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Copper and Silver Complexes Containing Organic Azide Ligands: Syntheses, Structures, and Theoretical Investigation of $[HB(3,5-(CF_3)_2Pz)_3]CuNNN(1-Ad)$ and $[HB(3,5-(CF_3)_2Pz)_3]AgN(1-Ad)NN$ (Where Pz = Pyrazolyl and 1-Ad = 1-Adamantyl)

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Treatment of $[HB(3,5-(CF_3)_2Pz)_3]Na(THF)$ with CF_3SO_3Cu followed by 1-azidoadamantane affords $[HB(3,5-(CF_3)_2Pz)_3]CuNNN(1-Ad)$ in 65% yield. The solid state structure shows that the copper atom is coordinated to the terminal nitrogen atom (N_T) of the azidoadamantane ligand. The related silver(I) adduct can be prepared in 80% yield by the treatment of $[HB(3,5-(CF_3)_2Pz)_3]Ag(THF)$ with 1-azidoadamantane. However, $[HB(3,5-(CF_3)_2Pz)_3]AgN(1-Ad)NN$ shows a different bonding mode where the silver atom coordinates to the alkylated nitrogen atom (N_A) of the azidoadamantane ligand. Asymmetric stretching bands of the azido group for copper and silver adducts appear at 2143 and 2120 cm^{-1}, respectively. Theoretical investigation shows that steric effects do not play a dominant role in determining the bonding mode of the azide ligand in these two metal complexes. Although the copper(I) ion affinity for the two coordinating sites N_T and N_A is nearly identical, copper−azide back-bonding interactions favor the copper−N_T mode of bonding over the copper−N_A mode. Silver (a very poor back-bonding metal) prefers the N_A site for coordination. The N_A site has a significantly higher proton affinity and slightly higher sodium ion affinity. Important structural parameters for $[HB(3,5-(CF_3)_2Pz)_3]CuNNN(1-Ad)$ and $[HB(3,5-(CF_3)_2Pz)_3]AgN(1-Ad)NN$ are as follows: Cu−N_T 1.861(3) Å, N_T−N 1.136(4) Å, N−N_A 1.219(4) Å, N_T−N−N_A 173.1(3)°; Ag−N_A 2.220(5) Å, N_T−N 1.143(12) Å, N−N_A 1.227(10) Å, N_T−N−N_A 176.8(12)°. Overall, the azidoadamantane ligand does not undergo any significant changes upon coordination to Cu(I) or Ag(I) ions.

Introduction

Organic azides (RNNN) are excellent starting materials for the preparation of a variety of organic and inorganic compounds.[1−6] Some of the organic compounds that can be synthesized using organo azides include amines, azomethines, nitriles, diazo compounds, and various nitrogen-containing heterocycles.[1,2] Organic azides (RNNN) are also a convenient source for the generation of nitrene (RN) fragments.[1−3] This process occurs with the elimination of N_2 and has been exploited in inorganic (e.g., synthesis of imidometal adducts),[4−6] organic (e.g., synthesis of azomethines),[1] biochemical (e.g., photoaffinity labeling),[2] and industrial (e.g., cross-linking of polymeric systems)[2] applications. Some of these transformations are mediated by main group and/or transition metal ions.[1,2] It is commonly believed that such processes involve organoazido-metal complexes as intermediates.[7−15] Although there is a significant interest in these intermediates, the isolation and characterization of such species are difficult mainly due to the rapid loss of nitrogen.[8,11] Overall, stable metal complexes containing organo azide ligands are extremely rare.

Since 1995, a small number of structurally characterized, metal−organo azide complexes have appeared in the literature (Figure 1). These include tantalum(V) complexes of NNNPh and $NNNC_6H_4$-*p*-NMe_2 (**1, 2**),[12,14] a vanadium(V) adduct (**3**) containing NNNMes,[13] a mixed-metallic zirconium(IV)−iridium(III) complex (**4**) containing a bridging NNNPh,[16] and palladium(II) (**5**) and copper(II) (**6**) adducts featuring a chelating 1-azido-2-pyrazolylcyclohexane ligand.[17] These compounds show interesting structures and properties. Organo azide metal adducts **1**−**4** feature significantly bent "NNN" moieties. They are best described as metal complexes of "diazenylimido" ligands.[12−14] In contrast, the organoazido complexes **5** and **6**

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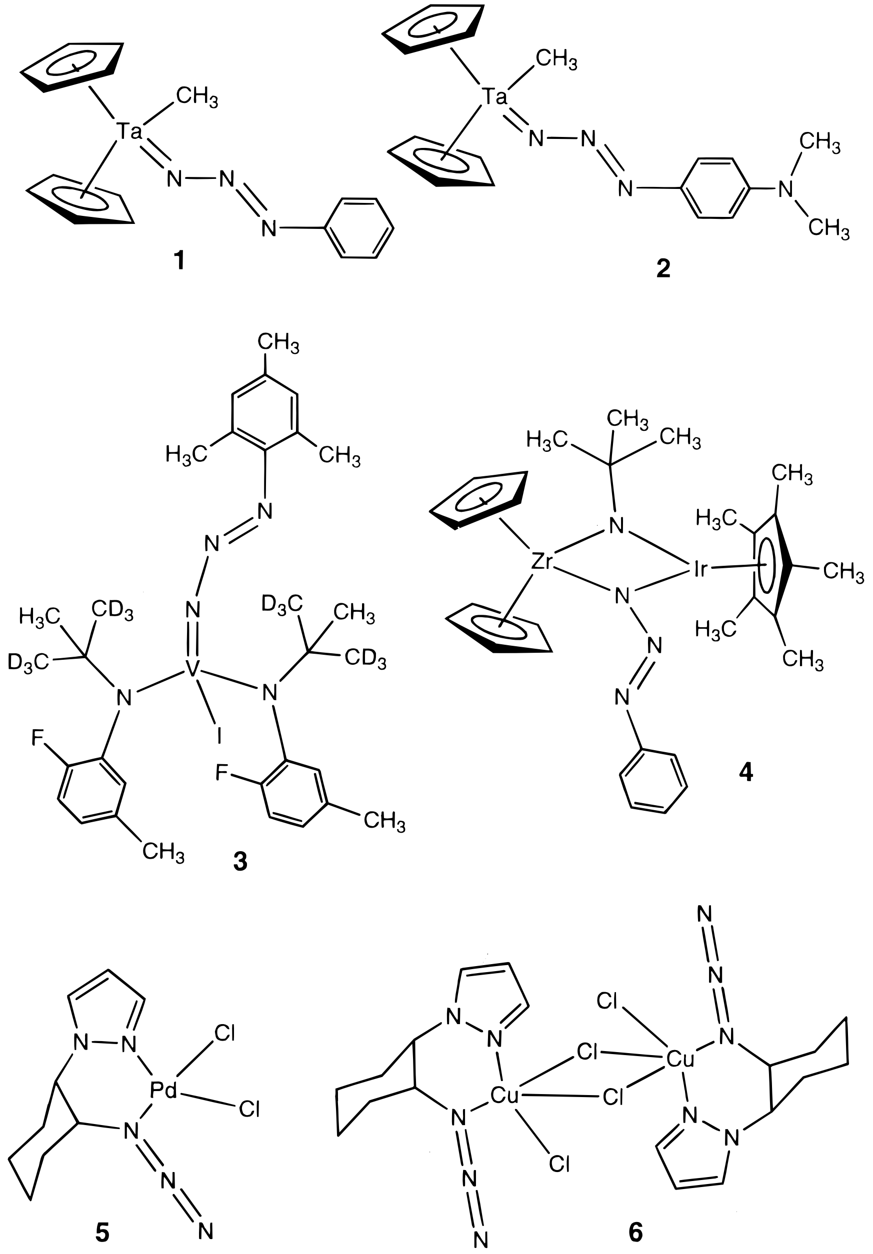

Figure 1. Structurally characterized metal−organo azide complexes.

contain essentially linear “NNN” groups. Compounds **1**−**3** lose nitrogen under relatively mild conditions to yield metalimido complexes.

We are currently interested in the chemistry of highly fluorinated poly(pyrazolyl)borate ligands.[18−28] Fluorinated ligands such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (where $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ = hydridotris(3,5-bis(trifluoromethyl)pyrazolyl)borate) are very useful in the stabilization of reactive and/or labile metal adducts. For example, we have successfully used $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ to isolate compounds such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-}C_2H_2)$,[28] $[HB(3,5\text{-}(CF_3)_2Pz)_3]AuCO$,[27] and $[HB(3,5\text{-}(CF_3)_2Pz)_3]$-Ga.[29] In this paper, we describe the utility of the $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand in the isolation of the first organoazido complexes of copper(I) and silver(I). We have also performed quantum mechanical calculations to investigate how steric/electronic effects influence the coordination mode of the organoazido ligand in $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuNNN(1\text{-}Ad)$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgN(1\text{-}Ad)NN$ (where 1-Ad = 1-adamantyl).

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen either using standard Schlenk techniques or in a Vacuum Atmospheres single-station drybox equipped with a

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−25 °C refrigerator. Solvents were purchased from commercial sources and distilled from conventional drying agents prior to use. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded at 25 °C on a JEOL Eclipse 500 spectrometer (^{1}H, 500.16 MHz; ^{13}C, 125.78 MHz; ^{19}F, 470.62 MHz). Proton and carbon chemical shifts are reported in parts per million vs Me_4Si. ^{19}F NMR chemical shifts were referenced relative to external $CFCl_3$. Infrared spectra were recorded on a JASCO FT-IR 410 spectrometer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed at the University of Texas at Arlington using a Perkin-Elmer Model 2400 CHN analyzer. Syntheses of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(THF)$[23] and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$[28] were carried out as reported previously. Bis(copper(I) trifluoromethanesulfonate)-benzene and 1-azidoadamantane were purchased from commercial sources.

Synthesis of $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuNNN(1\text{-}Ad)$. $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(THF)$ (0.228 g, 0.318 mmol) and bis(copper(I) trifluoromethanesulfonate)benzene (0.080 g, 0.159 mmol) were combined in THF (15 mL) and stirred for 20 min at 0 °C. The solution was allowed to warm to room temperature, and 1-azidoadamantane (0.056 g, 0.316 mmol in 2 mL of THF) was added. After stirring for 4 h, the solvent was removed under reduced pressure. The residue was extracted into toluene and filtered over Celite, and the toluene was removed from the filtrate under vacuum to obtain a white crystalline solid. It was recrystallized from toluene/hexane at 5 °C to obtain $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuNNN(1\text{-}Ad)$ as colorless crystals. Yield: 65%. Mp: 159−164 °C dec. ^{1}H NMR (C_6D_6): δ 1.37 (s, Ad), 1.78 (s, Ad), 1.86 (s, Ad), 6.17 (s, Pz-CH). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 30.2 (s, Ad), 35.7 (s, Ad), 41.5 (s, Ad), 106.6 (s, Pz-CH), 119.6 (q, $^{1}J(C,F) = 270$ Hz, CF_3), 120.7 (q, $^{1}J(C,F) = 270$ Hz, CF_3), 139.7 (q, $^{2}J(C,F) = 44$ Hz, CCF_3), 142.8 (q, $^{2}J(C,F) = 38$ Hz, CCF_3). ^{19}F NMR (C_6D_6): δ −58.9, −62.2. IR (Nujol), cm^{-1}: 3142 (Pz, C−H), 2923, 2628 (B−H), 2336, 2143 (N_3), 1560, 1496, 1267, 1166, 1075, 1044, 996, 967, 879, 847, 827, 779, 748, 737, 731, 696, 664. IR (KBr), cm^{-1}: 2137 (N_3). Anal. Calcd for $C_{25}H_{19}N_9BF_{18}Cu$: C, 34.84; H, 2.22; N, 14.63 Found: C, 35.26; H, 2.55; N, 14.26.

Synthesis of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgN(1\text{-}Ad)NN$. 1-Azidoadamantane (0.043 g, 0.244 mmol) and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ (0.200 g, 0.244 mmol) were combined in hexane at room temperature and stirred for 7 h. Solvent was removed under reduced pressure to obtain a white solid. It was recrystallized from hexane at 5 °C to obtain colorless, crystalline $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgN(1\text{-}Ad)NN$ in 80% yield. Mp: 107−111 °C. ^{1}H NMR (C_6D_6): δ 1.32 (q, Ad), 1.60 (m, Ad), 1.76 (s, Ad), 6.27 (s, Pz-CH). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 30.1 (s, Ad), 35.9 (s, Ad), 41.6 (s, Ad), 58.9 (s, Ad), 106.8 (s, Pz-CH), 119.7 (q, $^{1}J(C,F) = 271$ Hz, CF_3), 120.8 (q, $^{1}J(C,F) = 270$ Hz, CF_3), 140.5 (q, $^{2}J(C,F) = 48$ Hz, $\mathit{C}CF_3$), 143.6 (q, $^{2}J(C,F) = 39$ Hz, $\mathit{C}CF_3$). ^{19}F NMR (C_6D_6): δ −58.9 (d, $^{5}J(F,H) = 3.2$ Hz), −61.6. IR (Nujol), cm^{-1}: 3165 (Pz, C−H), 2630 (BH), 2377, 2120 (N_3), 1657, 1556, 1497, 1365, 1268, 1165, 1078, 1039, 991, 970, 891, 830, 778, 746, 737, 699, 682, 611. Anal. Calcd for $C_{25}H_{19}N_9BF_{18}Ag$: C, 33.14; H, 2.11; N, 13.91. Found: C, 33.27; H, 2.25; N, 13.06.

Crystallographic Data Collection and Structure Determinations. General Procedures. A suitable crystal covered with a layer of hydrocarbon oil was selected and mounted on a glass fiber with a small amount of 5-min epoxy. Data were collected on a Siemens P4 diffractometer at room temperature. Data were corrected for Lorentz, polarization, and absorption effects. The space group determination was based upon a check of Laue symmetry and symmetric absences present and was confirmed by the structure solution. Structures were solved by direct methods followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using the Bruker SHELXTL 5.1 software package.[30]

$[HB(3,5\text{-}(CF_3)_2Pz)_3]CuNNN(1\text{-}Ad)$. X-ray quality crystals were obtained from a toluene−hexane solution at 0 °C. Cell parameters were determined using 40 reflections. This compound crystallizes in the $P\bar{1}$ space group with a half-occupied toluene molecule in the asymmetric unit. This toluene molecule lies on an inversion center. A rotational disorder was observed for fluorines on C16, C26, and C36 carbon atoms and was modeled successfully. All non-hydrogen atoms were refined anisotropically. The hydrogen atom on boron was located from the difference map. The remaining hydrogens were included in the calculated positions.

$[HB(3,5\text{-}(CF_3)_2Pz)_3]AgN(1\text{-}Ad)NN$. X-ray quality crystals were obtained from a hexane−Et_2O solution at −25 °C. Cell parameters were determined using 53 reflections. This silver adduct crystallizes in the $P\bar{1}$ space group with two well-separated $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgN(1\text{-}Ad)NN$ molecules in the asymmetric unit. A rotational disorder was observed for fluorines on C16, C26, and C66 and was modeled successfully. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on boron were located from the difference map. The remaining hydrogens were included in the calculated positions. Crystals of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgN(1\text{-}Ad)NN$ obtained from a toluene−hexane mixture at −25 °C adopt a different crystal system. They crystallize in the monoclinic $P2_1/c$ space group with one molecule of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgN(1\text{-}Ad)NN$ in the asymmetric unit. Crystal data: $C_{25}H_{19}AgBF_{18}N_9$, $T = 293$ K, $a = 9.1469(9)$ Å, $b = 21.9567(19)$ Å, $c = 17.183(3)$ Å, $\beta = 92.251(10)°$, $V = 3448.3(7)$ Å^3, $Z = 4$. This structure can be solved and refined (R1 = 6.94%, wR2 = 13.39% for all data). However, it contains a disordered adamantyl group.

Cell dimensions and structure refinement data for $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuNNN(1\text{-}Ad)$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgN(1\text{-}Ad)NN$ are listed in Table 1. Selected bond lengths and angles are given in Tables 2 and 3. Full crystallographic data, atomic coordinates, a complete list of bond distances and angles, anisotropic thermal parameters, and the hydrogen coordinates are presented in the Supporting Information.

Computational Procedures. Quantum mechanical calculations were performed to investigate the factors responsible for the structural differences between the copper and silver azide complexes. However, due to the relatively large size of these azidometal systems, smaller model systems were employed for most of the calculations. The models considered were $[HB(Pz)_3]M(HN_3)$ and $[HB(Pz)_3]M(CH_3N_3)$ for the copper and silver species and $[HB(3\text{-}(CF_3)Pz)_3]M(HN_3)$ for the silver system (Figure 2). To examine the effects of zero-point energy (ZPE) differences on the energetics, we also employed a smaller model for the copper system: $[HB(NN(H))_3]Cu(N_3H)$ (Figure 2). ZPEs had a negligible effect (∼0.1 kcal/mol favoring N_T) and were therefore not considered further.

Both isomers for each model were optimized fully at the B3LYP[31] level of theory. The Wachters−Hay[32,33] basis set was used for the copper, while the standard 6-31G*[34] basis set was employed for all ligand atoms. For the silver atom, both all-electron (AE) and relativistic effective core potential (RECP) basis sets were considered. The AE basis set used for silver was a set of (18s12p9d) Gaussian functions contracted to [6s5p3d].[35] Four different RECP basis sets were considered: LanL2DZ,[36] Stevens−Basch−Krauss (CEP[37]), Stuttgart−Dresden (SDD),[38] and CRENBL.[39] All the RECPs replaced the inner 28 core electrons of silver. CEP used a [4211/4211/311] valance basis set. A [341/321/31] valence basis set was used in LanL2DZ. A [311111/2211/411] valence basis set was used in SDD, and a [11111/11111/1111] valence basis set was used in CRENBL. The remaining atoms were described by the all-electron 6-31G* basis set.

Results and Discussion

The copper(I) adduct $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(THF)$ was prepared in situ from $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(THF)$ and CF_3SO_3Cu in THF. This compound was then treated with 1-azido-

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Table 1. Crystal Data and Structure Refinement Parameters

	[HB(3,5-(CF$_3$)$_2$Pz)$_3$]CuNNN(1-Ad)	[HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgN(1-Ad)NN
formula	$C_{25}H_{19}BCuF_{18}N_9 \cdot 0.5(C_7H_8)$	$C_{25}H_{19}AgBF_{18}N_9$
fw	907.91	906.17
T (K)	293(2)	293(2)
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.4911(12)	13.2765(16)
b, Å	11.4778(12)	13.7870(11)
c, Å	16.139(2)	21.479(2)
α, deg	99.621(10)	97.805(6)
β, deg	108.817(11)	96.344(8)
γ, deg	90.081(9)	118.500(7)
V, Å^3	1810.5(4)	3353.0(6)
Z	2	4
λ(Mo Kα), Å	0.710 73	0.710 73
D (calcd), Mg/m^3	1.665	1.795
GOF on F^2	1.023	1.011
R indices[a] [$I > 2\sigma(I)$]	R1 = 0.0374 wR2 = 0.0957	R1 = 0.0475 wR2 = 0.1104
R indices[a] (all data)	R1 = 0.0458 wR2 = 0.1019	R1 = 0.0717 wR2 = 0.1238

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma |F_o|$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o2)^2]]^{1/2}$.

adamantane (NNN(1-Ad)) to obtain [HB(3,5-(CF$_3$)$_2$Pz)$_3$]CuNNN(1-Ad) in 65% yield. It is a colorless crystalline solid. The infrared spectrum of these crystals displays a strong absorption band at 2143 cm^{-1}. This can be assigned to the asymmetric stretching vibration of the azido group. The ν_{asym} (N$_3$) absorption of the parent ligand NNN(1-Ad) appears at a lower frequency (2110 cm^{-1}).[15] NMR (^{1}H, ^{13}C, ^{19}F) spectra display resonances for three equivalent pyrazolyl rings. Chemical shift values corresponding to the tris(pyrazolyl)borate moiety are very similar to those observed for previously reported [HB(3,5-(CF$_3$)$_2$Pz)$_3$]CuL (L = CO, NCCH$_3$) complexes.[19,25]

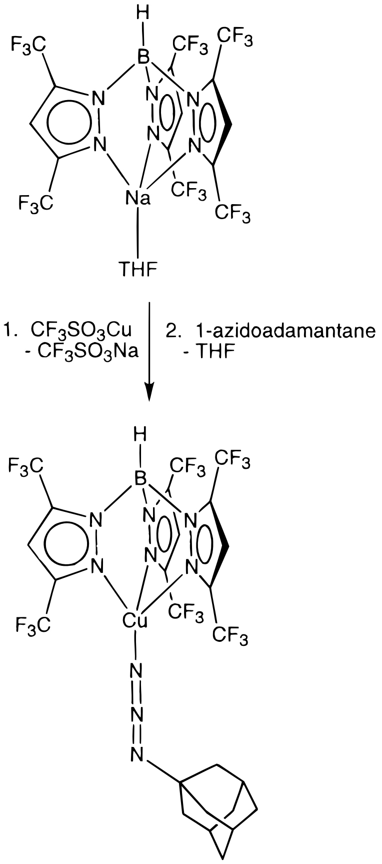


Table 2. Selected Bond Lengths (Å) and Angles (deg) for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]CuNNN(1-Ad)

Cu−N3	1.861(3)	N21−B	1.546(4)
Cu−N12	2.051(3)	N31−N32	1.354(3)
Cu−N32	2.087(2)	N31−B	1.565(4)
Cu−N22	2.092(3)	N1−N2	1.219(4)
N11−N12	1.359(3)	N1−C1	1.509(4)
N11−B	1.556(4)	N2−N3	1.136(4)
N21−N22	1.358(4)	Cu···B	3.056
N3−Cu−N12	125.20(12)	N21−B−N31	109.2(2)
N3−Cu−N32	126.07(13)	N11−B−N31	108.4(2)
N12−Cu−N32	90.62(10)	N2−N1−C1	116.1(3)
N3−Cu−N22	123.69(15)	N3−N2−N1	173.1(3)
N12−Cu−N22	90.43(11)	N2−N3−Cu	173.8(4)
N32−Cu−N22	90.09(10)	B···Cu−N3	178.5
N21−B−N11	109.6(2)		

Table 3. Bond Lengths (Å) and Angles (deg) for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgN(1-Ad)NN

Ag1−N1	2.236(5)	Ag2−N1′	2.203(6)
Ag1−N22	2.343(4)	Ag2−N42	2.369(5)
Ag1−N32	2.395(5)	Ag2−N52	2.389(5)
Ag1−N12	2.403(4)	Ag2−N62	2.389(5)
N1−N2	1.227(9)	N1′−N2′	1.228(12)
N1−C1	1.499(8)	N1′−C1′	1.496(9)
N2−N3	1.125(10)	N2′−N3′	1.162(14)
N11−N12	1.361(6)	N41−N42	1.350(6)
N11−B1	1.562(8)	N41−B2	1.540(8)
N21−N22	1.355(6)	N51−N52	1.350(6)
N21−B1	1.549(8)	N51−B2	1.563(8)
N31−N32	1.353(6)	N61−N62	1.361(6)
N31−B1	1.544(8)	N61−B2	1.551(8)
Ag1···B1	3.370	Ag2···B2	3.396
N1−Ag1−N22	156.5(2)	N1′−Ag2−N42	128.8(2)
N1−Ag1−N32	116.0(2)	N1′−Ag2−N52	139.5(2)
N22−Ag1−N32	81.39(16)	N42−Ag2−N52	80.68(15)
N1−Ag1−N12	115.6(2)	N1′−Ag2−N62	125.4(2)
N22−Ag1−N12	81.21(15)	N42−Ag2−N62	78.87(16)
N32−Ag1−N12	81.29(15)	N52−Ag2−N62	82.64(16)
N2−N1−C1	112.8(6)	N2′−N1′−C1′	111.4(7)
N2−N1−Ag1	117.9(5)	N2′−N1′−Ag2	118.6(6)
C1−N1−Ag1	129.2(4)	C1′−N1′−Ag2	129.4(5)
N3−N2−N1	176.0(9)	N3′−N2′−N1′	177.6(15)
N31−B1−N21	110.8(5)	N41−B2−N61	110.2(5)
N31−B1−N11	110.9(5)	N41−B2−N51	110.0(5)
N21−B1−N11	109.7(4)	N61−B2−N51	110.4(5)
B1···Ag1−N1	154.5	B2···Ag2−N1′	171.5

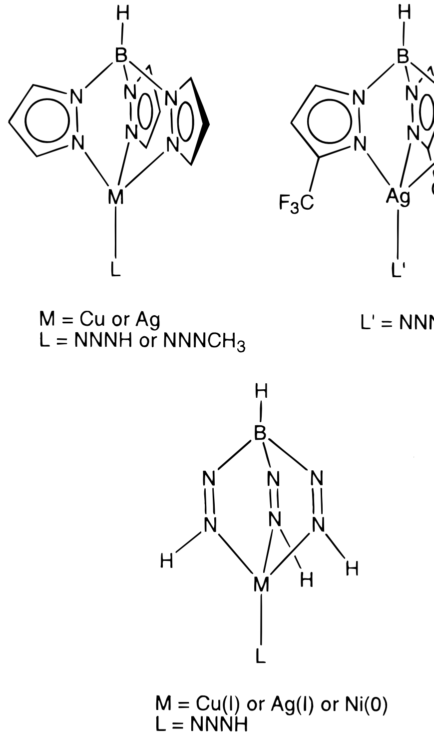


Figure 2. Model systems used in the calculations.

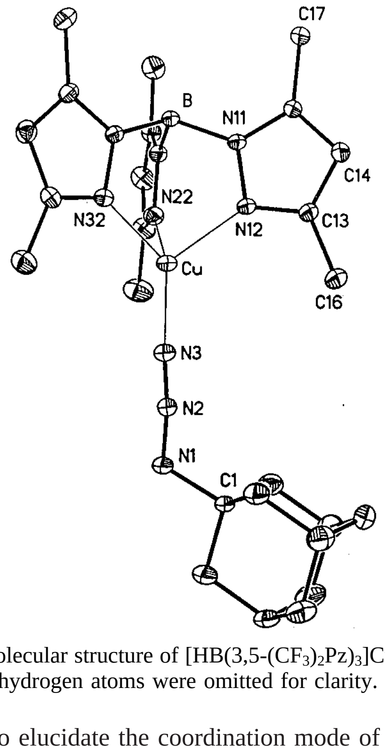
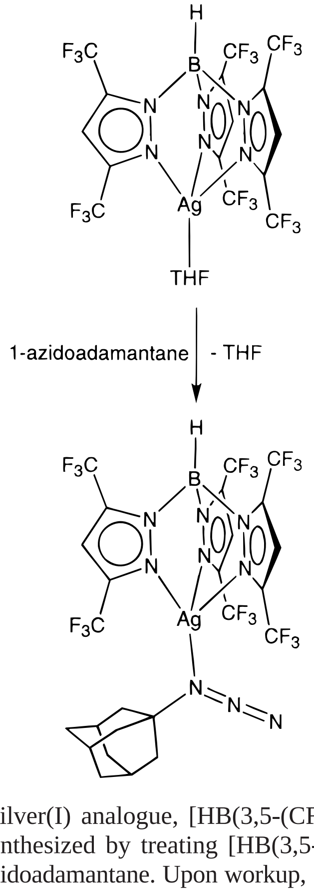


Figure 3. Molecular structure of [HB(3,5-$(CF_3)_2Pz)_3$]CuNNN(1-Ad). Fluorine and hydrogen atoms were omitted for clarity.

In order to elucidate the coordination mode of NNN(1-Ad) in [HB(3,5-$(CF_3)_2Pz)_3$]CuNNN(1-Ad), an X-ray diffraction analysis was undertaken. The molecular structure is illustrated in Figure 3. The azidoadamantane ligand coordinates to the copper atom via the terminal nitrogen atom (N_T). To our knowledge, there are no reports of organoazido copper(I) complexes in the literature.[40] However, there is a structurally characterized organic azide complex involving copper(II) (**6**).[17] In contrast to [HB(3,5-$(CF_3)_2Pz)_3$]CuNNN(1-Ad), the copper atom in **6** coordinates to the alkylated nitrogen atom (N_A) of the azide ligand.

The Cu−N_T distance of [HB(3,5-$(CF_3)_2Pz)_3$]CuNNN(1-Ad) is 1.861(3) Å. It is very similar to related copper−nitrogen bond lengths observed for [HB(3,5-$(CF_3)_2Pz)_3$]CuNCCH$_3$ (1.892(11) Å) and [HB(3,5-$(CF_3)_2Pz)_3$]CuNC(*t*-Bu) (1.878(7) Å).[41] It is, however, significantly shorter than the Cu−N_A distance of **6** (2.079(2) Å).[17] This may be due to differences in coordination numbers of the bonded atoms. [HB(3,5-$(CF_3)_2Pz)_3$]CuNNN(1-Ad) contains a 4-coordinate copper center and a 2-coordinate N_T site, whereas in **6**, coordination numbers of the copper and N_A site are 5 and 3, respectively. [HB(3,5-$(CF_3)_2Pz)_3$]CuNNN-(1-Ad) has an essentially linear azide moiety as is evident from the N_A−N−N_T bond angle of 173.1(3)° (cf. 174.5(2)° of **6**). The N_T−N and N_A−N bond distances are 1.136(4) and 1.219(4) Å, respectively. These values are very similar to those observed for free aliphatic azides.

Interestingly, despite all the differences, [HB(3,5-$(CF_3)_2Pz)_3$]-CuNNN(1-Ad) and **6** show remarkably similar ν_{asym} (N_3) values for the alkyl azide group (2143 and 2148 cm^{-1}, respectively). Compounds **1**−**4** contain RNNN ligands bonded to metals through the terminal nitrogen atom.[12−14,16] However, they all show significant structural changes in the organo azide ligand (Table 4). The most notable feature is that they all contain a bent "NNN" group (N_A−N−N_T bond angle ca. 114°). N_T−N bond distances are also significantly different compared to the corresponding distances of free ligands. Thus the organo azide ligands of metal adducts **1**−**4** are best described as "diazenylimido" ligands.[12−14] [HB(3,5-$(CF_3)_2Pz)_3$]CuNNN(1-Ad), in contrast, contains an essentially undisturbed organo azide ligand.



The related silver(I) analogue, [HB(3,5-$(CF_3)_2Pz)_3$]AgN(1-Ad)NN, was synthesized by treating [HB(3,5-$(CF_3)_2Pz)_3$]Ag-(THF) with 1-azidoadamantane. Upon workup, [HB(3,5-$(CF_3)_2$-Pz$)_3$]AgN(1-Ad)NN was isolated as an air-stable, colorless crystalline solid in 80% yield. The IR spectrum of [HB(3,5-$(CF_3)_2Pz)_3$]AgN(1-Ad)NN shows a strong absorption band at

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(40) *Cambridge Structural Database System (CSDS)*, Cambridge Crystallographic Data Centre, Cambridge, England, 1998.

(41) Dias, H. V. R.; Ayers, A. Unpublished work.

Table 4.[a] Selected Bond Distances (Å) and Angles (deg) for Metal Adducts Containing RNNN Ligands

	N_A−N	N_T−N	N_A−N−N_T	R−N_A−N	ref
A	1.219(4)	1.136(4)	173.1(3)	116.1(3)	this work
B	1.227(9)	1.125(10)	176.0(9)	112.8(6)	this work
	1.228(12)	1.162(14)	177.6(15)	111.4(7)	
B	1.238(8)	1.134(8)	176.6(8)	113.1(7)	data from $P2_1/c$ system
1	1.267(15)	1.282(16)	115.0(12)	110.7(12)	12
2	1.276(9)	1.310(9)	113.7(8)	112.2(7)	14
3	1.198(6)	1.339(5)	116.6(4)	118.1(4)	13
4	1.331(13)	1.320(13)	111.1(9)	111.6(10)	16
5	1.251(5)	1.129(5)	177.1(4)	114.3(3)	17
6	1.251(3)	1.123(3)	174.5(2)	114.93(17)	17

[a] **A** = [HB(3,5-$(CF_3)_2Pz)_3$]CuNNN(1-Ad), and **B** = [HB(3,5-$(CF_3)_2Pz)_3$]AgN(1-Ad)NN.

2120 cm^{-1}, corresponding to the ν_{asym} (N_3). This frequency is slightly lower than that of the copper adduct [HB(3,5-$(CF_3)_2$-$Pz)_3$]CuNNN(1-Ad), but marginally higher than the ν_{asym} (N_3) of the free ligand (2110 cm^{-1}). NMR spectra display resonances for three equivalent pyrazolyl rings and indicate, considering the crystal structure of [HB(3,5-$(CF_3)_2Pz)_3$]AgN(1-Ad)NN, fluxional behavior in solution.

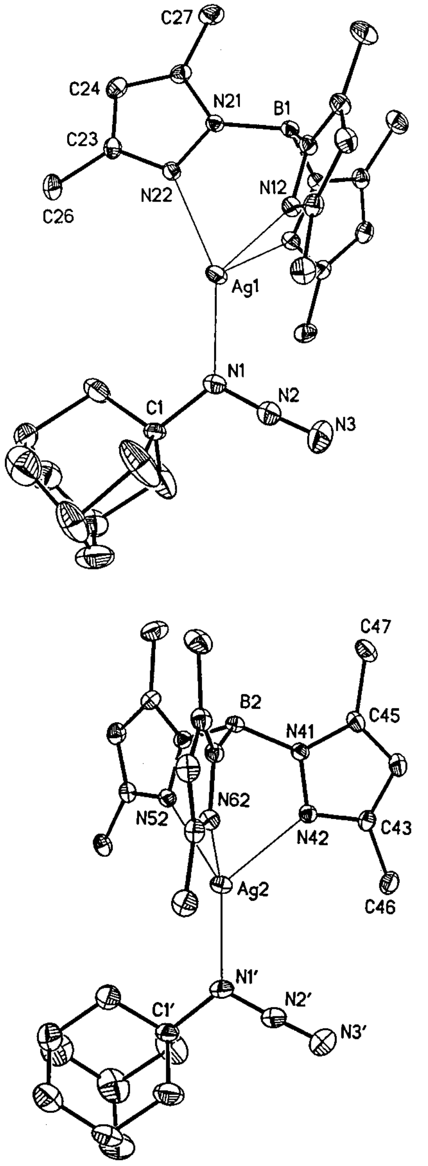


Figure 4. Molecular structure of [HB(3,5-$(CF_3)_2Pz)_3$]AgN(1-Ad)NN showing the geometry of the two molecules in the asymmetric unit. Fluorine and hydrogen atoms were omitted for clarity.

[HB(3,5-$(CF_3)_2Pz)_3$]AgN(1-Ad)NN crystallizes in the $P\bar{1}$ space group with two chemically similar but crystallographically different molecules in the asymmetric unit (Figure 4). These molecules contain η^1-bonded NNN(1-Ad) groups. In contrast to the copper analogue, the azide group in [HB(3,5-$(CF_3)_2Pz)_3$]-AgN(1-Ad)NN coordinates to silver through the alkylated nitrogen atom (N_A). The main difference between the two molecules in the asymmetric unit is the degree of distortion at the silver site. The molecule involving Ag1 shows the largest deviation from the ideal tetrahedral geometry. This is evident from the B$\cdots$Ag−N_A angle of 154.5° for the Ag1-containing molecule. The corresponding angle for the Ag2-containing molecule is 171.5°. Interestingly, structural parameters of the two "AgN(1-Ad)NN" units are nearly identical. The N_A−N (average 1.227 Å) and N_T−N (average 1.143 Å) bond distances are very similar to those of the copper(I) analogue (see Table 4). The azide group is also essentially linear (average N_A−N−N_T angle = 176.8(12)°) as in the copper system. These observations agree well with ν_{asym} (N_3) data of the two adducts. The average Ag−N_A distance of 2.220 Å in [HB(3,5-$(CF_3)_2$-$Pz)_3$]AgN(1-Ad)NN is longer than the Ag−N(CR) distance of [HB(3,5-$(CF_3)_2Pz)_3$]AgNC(*t*-Bu) (2.120(4) Å).[28] The larger value for [HB(3,5-$(CF_3)_2Pz)_3$]AgN(1-Ad)NN may most likely be a result of higher coordination number at the nitrogen site.

The bonding mode of the alkyl azide in [HB(3,5-$(CF_3)_2Pz)_3$]-AgN(1-Ad)NN is similar to those observed for copper(II) and palladium(II) adducts **5** and **6**. A similar mode of coordination has also been proposed for the intermediate formed during the $AlCl_3$-mediated rearrangement of 1-azidoadamantane.[15] It appears that the highly electrophilic metal sites prefer the alkylated nitrogen atom of the organo azide for bonding.

These results raise some interesting questions. Why do [HB-(3,5-$(CF_3)_2Pz)_3$]Cu and [HB(3,5-$(CF_3)_2Pz)_3$]Ag adducts of NNN(1-Ad) show different coordination modes? One possibility is that adverse steric interactions between the adamantyl and CF_3 groups force copper to coordinate via the N_T site. Alternatively, N_T may indeed be the preferred site of coordination for a copper(I) ion, possibly because π-back-bonding also plays a role. It is also interesting to compare [HB(3,5-$(CF_3)_2$-$Pz)_3$]CuNNN(1-Ad) with the copper(II) system **6**. Any number of factors such as the oxidation state of copper and the steric and/or electronic effects of the ligands may account for the different coordination mode in these two compounds. Furthermore, the coordination through the alkylated nitrogen of the azide in **6** is also most likely influenced by the formation of a six-membered metallacycle. On the other hand, N_A may be the preferred site for copper(II) ions even in the absence of chelate effects. In order to find answers to some of these questions, we have performed quantum mechanical calculations on several tris-(pyrazolyl)borato metal adducts.

The optimized geometrical parameters at the AE level for [HB$(Pz)_3$]Cu(HN_3) and [HB$(Pz)_3$]Cu(CH_3N_3) are given in Table 5. The computed [HB$(Pz)_3$]CuNNNH structure compared reasonably well with the experimental structure (which contains CF_3-substituted pyrazolyl rings and an adamantyl group on the azide ligand). The largest error in bond distances was 0.032 Å, and the largest bond angle error was 5.8°. In agreement with the crystal structure of the fully substituted systems, [HB$(Pz)_3$]-CuNNNH was found to be more stable than [HB$(Pz)_3$]CuN-(H)NN (ΔE = 0.6 kcal/mol). Thus, the intrinsic metal-ion affinities of the two coordinating sites of the HNNN ligand are nearly identical. The substituent effect of an alkyl group on the azide ligand was assessed with the model [HB$(Pz)_3$]Cu(CH_3N_3).

Table 5. Selected Geometrical Parameters[a]

[HB(Pz)$_3$]CuN(H)NN and [HB(Pz)$_3$]CuN(CH$_3$)NN

	(N(H)NN)	(N(CH$_3$)NN)
Cu−N$_A$	2.016	2.030
N$_A$−N	1.252	1.247
N−N$_T$	1.137	1.141
N−N$_A$−R	110.8	114.8
N$_A$−N−N$_T$	172.5	174.9
Cu−N$_A$−N	126.2	121.3
Cu−N$_{Tp}$	2.106; 2.109	2.073; 2.130

[HB(Pz)$_3$]CuNNNH and [HB(Pz)$_3$]CuNNNCH$_3$

	(NNNH)	(NNNCH$_3$)	exptl[b]
Cu−N$_T$	1.893	1.898	1.861
N$_T$−N	1.144	1.148	1.136
N−N$_A$	1.242	1.230	1.219
N−N$_A$−R	110.3	110.3	116.1
N$_T$−N−N$_A$	168.9	171.0	173.1
Cu−N$_T$−N	175.8	178.8	173.8
Cu−N$_{Tp}$	2.070; 2.123	2.074; 2.122	2.051; 2.092

[a] Å and deg, calculated at the AE B3LYP level, N$_{Tp}$ = N of tris(pyrazolyl)borate ligand. [b] Experimental data taken from crystal structure of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]CuNNN(1-Ad).

Table 6. Selected Geometrical Parameters[a]

[HB(Pz)$_3$]Ag(N(H)NN) (**C**), [HB(Pz)$_3$]Ag(N(CH$_3$)NN) (**D**), and [HB(3-(CF$_3$)Pz)$_3$]Ag(N(H)NN) (**E**)

	C	**D**	**E**	exptl[b]
Ag−N$_A$	2.384	2.395	2.367	2.220
N$_A$−N	1.248	1.243	1.241	1.227
N−N$_T$	1.135	1.139	1.139	1.143
Ag−N$_{Tp}$	2.380; 2.407	2.374; 2.415	2.431; 2.455	2.343; 2.403
N−N$_A$−R	110.9	115.3	115.8	112.1
N$_A$−N−N$_T$	172.6	174.5	175.2	176.8
Ag−N$_A$−N	128.3	123.1	120.7	118.2

[HB(Pz)$_3$]AgNNNH [F], [HB(Pz)$_3$]AgNNNCH$_3$ [G] and [HB(3-(CF$_3$)Pz)$_3$]AgNNNH [H]

	F	**G**	**H**
Ag−N$_T$	2.365	2.350	2.336
N$_T$−N	1.140	1.145	1.146
N−N$_A$	1.234	1.233	1.220
Ag−N$_{Tp}$	2.377; 2.395	2.385; 2.398	2.410; 2.493
N−N$_A$−R	111.3	117.8	118.3
N$_T$−N−N$_A$	171.1	172.8	172.1
Ag−N$_T$−N	179.2	173.9	151.0

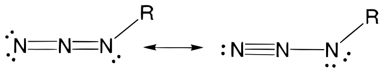
[a] Å and deg, calculated at the AE B3LYP level, N$_{Tp}$ = N of tris(pyrazolyl)borate ligand. [b] Experimental data taken from crystal structure of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgN(1-Ad)NN.

Inspection of Table 5 shows that the optimized structures for both isomers of [HB(Pz)$_3$]Cu(CH$_3$N$_3$) closely resemble those of [HB(Pz)$_3$]Cu(HN$_3$), especially with respect to the bond distances. The alkyl-substituted azide has almost no effect on the relative stability of the two isomers of the copper system (ΔE = 0.5 kcal/mol, compared to ΔE = 0.6 kcal/mol for the two unsubstituted isomers). We did not investigate the electronic effects of the CF$_3$ substituents in this system, although we will show below that they have a negligible effect on the energetics of the corresponding silver system.

Steric effects of the adamantyl group could also play a role in the copper system. The adamantyl group is relatively close to the CF$_3$-substituted pyrazolyl rings. To investigate these effects, we optimized [HB(3-(CF$_3$)Pz)$_3$]CuN(1-Ad)NN and [HB(3-(CF$_3$)Pz)$_3$]CuNNN(1-Ad) at the PM3 level. We find a closest nonbonded interaction of 2.37 Å between a hydrogen on the adamantyl group and a CF$_3$ fluorine on the pyrazolyl ring of the former species. No significant steric interactions should be present at that distance. However, single point B3LYP level calculations at the PM3 optimized geometries using the Wachters−Hay basis set on copper and the 3-21G basis set on the ligands yielded a ΔE of 4.3 kcal/mol for the fully substituted system favoring binding through N$_T$. This compares to a calculated value of 3.9 kcal/mol at the same theoretical level when the CF$_3$ groups are replaced with H and the adamantyl is replaced with CH$_3$. Therefore, we estimate steric effects at about 0.4 kcal/mol, roughly the same as electronic effects (and in the same direction favoring Cu−N$_T$ bonding). These steric effects will obviously be much less in the silver system.

The study of the silver−azide system was divided into two parts. In the first part we investigated the effects of various substituents by considering models of different sizes as describe above. The findings of this investigation are tabulated in Table 6. In general, the computed silver−azide distances for the various models described above were not satisfactory compared to the experiment. The silver−azide distance was consistently predicted to be 0.15−0.17 Å longer than the experimentally observed value. This is also true for the Ag−N distances for the nitrogens in the pyrazolyl rings (compare, for example, these distances for **E** in Table 6 with the experimental values). All models predicted the AgN(R)NN system to be more stable by 2−3 kcal/mol, again in agreement with the experimental observations. As we will see below, the use of relativistic effective core potentials leads to much more accurate geometries for the silver system, but has little effect on the calculated energetics. The completely unsubstituted model yielded a ΔE of 2.7 kcal/mol (where $\Delta E = E(\mathrm{Ag{-}N_T}) - E(\mathrm{Ag{-}N_A})$), while methyl substitution on the azide decreased the ΔE slightly to 2.1 kcal/mol, and CF$_3$ substitution on the pyrazolyl ring 3-positions resulted in a ΔE of 2.4 kcal/mol. Clearly, electronic substituent effects, whether on the pyrazolyl rings or the azide, cannot account for the structural differences seen in these two systems.

The intrinsic basicity of the terminal and alkylated nitrogens on the azide ligand favors N$_A$. For instance, at the G2[42] level we find that the proton affinity at the N$_A$ site with R = H is 22.0 kcal/mol greater than at the terminal N$_T$ site. This trend also applies to metals, but to a much lesser degree. We have calculated the relative sodium ion affinity for the two nitrogen sites (again with R = H) at the G2 level and find that the N$_A$ site is favored, but only by 1.6 kcal/mol. This result closely parallels our DFT results for the silver system, and we attribute the binding of silver through N$_A$ to be due to the greater basicity of this site. The basicity of this site may be understood from the perspective of the resonance structures as reflected in the molecular structure and a natural bond orbital (NBO) analysis.[43] Two obvious resonance structures are possible:



a **b**

At the AE B3LYP level, the N$_T$−N distance is 1.14 Å, while the N−N$_A$ distance is 1.24 Å and the H−N$_A$−N angle is 110.0°. These parameters compare reasonably well to the experimental values,[1,44] which are 1.13 Å (N$_T$−N), 1.24 Å (N−N$_A$), and 114° (H−N−N). The molecular structure therefore is consistent with **b** being the dominant resonance form. The NBO analysis is

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(42) Curtis, L. A.; Rajhavachan, K. R.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.
(43) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(44) Winnewisser, M.; Cook, R. L. *J. Chem. Phys.* **1964**, *41*, 999.

also consistent with **b**. For instance, the natural charges on N_T and N_A are $-0.05e^-$ and $-0.54e^-$, respectively, and the natural bond orbitals also correspond to **b**, with three N_T-N and one $N-N_A$ NBOs. Structure **b**, with a formal charge of -1 and an alkyl substituent on N_A, would clearly be expected to be more basic, and should be the preferred site of metal binding in the absence of more subtle effects.

Why then does the copper system bind through N_T? While both metals are formally in the +1 oxidation state with a d^{10} electronic configuration, as expected there is somewhat more back-bonding in the copper system. This is manifested by the calculated total d orbital populations, which are $7.95e^-$ (Cu) and $8.35e^-$ (Ag) for the species bound through N_A. Back-bonding is enhanced when the azide ligand binds through N_T. For binding through the terminal nitrogen, the corresponding d orbital populations are $7.89e^-$ (Cu) and $8.33e^-$ (Ag). Thus, there is a $0.06e^-$ drop in the total d orbital population upon going from N_A to N_T binding in the copper species, while the corresponding drop for the silver system is $0.02e^-$. This corresponds to enhanced back-bonding for the copper system bound through N_T and stabilizes this species. While the changes in d orbital populations are small, the corresponding energetic effects are also small (on the order of 3 kcal/mol). The greater d orbital depopulation in the copper system when the azide ligand is bound through N_T can also be correlated with the group charges of the NNNH moiety, which are $-0.07e^-$ (Cu system) and $+0.05e^-$ (Ag system). Further evidence for enhanced back-bonding in $[HB(Pz)_3]CuNNNH$ relative to $[HB(Pz)_3]CuN(H)NN$ comes from the calculated N_T-N stretching frequencies (calculated at the SDD RECP level), which are 2145 cm^{-1} for the CuNNNH isomer and 2161 cm^{-1} for the AgNNNH isomer. Frequency calculations were done on a smaller model, in which the carbons of the pyrazolyl rings were omitted and the nitrogen dangling bonds were terminated with hydrogen, i.e., $[HB(NN(H))_3]M(N_3H)$ (Figure 2). This model yields geometries and energies which are very similar to the those of the model with pyrazolyl rings. The calculated relative energies at the AE B3LYP level for this model are 0.4 kcal/mol for the copper system (favoring N_T) and 2.4 kcal/mol for the silver system (favoring N_A).

Finally, we have also calculated the relative binding energies of the N_T and N_A sites of NNNH to $[HB(Pz)_3]Cu^+$, in which copper is in the +2 oxidation state. We find that, for Cu(II), the N_A site is favored by 5.0 kcal/mol. Clearly, when copper assumes a higher oxidation state, back-bonding is suppressed and Cu(II) behaves more like Ag(I) and Na(I), which exhibit little (Ag(I)) or no (Na(I)) π-donating ability. It is reasonable to assume that if back-bonding effects are important in the Cu(I) system, they should be even more important in the hypothetical $\{[HB(Pz)_3]Ni(N_3H)\}^-$ system, in which nickel is in the zero oxidation state. We have used the model $\{[HB(NN(H))_3]Ni(N_3H)\}^-$ to estimate the effects of substituting Ni(0) for Cu(I). We find that the ΔE for this species is 22 kcal/mol, favoring binding through N_T. The species bound through N_T exhibits a bent azide ligand with $Ni-N_T = 1.77$ Å, $N_T-N = 1.20$ Å, $N-N_A = 1.31$ Å, and $N_T-N-N_A = 133°$. The species bound through N_A has a nearly linear azide ligand, with $Ni-N_A = 1.98$ Å, $N_A-N = 1.26$ Å, $N-N_T = 1.16$ Å, and $N_T-N-N_A = 167°$.

The second part of the study on the silver system addresses the large error in the calculated silver−azide bond length. Test calculations using four different RECPs were performed on both isomers of $[HB(Pz)_3]Ag(HN_3)$ (Table 7). As expected, description of the silver atom with a RECP produces a shorter $Ag-N_A$ bond compared to the structure obtained with the AE basis set. However, the choice of RECP significantly affects the accuracy of the $Ag-N_A$ bond length. The SDD RECP predicts a smallest error (0.070 Å) in the $Ag-N_A$ bond. In spite of the poor distances calculated with the AE basis set, the energetics seems to be largely unaffected. For the completely unsubstituted silver system, the SDD RECP calculations predict a ΔE of 2.7 kcal/mol, favoring binding through the nitrogen carrying the substituent. This is exactly the same value obtained with the AE basis set.

Table 7

Selected Geometrical Parameters for $[HB(Pz)_3]Ag(HN_3)$ Obtained from SDD RECP Calculations[a]

	isomer 1 (N(H)NN)		isomer 2 (NNNH)
	exptl	computed	computed
$Ag-N_A/Ag-N_T$	2.220	2.290	2.224
N_A-N	1.227	1.250	1.235
N_T-N	1.143	1.135	1.141
$Ag-N_{Tp}$	2.343; 2.403	2.321; 2.379	2.324; 2.353
$N-N_A-R$	112.1	111.1	111.1
N_A-N-N_T	176.8	172.5	170.6
$Ag-N_A-N/Ag-N_T-N$	118.2	127.7	174.8
ΔE(B3LYP/AE+SDD)		0.0	2.7 kcal/mol

Ag−Ligand Distances for $[HB(Pz)_3]AgN(H)NN$ Obtained from Various (AE+RECP) Calculations

	$Ag-N_A$	$Ag-N_{Tp}$
CEP	2.322	2.33; 2.391
LANL2DZ	2.337	2.347; 2.375
CRENBL	2.300	2.324; 2.389

[a] Å and deg, N_{Tp} = N of tris(pyrazolyl)borate ligand, RECP on Ag only.

Conclusion

With the aid of the highly fluorinated tris(pyrazolyl)borate $[HB(3,5-(CF_3)_2Pz)_3]^-$ ligand, the copper(I) and silver(I) complexes of 1-azidoadamantane can be isolated as thermally stable solids. Solid state structures show two different bonding modes. Theoretical calculations indicate that, in the absence of back-bonding, the azide ligand prefers, if only slightly, binding through the more basic N_A site. This is what is observed in the silver(I) adduct $[HB(3,5-(CF_3)_2Pz)_3]AgN(1-Ad)NN$. Calculations also predict that Na(I) and Cu(II) ions would prefer the N_A site. Copper(I) exhibits enough π-donating ability to favor binding through the terminal nitrogen. $[HB(3,5-(CF_3)_2Pz)_3]CuNNN(1-Ad)$ shows this type of interaction. Remarkably, steric effects are not dominant in determining the binding preferences of NNN(1-Ad) to the $[HB(3-(CF_3)Pz)_3]Cu$ moiety. This should also be applicable for the related $[HB(3,5-(CF_3)_2Pz)_3]Cu$ system.[25] $[HB(3,5-(CF_3)_2Pz)_3]CuNNN(1-Ad)$ and $[HB(3,5-(CF_3)_2Pz)_3]AgN(1-Ad)NN$ are rare examples of organoazido metal complexes. We are currently exploring the chemistry of these systems.

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Supporting Information Available: Tables of Cartesian coordinates and total energies for the optimized structures and an X-ray crystallography file in CIF format for the structure determination of $[HB(3,5-(CF_3)_2Pz)_3]CuNNN(1-Ad)$ and $[HB(3,5-(CF_3)_2Pz)_3]AgN(1-Ad)NN$. This material is available free of charge via the Internet at http://pubs.acs.org.

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