direct methods and completed from difference Fourier maps. A molecule of CH$_2$Cl$_2$, the recrystallization solvent, was located in the crystal lattice for **3**. The fluorine atoms in the PF$_6^-$ counterion in **6** were highly disordered; attempts to model the disorder were only partially successful. For **3**, only the Cu, N, and C atoms in CH$_3$CN were anisotropically refined, and for **6**, only the Cu and CO group atoms were refined anisotropically. Hydrogen atom contributions were idealized. All computations used SHELXTL 5.1 software (G. Sheldrick, Siemens XRD, Madison, WI).

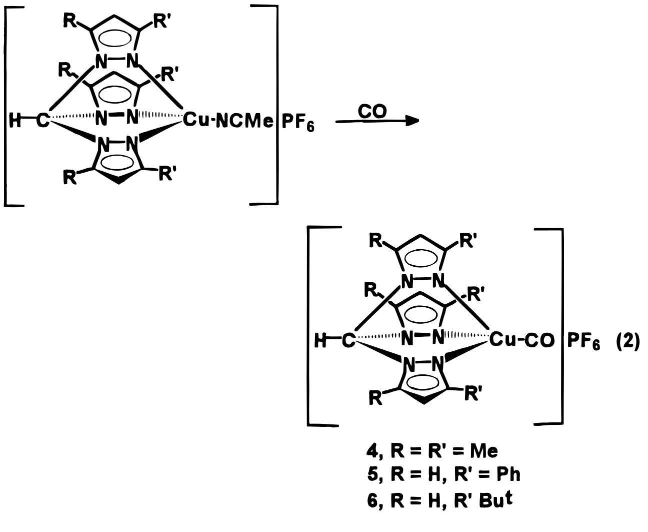
Results

Syntheses and Properties. Reaction of [Cu(NCMe)$_4$]-PF$_6$ with equimolar amounts of the neutral tris(pyrazolyl)methane ligands L (L = HC(3,5-Me$_2$pz)$_3$, HC(3-Phpz)$_3$, and HC(3-Bu^{t}pz)$_3$) in CH$_2$Cl$_2$ yields the respective LCu(NCMe)PF$_6$ salts (eq 1). These complexes were



characterized by ^{1}H NMR, mass spectral, and elemental analyses. Low-resolution FAB mass analyses of each complex showed clusters with the appropriate isotopic pattern for the cation resulting from the loss of acetonitrile. The solubility of these copper(I) monocations in CH_2Cl_2 decreases in the order $\{[HC(3\text{-}Bu^tpz)_3]Cu(NCMe)\}PF_6 > \{[HC(3\text{-}Phpz)_3]Cu(NCMe)\}PF_6 > \{[HC(3,5\text{-}Me_2pz)_3]Cu(NCMe)\}PF_6$. All three are moderately air stable even as solutions. Bubbling dioxygen into CH_2Cl_2 solutions at −78 °C provides no color change, though a faint green solution results upon warming to room temperature. The complex $\{[HC(3\text{-}Bu^tpz)_3]Cu(NCMe)\}PF_6$ was characterized in the solid state by X-ray crystallography.

The acetonitrile in the three copper(I) cations **1**−**3** can be readily substituted with carbon monoxide under mild conditions. The respective carbon monoxide adducts $\{LCu(CO)\}PF_6$ are prepared by precipitation from CH_2Cl_2 solutions of the complexes with hexanes under an atmosphere of carbon monoxide (eq 2). Alternatively, complexes **4** and **6** can be prepared by mixing $[Cu(NCMe)_4]PF_6$ with the ligand $HC(3,5\text{-}Me_2pz)_3$ or $HC(3\text{-}Bu^tpz)_3$ under CO, followed by precipitation with hexanes. Complex **5** forms a mixture (ca. 1/1) of the carbonyl and acetonitrile adducts under these conditions. The three CO complexes were characterized by solid-state IR spectroscopy (Nujol mull) as well as ^{1}H NMR, high-resolution FAB mass analyses, and elemental analyses. Surprisingly, the carbon monoxide ligand remains associated with the copper(I) complexes in the mass spectral analyses. These complexes are also moderately air stable in solution. The solid-state structure of $\{[HC(3\text{-}Bu^tpz)_3]Cu(CO)\}PF_6$ was determined by X-ray crystallography.



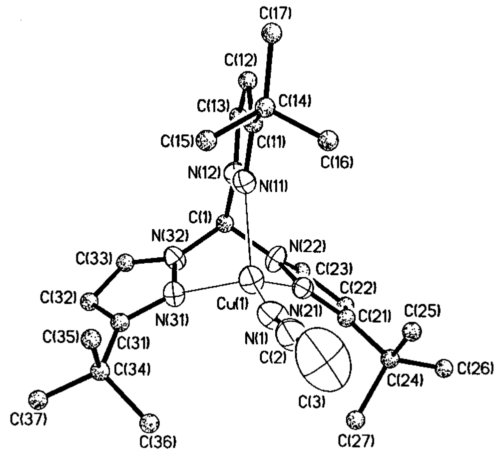


Figure 1. Diagram of $\{[HC(3\text{-}Bu^tpz)_3]Cu(NCMe)\}^+$.

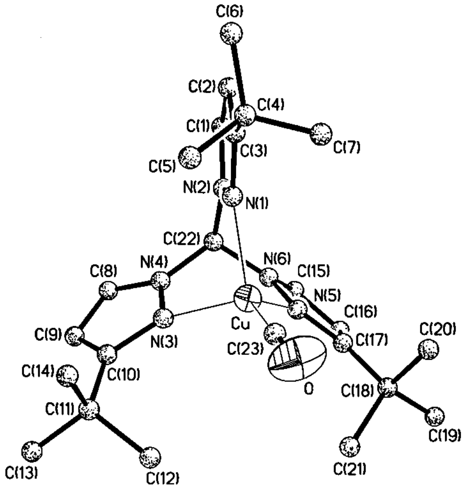


Figure 2. Diagram of $\{[HC(3\text{-}Bu^tpz)_3]Cu(CO)\}^+$.

Solid-State Structures of $\{[HC(3\text{-}Bu^tpz)_3]Cu(NCMe)\}PF_6$ (3) and $\{[HC(3\text{-}Bu^tpz)_3]Cu(CO)\}PF_6$ (6). Diagrams of the cations in **3** and **6** are provided in Figures 1 and 2. Selected bond distances and angles are given in Table 2. In both structures, the coordination geometry around the copper atom is best described as a trigonally distorted tetrahedron. The intraligand N−Cu−N angles are restrained by the chelate rings to 89°, and the average angles from these nitrogen donor atoms to the CO or NCMe donor atom open to 126°.

In the structure of **3**, the Cu−N distances for the tridentate ligand vary from 2.061(9) to 2.138(9) Å (average 2.107 Å). The fourth Cu−N distance is much shorter at 1.873(9) Å. These values are comparable to those reported previously in the structure of $[Cu(tris(1\text{-}ethyl\text{-}4\text{-}isopropylimidazolyl)phosphine)(CH_3CN)]PF_6$ of 2.075(8) and 1.901(10) Å, respectively.[12]

Significant metrical parameters in the structure of **6** are very similar to those in **3** and in previously reported analogous copper(I) carbonyl complexes of hydrotris(pyrazolyl)borate ligands[1b,2b,d] and the four-coordinate

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Table 2. Selected Bond Distances and Angles for $\{[HC(3\text{-}Bu^tpz)_3]Cu(NCMe)\}PF_6$ (3) and $\{[HC(3\text{-}Bu^tpz)_3]Cu(CO)\}PF_6$ (6)

3·CH_2Cl_2		**6**	
Bond Distances (Å)			
Cu(1)−N(11)	2.138(9)	Cu−N(1)	2.076(6)
Cu(1)−N(21)	2.122(9)	Cu−N(3)	2.075(5)
Cu(1)−N(31)	2.061(9)	Cu−N(5)	2.088(5)
Cu(1)−N(1)	1.873(9)	Cu−C(23)	1.778(10)
C(2)−N(1)	1.105(13)	C(23)−O	1.133(9)
C(2)−C(3)	1.48(2)		
N(11)···N(21)	2.987(8)	N(1)···N(3)	2.898(7)
N(11)···N(31)	2.968(9)	N(1)···N(5)	2.995(6)
N(21)···N(31)	2.926(9)	N(3)···N(5)	2.851(7)
Bond Angles (deg)			
Cu(1)−N(1)−C(2)	174.1(14)	Cu−C(23)−O	176.8(9)
N(1)−Cu(1)−N(11)	122.9(4)	C(23)−Cu−N(1)	123.7(3)
N(1)−Cu(1)−N(21)	125.7(4)	C(23)−Cu−N(3)	128.9(3)
C(1)−Cu(1)−N(31)	128.7(5)	C(23)−Cu−N(5)	125.4(3)
N(11)−Cu(1)−N(21)	89.0(4)	N(1)−Cu−N(3)	88.6(2)
N(11)−Cu(1)−N(31)	89.9(4)	N(1)−Cu−N(5)	92.0(2)
N(21)−Cu(1)−N(31)	88.8(4)	N(3)−Cu−N(5)	86.5(2)
Torsion Angles (deg)			
Cu(1)N(11)−N(12)C(13)	172.6(9)	CuN(1)−N(2)C(1)	172.8(2)
Cu(1)N(21)−N(22)C(23)	171.1(8)	CuN(3)−N(4)C(8)	175.6(2)
Cu(1)N(31)−N(32)C(33)	172.0(9)	CuN(5)−N(6)C(15)	173.6(2)

Table 3. Carbonyl Stretching Frequencies for [Tris(pyrazolyl)methane]- and [Tris(pyrazolyl)borato]copper(I) Carbonyl Complexes

complex	ν(CO) (cm^{-1})	complex	ν(CO) (cm^{-1})
$\{[HC(3,5\text{-}Me_2pz)_3]CuCO\}^+$	2113	$[HB(3,5\text{-}Me_2pz)_3]CuCO$[2a]	2066
$\{[HC(3\text{-}Phpz)_3]CuCO\}^+$	2104	$[HB(3,5\text{-}Ph_2pz)_3]CuCO$[2b]	2086
$\{[HC(3\text{-}Bu^tpz)_3]CuCO\}^+$	2100	$[HB(3\text{-}Bu^tpz)_3]CuCO$[2c]	2069

cationic complex $[Cu(dien)CO]BPh_4$.[13] Specifically, the average Cu−N bond distance (2.080 Å) and the Cu−CO bond distance of 1.778(10) Å fall within typical ranges observed in the cationic and neutral copper(I) carbonyl complexes studied previously.

Discussion

The complexes **1**−**6** are the first reported copper(I) derivatives of the tris(pyrazolyl)methane ligands,[14] and complexes **3** and **6** are the first reported complexes on any metal of the bulky ligand $HC(3\text{-}Bu^tpz)_3$. The change from negatively charged tris(pyrazolyl)borate ligands to these neutral analogs does not appear to change the stability of the carbonyl complexes. Table 3 shows a comparison of the carbonyl stretching frequencies of the matched complexes (the substitution for the phenyl derivative is different). As expected, the values for the cationic complexes are higher, indicating weaker π back-bonding with the CO ligand. A similar increase in stretching frequency was noted previously for the comparison of analogous neutral tris(pyrazolyl)borate and cationic tris(imidazolyl)phosphine complexes.[3]

Even though a CO ligand is a weak σ donor and strong π back-bonding ligand, whereas the NCMe ligand is viewed as a moderate σ donor and very weak π acceptor,[15] the two cations have very similar geometries in the solid state. The average tris(pyrazolyl)methane Cu−N bond length in **3** is 0.03 Å greater than that observed in **6**, although the shortest individual distance is found in **3**. The shortening in **6** can be attributed to the carbonyl ligand donating less electron density than the acetonitrile ligand to the copper, causing the nitrogen donor atoms from the tridentate ligand to bond more strongly, but the effect is small.

Another feature worth noting is that in both structures there is very little tilting of the pyrazolyl rings with respect to the C_{3v} axis of the molecule. Thus, the Cu−N−N−C torsion angles of the pyrazolyl rings average 172° for **3** and 174° for **6**. For complexes with planar pyrazolyl rings, as observed with these complexes, the deviation of this angle from 180° defines the degree of tilting of the rings. This lack of tilting contrasts with our earlier results in thallium[6a] and cadmium[6b] structures containing the ligand $HC(3,5\text{-}Me_2pz)_3$. In the most distorted case of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$, this M−N−N−C torsion angle is 123.2°. We attributed this distortion to the size of the metal atom being large in comparison to the intrinsic "bite" of the ligand. In the present structures, no distortion is necessary because the small size of copper(I) matches the bite of the ligand.

Previously, Kitjima reported that addition of dioxygen to the copper(I) species $[HB(3,5\text{-}i\text{-}Pr_2pz)_3]Cu$ at low temperatures is facile and results in a deep purple solution.[2b] The product that forms is a μ-η^2:η^2-dioxygen dimer, as determined by low-temperature X-ray crystallography. All but the most sterically hindered cationic copper(I) complexes of the tris(imidazolyl)phosphine ligands also turn purple in the presence of oxygen at low temperatures.[3,12] In contrast, compounds **1**−**3** are resistant toward forming this purple solution under similar conditions and are surprisingly stable.

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Supporting Information Available: Tables of complete data collection information, bond distances, angles, positional parameters, and anisotropic thermal parameters for **3** and **6** (13 pages). Ordering information is given on any current masthead page.

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