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Syntheses and Characterization of Cationic (Tris(pyrazolyl)methane)silver(I) Complexes. Solid-State Structures of $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}(O_3SCF_3)$, $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$, and $\{[HC(3\text{-}Bu^tpz)_3]Ag(CNBu^t)\}(O_3SCF_3)$

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Reaction of $Ag(O_3SCF_3)$ with 2 equiv of $HC(3,5\text{-}Me_2pz)_3$ in thf provides the stable six-coordinate "sandwich" complex $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}(O_3SCF_3)$. The solid-state structure shows that the coordination geometry about the silver is a trigonally distorted octahedron. Substantial tilting of the pyrazolyl rings away from alignment with the metal is observed in this six-coordinate complex, with the average AgN−NC torsion angles of the rings = 137°. Reaction of equimolar amounts of $Ag(O_3SCF_3)$ and $HC(3\text{-}Bu^tpz)_3$ yields $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$. Addition of 1 molar equiv of Bu^tNC to a CH_2Cl_2 solution of $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$ yields $\{[HC(3\text{-}Bu^tpz)_3]Ag(CNBu^t)\}(O_3SCF_3)$. The solid-state structures of both cations are very similar and show pseudotetrahedral geometry about silver. An oxygen atom from the triflate group provides the fourth donor atom in the structure of $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$.

Introduction

We have initiated an investigation into the coordination chemistry of the neutral tris(pyrazolyl)methane ligands with a variety of post-transition and transition metals.[1] An objective in this research is to demonstrate the ability of these ligands to control the coordination chemistry of various metals through careful choice of substituents on the ligands. As part of this study, we have reported the syntheses of stable copper(I) carbonyls[1c] using the ligand $HC(3,5\text{-}Me_2pz)_3$[2] and the bulky "second generation" ligands $HC(3\text{-}Phpz)_3$[3] and $HC(3\text{-}Bu^tpz)_3$.[4] The chemistry of silver(I) with these ligands is unexplored. Bruce has prepared a variety of silver(I) complexes employing anionic poly(pyrazolyl)borate ligands,[5] and very recently Dias reported the isolation and structural characterization of rare silver(I) carbonyl and silver(I) isonitrile complexes employing the highly fluorinated tris(pyrazolyl)borate ligand $[HB(3,5\text{-}(CF_3)_2pz)_3]^-$.[6] Lobbia has reported the synthesis of $\{[Me_2C(pz)_2]_2Ag\}(ClO_4)$, a tetrahedral four-coordinate complex of a bis(pyrazolyl)methane ligand,[7a] and silver(I) complexes using the $HC(pz)_3$ ligand, complexes with limited solubility.[7b] Presented here are the results of a study on silver(I) with the tris(pyrazolyl)methane ligands $HC(3,5\text{-}Me_2pz)_3$ and $HC(3\text{-}Bu^tpz)_3$. The syntheses and solid-state structures of $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}(O_3SCF_3)$, $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$, and $\{[HC(3\text{-}Bu^tpz)_3]Ag(CNBu^t)\}(O_3SCF_3)$ are reported, as well as efforts to prepare a carbonyl complex.

Experimental Section

General Procedures. All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. ^1H and ^{13}C NMR chemical shifts are reported in ppm versus TMS. Silver(I) trifluoromethanesulfonate was purchased from Strem Chemicals. *tert*-Butyl isocyanide was purchased from Aldrich Chemicals. $HC(3,5\text{-}Me_2pz)_3$[2] and $HC(3\text{-}Bu^tpz)_3$[4] were prepared according to literature procedures. Elemental analyses were performed by National Chemical Consulting, Inc.

$\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}(O_3SCF_3)$ (1). A thf (5 mL) solution of $Ag(O_3SCF_3)$ (0.26 g; 1.0 mmol) was treated dropwise with a thf (15 mL) solution of $HC(3,5\text{-}Me_2pz)_3$ (0.60 g; 2.0 mmol). A white solid began to precipitate during the addition. After being stirred overnight, the reaction mixture was filtered and the remaining white solid was washed with hexanes (3 × 5 mL). This solid was dried under vacuum (0.68 g; 0.80 mmol; 79%), mp = 334−336 °C. ^1H NMR (acetone-d_6, δ): 8.23 (s; 2;

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[2] (a) Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118. (b) Julia, S.; del Mazo, J.; Avila, L.; Elguero, J. *Org. Prep. Procedures Int.* **1984**, *16* (5), 299.

[3] This ligand has been prepared by D. L. Jameson and R. K. Castellano, Gettysburg College, personal communication: Jameson, D. L.; Castellano, R. K. *Inorg. Synth.*, submitted for publication.

[4] This ligand has been prepared by D.L.R. and J.E.C. in a collaborative effort with D. L. Jameson and R. K. Castellano, personal communication: Reger, D. L.; Collins, J. E.; Jameson, D. L.; Castellano, R. K. *Inorg. Synth.*, submitted for publication.

[5] (a) Bruce, M. I.; Walsh, J. D. *Aust. J. Chem.* **1979**, *32*, 2753. (b) Abu Salah, O. M.; Ashby, G. S.; Bruce, M. I.; Pederzolli, E. A.; Walsh, J. D. *Aust. J. Chem.* **1979**, *32*, 1613.

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Table 1. Crystallographic Data for the Structural Analyses of {[HC(3,5-$\mathrm{Me_2pz)_3]_2Ag\}(O_3SCF_3)}$ (1), {[HC(3-Bu^tpz)$_3$]Ag}($\mathrm{O_3SCF_3}$) (2), and {[HC(3-Bu^tpz)$_3$]Ag(CNBu^t)}($\mathrm{O_3SCF_3}$) (3)

	1	2	3
formula	$\mathrm{C_{33}H_{44}AgF_3N_{12}O_3S}$	$\mathrm{C_{23}H_{34}AgF_3N_6O_3S}$	$\mathrm{C_{28}H_{43}AgF_3N_7O_3S}$
fw	853.73	639.48	722.62
space group	$P2_1/c$	$P2_1/n$	$Pna2_1$
a, Å	9.152(2)	9.953(12)	20.091(2)
b, Å	12.968(7)	16.769(4)	16.882(2)
c, Å	16.312(2)	17.044(12)	10.631(1)
β, deg	90.41(2)	91.93(7)	
V, Å^3	1936(1)	2843(4)	3605.8(5)
Z	2	4	4
cryst color	colorless block	colorless block	colorless block
D(calc), g cm^{-3}	1.465	1.494	1.331
μ(Mo Kα), cm^{-1}	6.39	8.3	6.69
temp, K	298	293	298
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
$R(F)$,[a] R(wF),[b] R(wF^2),[c] %	6.05, -, 12.75	5.6, 6.5, -	4.48, -, 8.79

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

*H*C($\mathrm{Me_2pz)_3}$); 6.09 (s; 6; 4-*H* pz); 2.50, 1.95 (s, s; 18, 18; $\mathrm{Me_2}$-pz). ^{13}C NMR (acetone-d_6, δ): 151.0 (3-*C* pz); 141.3 (5-*C* pz); 107.4 (4-*C* pz); 72.1 (H*C*($\mathrm{Me_2pz)_3}$); 13.9, 10.6 ($\mathrm{Me_2}$pz). The *C*F$_3$ carbon atom resonance was not detected. Accurate FAB high resolution mass spectrum for {[HC(3,5-$\mathrm{Me_2pz)_3]_2Ag\}^+}$ (m/z): calcd for $\mathrm{C_{32}H_{44}{}^{107}AgN_{12}}$, 703.2863; found, 703.2827. Crystals suitable for an X-ray structural analysis and the analytical sample were grown by slow diffusion of hexanes into a saturated $\mathrm{CH_2Cl_2}$ solution. Anal. Calcd for $\mathrm{C_{33}H_{44}AgF_3N_{12}O_3S}$: C, 46.43; H, 5.19. Found: C, 46.53; H, 5.18.

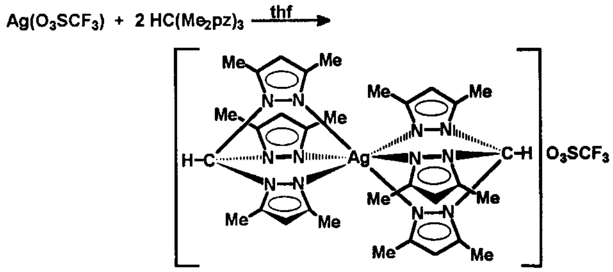
{[HC(3-Bu^tpz)$_3$]Ag}($\mathrm{O_3SCF_3}$) (2). A $\mathrm{CH_2Cl_2}$ (6 mL) suspension of Ag($\mathrm{O_3SCF_3}$) (0.125 g; 0.486 mmol) was treated with a $\mathrm{CH_2Cl_2}$ (4 mL) solution of HC(3-Bu^tpz)$_3$ (0.190 g; 0.49 mmol) by slow cannula transfer. The mixture was allowed to stir 2 h in the dark. Hexanes (20 mL) were added, and the mixture was cooled at −20 °C for 3 h and then filtered. The remaining white solid was dried under vacuum (0.164 g; 0.254 mmol; 52%) and stored in the dark, mp = 238−252 °C. ^{1}H NMR (acetone-d_6, δ): 9.31 (s; 1; *H*C(3-Bu^tpz)$_3$); 8.24 (d, 3, $J_{\mathrm{HH}} = 2.6$ Hz; 5-*H* pz); 6.43 (d, 3, $J_{\mathrm{HH}} = 2.6$ Hz; 4-*H* pz); 1.40 (s; 27; C(C*H*$_3$)$_3$). ^{13}C NMR (acetone-d_6, δ): 164.6 (s; 3-*C* pz); 133.0, 103.5 (s, s; 4,5-*C*'s pz); 77.8 (s; H*C*(3-Bu^tpz)$_3$); 31.7 (s; *C*(CH$_3$)$_3$); 29.7 (s; C(*C*H$_3$)$_3$). The *C*F$_3$ carbon atom resonance was not detected. Accurate FAB high resolution mass spectrum for {[HC(3-Bu^tpz)$_3$]Ag}$^+$ (m/z): calcd for $\mathrm{C_{22}H_{34}{}^{107}AgN_6}$, 489.1896; found, 489.1879. Crystals suitable for an X-ray structure and the analytical sample were grown by slow diffusion of hexanes into a saturated $\mathrm{CH_2Cl_2}$ solution. Anal. Calcd for $\mathrm{C_{23}H_{34}AgF_3N_6O_3S}$: C, 43.20; H, 5.36; N, 13.14. Found: C, 43.03; H, 5.32; N, 13.42.

{[HC(3-Bu^tpz)$_3$]Ag(CNBu^t)}($\mathrm{O_3SCF_3}$) (3). A $\mathrm{CH_2Cl_2}$ (8 mL) suspension of Ag($\mathrm{O_3SCF_3}$) (0.26 g; 1.0 mmol) was treated with a $\mathrm{CH_2Cl_2}$ (7 mL) solution of HC(3-Bu^tpz)$_3$ (0.38 g; 1.0 mmol) by slow cannula transfer. The solution became homogeneous and was allowed to stir 30 min in the dark before addition of Bu^tNC (8.3 mL of a 0.01 g/mL hexane solution; 1.0 mmol). The reaction mixture was allowed to stir overnight. $\mathrm{CH_2Cl_2}$ was removed under vacuum, and the remaining pale yellow solid was washed with hexanes prior to drying under vacuum. The solid was stored in the dark, mp = 148-153 °C (0.56 g; 0.77 mmol; 76%). ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 9.3 (s; 1; *H*C(3-Bu^tpz)$_3$); 8.22 (br; 3; 5-*H* pz); 6.12 (d, $J_{\mathrm{HH}} = 3$ Hz; 3; 4-*H* pz); 1.61 (s; 9; CNC(C*H*$_3$)$_3$); 1.35 (s; 27; C(C*H*$_3$)$_3$). ^{13}C NMR ($\mathrm{CDCl_3}$, δ): 163.8 (s; 3-*C* pz); 133.2, 103.3 (s, s; 4,5-*C*'s pz); 76.9 (s; H*C*(3-Bu^tpz)$_3$); 32.0 (s; *C*(CH$_3$)$_3$); 30.4 (s; C(*C*H$_3$)$_3$ pz); 30.2 (s; CNC(*C*H$_3$)$_3$). The *C*N and *C*F$_3$ carbon atom resonances were not detected. IR spectrum (Nujol mull; cm^{-1}): 2202 (CN). Accurate FAB high resolution mass spectrum for {[HC(3-Bu^tpz)$_3$]Ag(CNBu^t)}$^+$ (m/z): calcd for $\mathrm{C_{27}H_{43}{}^{107}AgN_7}$, 572.2631; found, 572.2614. Crystals suitable for an X-ray structural analysis and the analytical sample were grown by slow diffusion of hexanes into a saturated $\mathrm{CH_2Cl_2}$ solution. Anal. Calcd for $\mathrm{C_{28}H_{43}AgF_3N_7O_3S}$: C, 46.54; H, 6.00; N, 13.57. Found: C, 46.65; H, 5.87; N, 13.69.

Crystallographic Studies. Crystal, data collection, and refinement parameters are given in Table 1. The systematic absences in the diffraction data are uniquely consistent with $P2_1/c$ for {[HC(3,5-$\mathrm{Me_2pz)_3]_2Ag\}(O_3SCF_3)}$ (**1**), consistent with $P2_1/n$ for {[HC(3-Bu^tpz)$_3$]Ag}($\mathrm{O_3SCF_3}$) (**2**), and consistent with either $Pna2_1$ or $Pnma$ for {[HC(3-Bu^tpz)$_3$]Ag(CNBu^t)}($\mathrm{O_3SCF_3}$) (**3**). The absence of a molecular mirror plane in **3** suggested the noncentrosymmetric space group which resulted in chemically reasonable and computationally stable results of refinement. The structures of **1** and **3** were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. The structure of **2** was solved by the Patterson heavy atom method, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semi-empirical absorption corrections were applied to **3** but were not required for **1** or **2** because of less than 10% variation in the integrated ψ-scan intensities. Lorentz and polarization corrections were applied to the data for **2**. The Flack parameter refined to −0.04(4) for **3** indicating that the correct absolute hand of the structure was determined. The non-hydrogen atoms on the CNBu^t ligand in **3** and the oxygen atoms on the triflate counterion in **2** were refined isotropically to conserve data. All other non-hydrogen atoms were refined with anisotropic displacement coefficients. Each ion in **1** was located on an inversion center. The triflate ion in **1** is end-for-end disordered through an inversion center with the sulfur and carbon atom pair modeled as a reduced-occupancy sulfur atom and the oxygen and fluorine atom pairs modeled as increased-occupancy oxygen atoms. Both disordered pairs were refined with occupancies reflecting 50/50 distribution. The oxygen and fluorine atoms in the triflate anion for the structure of **2** were disordered around the C−S axis. No attempts were made to model this disorder. Hydrogen atoms were treated as ideal factors for **1** and **3** are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI). The software and sources of the scattering factors for **2** are contained in the MolEN program library: an interactive structure solutions procedure (Enraf-Nonius, Delft, The Netherlands).

Results

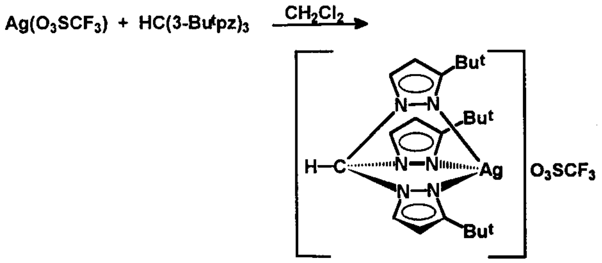
The reaction of Ag($\mathrm{O_3SCF_3}$) with 2 molar equiv of HC(3,5-$\mathrm{Me_2pz)_3}$ in thf results in the immediate precipitation of {[HC(3,5-$\mathrm{Me_2pz)_3]_2Ag\}(O_3SCF_3)}$ (eq 1). A product with a ligand to metal ratio of 1/1 could not be obtained using the HC(3,5-$\mathrm{Me_2pz)_3}$ ligand. The complex {[HC(3,5-$\mathrm{Me_2pz)_3]_2Ag\}(O_3SCF_3)}$ is slightly soluble in



(1)

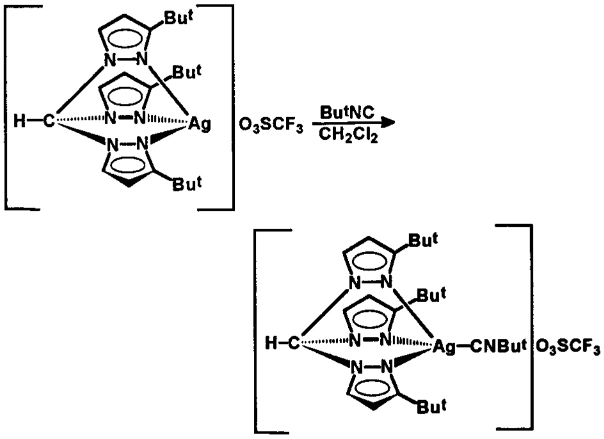
CH_2Cl_2 and acetone. It is air stable and melts at a high temperature.

A 1/1 ligand to metal product could be obtained with the bulky $HC(3\text{-}Bu^tpz)_3$ ligand. Addition of an equimolar amount of $HC(3\text{-}Bu^tpz)_3$ to a CH_2Cl_2 suspension of $Ag(O_3SCF_3)$ affords the complex $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$ (eq 2). As expected, a product with a ligand to metal ratio of 2/1 could not be obtained by addition of excess $HC(3\text{-}Bu^tpz)_3$. The bulky *tert*-butyl substituents in the 3-positions of the rings block the formation of these two ligand products.[8] These aliphatic substituents also enhance the solubility of $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$ in common polar organic and halogenated solvents. The complex $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$ is air stable, yet it is sensitive to light over extended periods.



(2)

The stable four-coordinate complex $\{[HC(3\text{-}Bu^tpz)_3]Ag(CNBu^t)\}(O_3SCF_3)$ was prepared upon addition of 1 molar equiv of *tert*-butyl isocyanide to a CH_2Cl_2 solution of $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$ (eq 3). This complex is highly soluble in common polar organic and halocarbon solvents. It is air stable yet decomposes slowly when exposed to light.



(3)

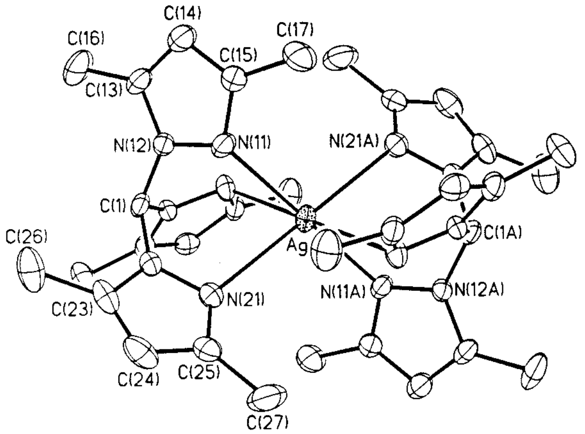


Figure 1. ORTEP diagram of $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}^+$.

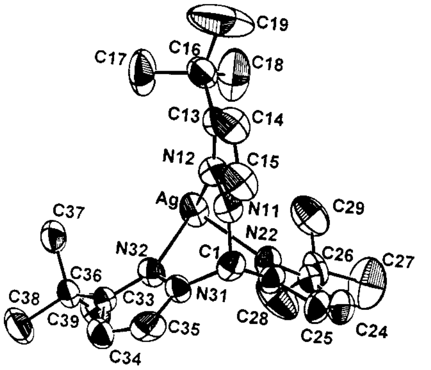


Figure 2. ORTEP diagram of $\{[HC(3\text{-}Bu^tpz)_3]Ag\}^+$.

Stirring a CH_2Cl_2 solution of $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$ under an atmosphere of carbon monoxide does not produce any indication of a CO complex. In contrast, under the same conditions $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(BF_4)$, prepared from mixing $AgBF_4$ and $HC(3\text{-}Bu^tpz)_3$ in CH_2Cl_2, leads to the formation of a carbon monoxide complex. Evidence supporting this claim is the observation of a new band in the IR spectrum of this solution at 2154 cm^{-1}, a band that is not observed in carbon monoxide saturated solutions that contain only $AgBF_4$. Also, a solid-state IR analysis (Nujol) of the solid formed by addition of hexane to the CO-saturated CH_2Cl_2 solution shows a CO stretching frequency at 2160 cm^{-1}. This solid readily loses carbon monoxide upon standing or when redissolved in CH_2Cl_2. Unfortunately, crystals suitable for an X-ray structural determination or an analytical sample could not be obtained due to this lability of the carbon monoxide ligand.

Solid State Structures of $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}(O_3SCF_3)$, $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$, and $\{[HC(3\text{-}Bu^tpz)_3]Ag(CNBu^t)\}(O_3SCF_3)$. ORTEP diagrams of the cations of each complex are provided in Figures 1–3, respectively. Crystallographic data are presented in Table 1. Selected bond distances and angles are given in Tables 2–4, respectively.

A six-coordinate trigonally distorted octahedral geometry about the silver(I) ion is observed in the structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}(O_3SCF_3)$. The intraligand Ag–N bond distances vary with two similar (2.461(7), 2.487(7) Å) and one longer (2.596(7) Å) distance (average = 2.51 Å). Small intraligand N–Ag–N bond angles (average = 77°) are observed with correspondingly larger interligand N–Ag–N bond angles (average = 103°). The two planes formed by the three nitrogen

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[8] (a) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507. (b) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (c) Parkins, G. *Adv. Inorg. Chem.* **1995**, *42*, 291. (d) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419.

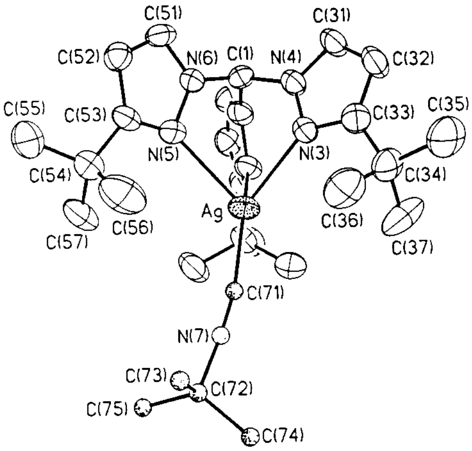

Figure 3. ORTEP diagram of {[HC(3-Bu^{t}pz)$_3$]Ag(CNBu^t)}$^+$.

Table 2. Selected Bond Distances and Angles for {[HC(3,5-Me$_2$pz)$_3$]$_2$Ag}(O$_3$SCF$_3$)

Bond Distances (Å)			
Ag−N(11)	2.461(7)	C(1)−N(12)	1.463(11)
Ag−N(21)	2.487(7)	C(1)−N(22)	1.425(9)
Ag−N(31)	2.596(7)	C(1)−N(32)	1.421(10)
Bond Angles (deg)			
N(11)−Ag−N(21)	75.6(2)	N(21)−Ag−N(31a)	101.4(2)
N(11)−Ag−N(31)	75.8(2)	N(12)−C(1)−N(22)	111.1(8)
N(21)−Ag−N(31)	78.6(2)	N(12)−C(1)−N(32)	111.7(6)
N(11)−Ag−N(21a)	104.4(2)	N(22)−C(1)−N(32)	112.5(9)
N(11)−Ag−N(31a)	104.2(2)		

Table 3. Selected Bond Distances and Angles for {[HC(3-Bu^{t}pz)$_3$]Ag}(O$_3$SCF$_3$)

Bond Distances (Å)			
Ag−N12	2.410(6)	C1−N11	1.44(1)
Ag−N22	2.394(7)	C1−N21	1.44(1)
Ag−N32	2.343(6)	C1−N31	1.45(1)
Bond Angles (deg)			
N12−Ag−N22	80.0(2)	N11−C1−N21	113.5(7)
N12−Ag−N32	80.0(2)	N11−C1−N31	112.8(7)
N22−Ag−N32	80.5(2)	N21−C1−N31	112.1(6)

Table 4. Selected Bond Distances and Angles for {[HC(3-Bu^{t}pz)$_3$]Ag(CNBu^t)}(O$_3$SCF$_3$)

Bond Distances (Å)			
Ag−N(1)	2.301(6)	C(1)−N(2)	1.437(8)
Ag−N(3)	2.361(5)	C(1)−N(4)	1.467(9)
Ag−N(5)	2.449(6)	C(1)−N(6)	1.438(10)
Ag−C(71)	2.053(7)	C(71)−N(7)	1.150(7)
Bond Angles (deg)			
N(1)−Ag−N(3)	81.1(2)	C(71)−N(7)−C(72)	175.6(6)
N(1)−Ag−N(5)	80.8(2)	Ag−C(71)−N(7)	168.2(6)
N(1)−Ag−C(71)	136.8(3)	N(2)−C(1)−N(4)	111.0(7)
N(3)−Ag−N(5)	80.2(2)	N(2)−C(1)−N(6)	115.0(8)
N(3)−Ag−C(71)	133.9(2)	N(4)−C(1)−N(6)	111.5(6)
N(5)−Ag−C(71)	123.0(2)		

donor atoms of each ligand are parallel, a consequence of the silver ion residing on a crystallographic center of inversion.

The pyrazole rings are significantly tilted with respect to the C_3 axis formed by the metal and the two methyne carbon atoms (a propeller-like distortion). Ideally, for maximum overlap with the lone pair on the donor nitrogen atoms the metal would lie in the plane of each pyrazole ring. Any deviation where the metal lies out of this planarity can be measured by the AgN(n1)-N(n2)C(n3) (where n denotes the ring number) torsion angle, an angle that is ideally 180° for these planar rings. These torsion angles range from 126.5 to 145.9° (average = 137°).

In the structure of [HC(3-Bu^{t}pz)$_3$]Ag}(O$_3$SCF$_3$), the coordination geometry about the silver atom is pseudotetrahedral. The three Ag−N bond distances vary in this structure from 2.343(6) to 2.410(6) Å (average = 2.38 Å). A bonding interaction exists with an oxygen atom from the triflate anion, yet the anion is disordered which precludes an accurate determination of the Ag−O bonding distance. Intraligand N−Ag−N bond angles are restrained by the chelate rings to an average of 80°. Tilting of the pyrazolyl rings in this structure is minimal (average AgN−NC torsion angle = 178°).

The silver atom in the structure of {[HC(3-Bu^{t}pz)$_3$]-Ag(CNBu^t)}(O$_3$SCF$_3$) is also four coordinate with a pseudotetrahedral geometry. The Ag−N bond distances vary greatly, 2.301(6)−2.449(6) Å, yet the average distance (2.37 Å) is comparable to that observed in the structure of {[HC(3-Bu^{t}pz)$_3$]Ag}(O$_3$SCF$_3$). Intraligand N−Ag−N bond angles are again restricted by the chelate rings to an average of 81°. The AgN−NC torsion angles range from 159.4 to 172.1° (average = 164.5°). The ring with the greatest tilting correlates to the longest Ag−N bond distance. The isonitrile ligand in this structure is slightly bent with a Ag−C(71)−N(7) bond angle of 168.2(6)° and a C(71)−N(7)−C(72) bond angle of 175.6(6)° and possesses a normal C≡N bond distance (1.150(7) Å).[9] The Ag−C(1) bond distance (2.053(7) Å) is very similar to the one recently reported in [HB(3,5-(CF$_3$)$_2$pz)$_3$]Ag(CNBu^t) (2.059(4) Å)[6] and those in other previously reported silver(I) isonitrile complexes.[10]

Discussion

Both four- and six-coordinate silver(I) complexes can be prepared by adjusting the steric bulk of the tris(pyrazolyl)methane ligand. The HC(3,5-Me$_2$pz)$_3$ ligand allows for the preparation of the six-coordinate silver(I) complex. It has not proven possible to prepare analogous complexes with poly(pyrazolyl)borate ligands. Bruce has shown that mainly oligomeric complexes with 1/1, ligand/silver, stoichiometry form in the reaction of silver(I) with the anionic polypyrazolylborate ligands [Ph$_2$B(pz)$_2$]$^-$, [HB(pz)$_3$]$^-$, [HB(3,5-Me$_2$pz)$_3$]$^-$, and [B(pz)$_4$]$^-$.[5]

While several silver(I) complexes with N$_6$ donor sets have been reported,[12] {[HC(3,5-Me$_2$pz)$_3$]$_2$Ag}(O$_3$SCF$_3$) represents only the second *mononuclear* complex in this family of "sandwich" compounds. Previously, Wieghardt[12a] has reported the complex [L$_2$Ag]PF$_6$ (L =

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1,4,7-trimethyl-1,4,7-triazacyclononane) where the silver resides in a pseudooctahedral environment. These two structures are closely related. The average Ag−N bonding distance in $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}(O_3SCF_3)$ (2.51 Å) is just slightly less than in the $[L_2Ag]PF_6$ structure (2.57 Å). Both structures possess small intraligand N−Ag−N bond angles that are restricted by the ligands and correspondingly larger interligand N−Ag−N bond angles.[12a] In light of the similarity between these two structures, an analogy can be drawn between the $HC(3,5\text{-}Me_2pz)_3$ and the more heavily studied 1,4,7-triazacyclononane ligands. Both are neutral tridentate N_3 donor ligands that facially coordinate to metal centers. Also, the steric properties of both ligands can be increased by substitution of appropriate alkyl groups in the ligands.[13]

The structures of $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}^+$ and its isoelectronic cadmium analog, $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$,[1b] are very similar. One notable difference is that the average Ag−N bond distance in $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}(O_3SCF_3)$ is 0.19 Å greater than the average Cd−N bond distance (2.32 Å) in $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$. This result is expected given that the difference in ionic radii between the two metal ions for six coordination is 0.20 Å.[14] Of interest is the fact that the tilting of the pyrazolyl rings in the structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}^+$ (137°) is only slightly greater than in $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$ (141°). In the structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}^+$,[1a] where the Tl−N bond distances are much longer (average 2.92 Å), a greater tilting (average torsion angle is 123°) was observed. This tilting was attributed to the large size of the metal in comparison to the intrinsic bite size of the ligand.[1a] Changing the M−N bond distance from 2.32 to 2.51 Å does not greatly change the tilting in the cadmium and silver structures.

As expected, the $HC(3\text{-}Bu^tpz)_3$ ligand supports the formation of tetrahedral complexes. The cationic isocyanide complex $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(CNBu^t)\}(O_3SCF_3)$ forms readily and is stable. Only one isocyanide complex of silver(I) supported by poly(pyrazolyl)borate ligands, $[HB(3,5\text{-}(CF_3)_2pz)_3]Ag(CNBu^t)$, has been previously structurally characterized.[6] The Ag−C and average Ag−N bond distances in $\{[HC(3\text{-}Bu^tpz)_3]Ag(CNBu^t)\}(O_3SCF_3)$ closely match those observed in $[HB(3,5\text{-}(CF_3)_2pz)_3]Ag(CNBu^t)$, in spite of the difference in charge between the two species and the change in pyrazolyl-ring substitution from a bulky electron-donating group to a small electron-withdrawing group. We have previously noted the structures of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$ and $\{[HB(3,5\text{-}Me_2pz)_3]_2Cd\}$ are very similar.[1b] The structures of complexes containing tris(pyrazolyl)borate and tris(pyrazolyl)methane ligands are similar because the tripodal arrangement of the pyrazolyl rings is the dominant controlling factor. The difference in the charge of the two ligands has a surprisingly small influence on the structures of analogous complexes.

The small influence of charge is also emphasized by the fact that neutral $[HB(3,5\text{-}(CF_3)_2pz)_3]Ag(CNBu^t)$ has a higher υ_{CN} at 2214 cm^{-1} than in cationic $\{[HC(3\text{-}Bu^tpz)_3]Ag(CNBu^t)\}^+$ at 2202 cm^{-1}. Both of these values are considerably higher than in free $CNBu^t$ (2138 cm^{-1}), indicating that the bonding is dominated by the σ-donation ability of the ligand. The electron-withdrawing ability of the fluorinated poly(pyrazolyl)borate ligand makes the silver a better Lewis acid in its complex than the positive charge on the tris(pyrazolyl)methane complex. Silver(I) carbonyl complexes are rare.[6,11]

Although it could not be isolated in pure form, the CO complex $\{[HC(3\text{-}Bu^tpz)_3]AgCO\}(BF_4)$ can be observed in solution and in the solid phase by IR spectroscopy. A similar CO complex could not be observed if the more strongly coordinating counterion $(O_3SCF_3)^-$ was present. The observed CO stretching frequency at 2160 cm^{-1} (solid) is lower than that reported for $[HB(3,5\text{-}(CF_3)_2pz)_3]AgCO$ of 2178 cm^{-1}.[6] The greater stability of $[HB(3,5\text{-}(CF_3)_2pz)_3]AgCO$ must be a result of the electron-withdrawing ability of the ligand, as noted above for the isonitrile complexes.

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Supporting Information Available: Tables of complete data collection information, bond distances and angles, anisotropic thermal parameters, and positional and *B* parameters (20 pages). Ordering information is given on any current masthead page.

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