Inorg. Chem. **2007**, *46*, 9708–9714

Inorganic Chemistry

Article

Small Scorpionate Ligands: Silver(I)-Organophosphane Complexes of 5-CF$_3$-Substituted Scorpionate Ligand Combining a B–H···Ag Coordination Motif

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Received May 29, 2007

The first 5-substituted trihydro(azolyl)borate system, the sodium trihydro(5-CF$_3$-pyrazol-1-yl)borate, Na[H$_3$B(5-(CF$_3$)-pz)], has been synthesized by the reaction of 3-trifuoromethyl-pyrazole with NaBH$_4$ in high yield. Na[H$_3$B(5-(CF$_3$)-pz)] reacts with AgNO$_3$ in the presence of monodentate tertiary phosphanes PR$_3$ (PR$_3$ = P(C$_6$H$_5$)$_3$, P(*p*-C$_6$H$_4$CH$_3$)$_3$, P(*m*-C$_6$H$_4$CH$_3$)$_3$, P(*o*-C$_6$H$_4$CH$_3$)$_3$, or PCH$_3$(C$_6$H$_5$)$_2$) to afford silver(I) bis(phosphane) adducts. These compounds have been characterized by elemental analyses, FTIR, ESI-MS, and multinuclear (^{1}H, ^{19}F, and ^{31}P) NMR spectroscopy. Solid-state structures of {[H$_3$B(5-(CF$_3$)pz)]Ag[P(C$_6$H$_5$)$_3$]$_2$} and {[H$_3$B(5-(CF$_3$)pz)]Ag[P(*p*-C$_6$H$_4$CH$_3$)$_3$]$_2$} are also reported. They feature κ^2-N,H-bonded trihydro(pyrazolyl)borate ligands and pseudo-tetrahedral silver atoms.

Introduction

Since the first report of Trofimenko,[1] poly(pyrazolyl)borates and related scorpionates[2] have been extensively employed as anionic σ-donor ligands in a variety of metal complexes, and they have found wide applications in coordination, organometallic, and bioinorganic chemistry.[3] A critical issue in the synthesis of poly(pyrazolyl)borate ligands obtained from pyrazoles whose anions are not of C_{2v} symmetry is the regiochemistry of the B−N bond formation. Usually, the larger substituents end up at the pyrazolyl ring 3-position (more distant from the boron center). This tendency is most pronounced when the size differences between the substituents at 3- and 5-positions are large. This regioselectivity was first demonstrated in the reaction of 3(5)-methylpyrazole, leading to [H$_2$B(3-(Me)pz)$_2$]$^-$ [4] and to [HB(3-(Me)pz)$_3$]$^-$ [5] as well as in the regiospecific synthesis of [HB(3-(Ph)pz)$_3$]$^-$ [6] and [HB(3-(Bu^t)pz)$_3$]$^-$.[7] A mixture containing 3,3,5-substituted tris(pyrazolyl)borates, where two substituents are at the 3-position and the other one is at the 5-position, is obtained when the steric differences between the pyrazolyl ring substituents in the 3- and in the 5-position are less substantial.[8] However, a few exceptions like the formation of [HB(3-(Mes)pz)$_2$(5-(Mes)pz)] ligand[9,10] or the rearrangement of a 3,3,3-substituted ligand during the formation of a metal adduct (e.g., octahedral [HB(3-(Pr^i)-pz)$_2$(5-(Pr^i)pz)]$_2$M)[11] are also known. The probable reason for 3,3,3-regioselectivity is that the B−N bond formation, involving a concerted loss of hydrogen, proceeds through a less sterically encumbered transition state, when bonding occurs to the less hindered nitrogen (Scheme 1, path b).

Electronic effects may also control the regiochemical course of the ligands' syntheses, with electron-withdrawing

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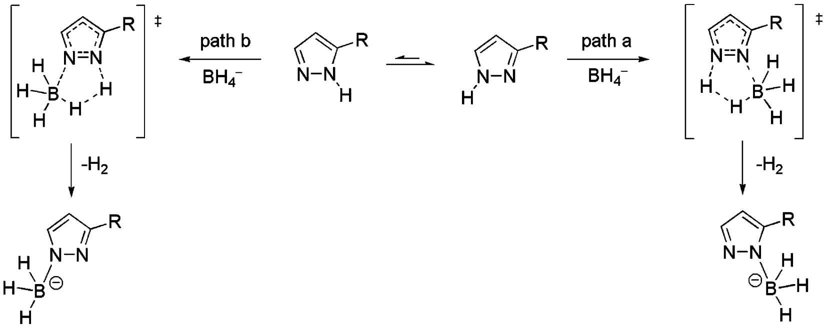
10.1021/ic701041k CCC: $37.00

Scheme 1



groups preferring the 3-position. This tendency is most clearly manifested in ligands like $[HB(3\text{-}(CF_3)\text{-}5\text{-}(Me)pz)_3]^-$[12] and $[HB(3\text{-}(CF_3)\text{-}5\text{-}(thionyl)pz)_3]^-$,[13] in which electronically quite different substituents are present. The syntheses of these ligands are highly regioselective with the more-electron-withdrawing CF_3 group residing exclusively in the 3-position of the final product. However, in these molecules, the steric factors may also contribute to the formation of the 3,3,3-isomer because the CF_3 is also the larger substituent. The electronic control is more clearly manifested when benzopyrazole (or indazole) and its derivatives containing alkyl or aryl substituents in the 3-, 4-, 5-, or 6-positions,[14,15] or 3-(Ar)-4,5-dibromopyrazoles[16] are used as azole precursors in the scorpionate ligand synthesis. They afford scorpionates in which the boron is bonded to the more-hindered nitrogen (Scheme 1, path a). This happens, presumably, because electronic effects outweigh steric ones. The preference of an electron-withdrawing group for the 3-position in tris(pyrazolyl)borate ligands can be explained via an argument analogous to that invoked to rationalize the equilibrium between the pyrazole tautomers $[3\text{-}(CF_3)pz]H$ and $[5\text{-}(CF_3)pz]H$. The inductive electron-withdrawing effect of the CF_3 group makes the distal nitrogen more basic, favoring the tautomer with the CF_3 group in the 3 position, $[3\text{-}(CF_3)pz]H$.[17]

It has been suggested that the B−N bond preference is kinetic in origin, the less-favored tautomer $[5\text{-}(CF_3)pz]H$ leading to the more-favorable transition state during the course of its reaction with BH_4^-. In view of the facility of borotropic rearrangements and the ease of pyrazole exchange processes under the thermolytic synthetic condition used, however, one must also consider that the isomeric preference is derived from the greater thermodynamic stability of the system when the boron binds to the more-basic nitrogen atom.[18] Under nonthermolytic conditions, we can suggest that the more-favored tautomer $[3\text{-}(CF_3)pz]H$ leads to the transition state with boron bonding to the less-basic nitrogen azole atom (Scheme 1, path a).

Despite the impressive chemistry based on bis-, tris-, and tetrakis-(azolyl)borates, no studies have been done on the syntheses of poly(pyrazolyl)borate systems under nonthermolytic conditions. In these conditions, the interplay of steric and electronic influence coupled with the kinetic B−N bond preference and the thermodynamic stability of the product seem to favor the 5-substituted pyrazolylborate $[H_3B(5\text{-}(CF_3)pz)]^-$. On this basis, we evaluated the possibility of preparing trihydro(pyrazolyl)borates, starting from 3-trifuoromethylpyrazole ($[3\text{-}(CF_3)pz]H$). This novel class of scorpionates, if acting as κ^3-H,H,N or κ^2-H,N chelators, will allow for the synthesis of complexes with new or uncommon coordinating features.

Unlike the common chelate tripodale κ^3-N′,N″,N‴ or bidentate κ^2-N,N′ coordination mode[2] (parts a and b of Figure 1), the κ^3-N,N′,H (part c of Figure 1)[19−21] bonding is somewhat rare among poly(pyrazolyl)borates. Recently, an unusual coordination mode (part d of Figure 1) for the bis(pyrazolyl)borate in $[H_2B(3,5\text{-}(CF_3)_2pz)_2]Cu(PPh_3)_2$,[22] that represents the first structurally characterized bis(pyrazolyl)borate compound showing the κ^2-H,N coordination mode, has also been reported. On the basis of the spectroscopic data, very similar coordination behavior has been suggested for $[H_2B(3,5\text{-}(CF_3)_2pz)_2]RuH(H_2)(PCy_3)_2$.[23] A tris(pyrazolyl)borate adduct ($[HB(4\text{-}Cl\text{-}3,5\text{-}(CH_3)_2pz)_3]Rh(CO)(PMePh_2)_2$) featuring rare κ^2-N,H coordination has also been reported.[24] The main reason for unusual modes of coordination in these poly(pyrazolyl)borate systems is believed to be steric in origin.[25] To our knowledge, only a limited number of complexes exhibiting the general κ^2-H,E or κ^3-H,H,E coordinating features are known (E = P),[26−29] but all of them are based on borane ligands. Santos and co-workers have

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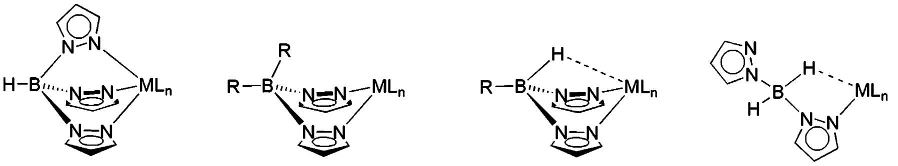
(a) κ^3-N',N'',N''' (b) κ^2-N',N'' (c) κ^3-N,N',H (d) κ^2-N,H

Figure 1. Examples of poly(pyrazolyl)borate coordination modes.

recently reported the synthesis of a new class of soft trihydro(mercaptoazolyl)borates able to coordinate to metals in κ^3-H,H,S fashion.[30] In this article, we report the synthesis of a mono(pyrazolyl)borate and its silver coordination chemistry. X-ray structures of $\{[H_3B(5\text{-}(CF_3)pz)]Ag[P(C_6H_5)_3]_2\}$ and $\{[H_3B(5\text{-}(CF_3)pz)]Ag[P(p\text{-}C_6H_4CH_3)_3]_2\}$ show uncommon κ^2-N,H poly(pyrazolyl)borate ligand coordination modes and rare Ag···HB contacts.

Experimental Section

Materials and General Methods. All of the syntheses and handling were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques or a glove box. All of the solvents were dried, degassed, and distilled prior to use. Elemental analyses (carbon, hydrogen, nitrogen, and sulfur) were performed in-house with a Fisons Instruments 1108 CHNS−O Elemental Analyser. Melting points were taken on an SMP3 Stuart Scientific Instrument. IR spectra were recorded from 4000 to 100 cm^{-1} with a PerkinElmer System 2000 FTIR instrument. IR annotations used: m = medium, mbr = medium broad, s = strong, sbr = strong broad, sh = shoulder, w = weak. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on an Oxford-400 Varian spectrometer (400.4 MHz for ^1H, 100.1 MHz for ^{13}C, 376.8 MHz for ^{19}F, and 162.1 MHz for ^{31}P). Chemical shifts, in ppm, for ^1H NMR spectra are relative to internal Me_4Si. ^{13}C NMR spectra were run with ^1H decoupling, and the chemical shifts are reported in ppm versus Me_4Si. ^{19}F NMR and ^{31}P NMR chemical shifts were referenced to an external $CFCl_3$ and an 85% H_3PO_4 standard, respectively. The ^{31}P NMR spectroscopic data were accumulated with ^1H decoupling. NMR annotations used: d = doublet, dd = double doublet, dbr = broad doublet, m = multiplet, m = broad multiplet, s = singlet, sbr = broad singlet, t = triplet. Electrospray mass spectra (ESI-MS) were obtained in the positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer, using an acetone mobile phase. The compounds were added to reagent grade methanol to give solutions of an approximate concentration of 0.1 mM. These solutions were injected (1 μL) into the spectrometer via a HPLC HP 1090 Series II fitted with an autosampler. The pump delivered the solutions to the mass spectrometer source at a flow rate of 300 $\mu L\ min^{-1}$, and nitrogen was employed both as a drying and nebulizing gas. Capillary voltages were typically 4000 and 3500 V for the positive- and negative-ion mode, respectively. Confirmation of all of the major species in this ESI-MS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter calculated using the *IsoPro 3.0* computer program.

Synthesis of the Ligand. Sodium trihydro(5-CF_3-pyrazol-1-yl)borate, $Na[H_3B(5\text{-}(CF_3)pz)]$ (1). To a mixture of sodium borohydride (0.760 g, 20.0 mmol) and 3-(trifluoromethyl)-1H-pyrazole (2.720 g, 20.0 mmol), 30 mL of THF were added, and the resulting suspension was stirred at room temperature. Release of H_2 was observed immediately after addition of the solvent. After 5 days of stirring at room temperature, ^1H NMR and ESI-MS analysis of one aliquot of the reaction mixture showed the complete consumption of the pyrazole and the nearly quantitative formation of the ligand. The solution was concentrated under a vacuum and treated with *n*-hexane (50 mL) to precipitate a microcrystalline white solid. It was filtered, purified by recrystallization from CH_2Cl_2/*n*-hexane (1:3), and dried at reduced pressure to yield ligand **1** in 87% yield. Mp. 80−82 °C. ^1H NMR (DMSO-d_6, 293K): δ 2.10 (qbr, 3H, ^1J(B,H) = 90 Hz, BH_3), 6.30 (d, 1H, 4-CH), 7.17 (d, 1H, 3-CH). ^1H NMR (Acetone, 293K): δ 2.32 (qbr, 3H, ^1J(B,H) = 89 Hz, BH_3), 6.34 (d, 1H, 4-CH), 7.24 (d, 1H, 3-CH). ^1H NMR (CD_3-OD, 293K): δ 2.38 (qbr, 3H, BH_3), 6.38 (d, 1H, 4-CH), 7.31 (d, 1H, 3-CH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 293K): δ 104.28 (s, 4-CH), 122.20 (q, ^1J(C,F) = 267.0 Hz, CF$_3$), 133.79 (q, ^2J(C,F) = 35.8 Hz, 5-CCF$_3$), 135.85 (s, 3-CH), ^{19}F NMR (DMSO-d_6, 293K): δ −57.45 (s). ^{19}F NMR (Acetone, 293K): δ −59.51 (s). IR (nujol, cm^{-1}): 3180m (CH); 2357sh, 2318m, 2271m (BH); 1529m (C=C + C=N); 660s, 636m, 627m, 553m, 535br, 463sbr, 434s, 382s, 324w, 282w, 270w, 256w, 236br. ESI-MS (major negative-ions, CH_3OH), *m*/*z* (%): 149 (100) $[H_3B(5\text{-}(CF_3)pz)]^-$. Anal. Calcd for $C_4H_5BF_3N_2Na$: C, 27.95; H, 2.93; N, 16.30. Found: C, 27.84; H, 3.02; N, 16.16.

Syntheses of Silver Complexes. $\{[H_3B(5\text{-}(CF_3)pz)]Ag[P(C_6H_5)_3]_2\}$ (2). To a methanol solution (20 mL) of $AgNO_3$ (0.085 g, 0.5 mmol), triphenylphosphine (0.262 g, 1.0 mmol) was added at room temperature and stirred for 12 h to give a colorless solution. A methanol solution (5 mL) of sodium trihydro(5-CF_3-pyrazol-1-yl)borate, $Na[H_3B(5\text{-}(CF_3)pz)]$ (0.86 g, 0.5 mmol) was added dropwise to the previous mixture. After addition, the reaction mixture was stirred for 2 h; the solution was filtered and concentrated under a vacuum. The resulting brown solid was filtered off and recrystallized from $CHCl_3$/*n*-hexane (1:2), to give **2** in 82% yield. Crude **2** was dissolved in $CHCl_3$/diethyl ether (1:2) solution and a single-crystal suitable for X-ray diffraction analysis was obtained. Mp. 135−137 °C. ^1H NMR (DMSO-d_6, 293K): δ 6.50 (d, 1H, 4-CH), 7.24−7.48 (m, 30H, C_6H_5), 7.50 (d, 1H, 3-CH). ^1H NMR ($CDCl_3$, 293K): δ 6.45 (d, 1H, 4-CH), 7.20−7.40 (m, 30H, C_6H_5), 7.65 (d, 1H, 3-CH). ^{19}F NMR (DMSO-d_6, 293K): δ −58.48 (s). ^{31}P NMR ($CDCl_3$, 293K): δ 8.25 (s). ^{31}P NMR ($CDCl_3$, 223K): δ 9.31 (d, $J(^{31}P\text{−}Ag)$ = 417 Hz). IR (nujol, cm^{-1}): 3190w (CH); 2371m, 2302m (BH); 1522m (C=C + C=N); 695s, 618m, 568w, 553m; 523m, 516sbr, 501s, 495s (PR_3); 458w, 445w, 420w, 398w, 376w, 352w, 325w, 303w, 280m, 254w, 247m, 227m, 202m. ESI-MS (major negative-ions, CH_3OH), *m*/*z* (%): 135 (10) $[5\text{-}(CF_3)pz]^-$, 149 (100) $[H_3B(5\text{-}(CF_3)pz)]^-$. ESI-MS (major positive-ions, CH_3OH), *m*/*z* (%): 632 (100) $\{Ag[P(C_6H_5)_3]_2\}^+$. Anal.

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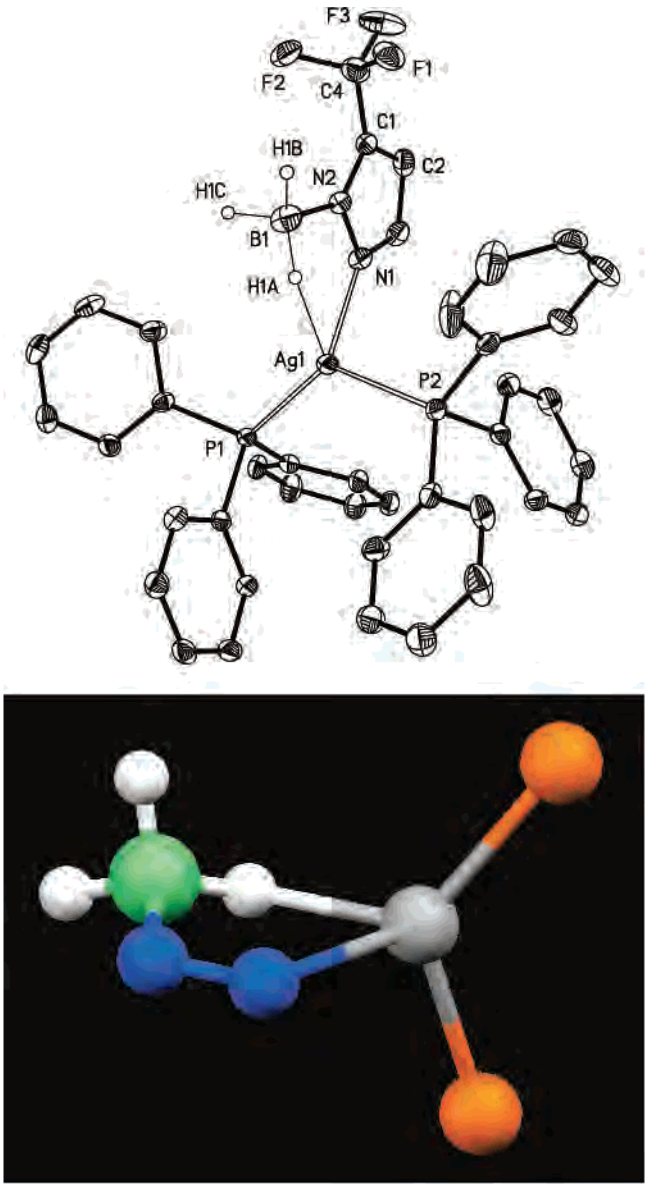


Figure 2. (a) (top) Basic structural unit of $\{[H_3B(5\text{-}(CF_3)pz)]Ag[P(C_6H_5)_3]_2\}$ (**2**) showing the atom numbering scheme at 35% probability level. All of the hydrogen atoms except those on boron have been omitted for clarity. Only one of the two molecules in the symmetric unit is shown here. (b) (bottom) A view of $\{[H_3B(5\text{-}(CF_3)pz)]Ag[P(C_6H_5)_3]_2\}$ showing coordination geometry at silver (only selected atoms are included). Selected bond distances (Å) and angles (°): Ag(1)−N(1) 2.335(3), Ag(1)−P(1) 2.4285(10), Ag(1)−P(2) 2.4736(10), Ag(1)−H(1A) 2.0336(3), Ag(2)−N(3) 2.312(3), Ag(2)−P(3) 2.4127(10), Ag(2)−P(4) 2.4553(10), Ag(2)−H(2A) 2.11(5), N(2)−B(1) 1.576(6), N(4)−B(2) 1.592(5); N(1)−Ag(1)−P(1) 116.54(8), N(1)−Ag(1)−P(2) 107.12(8), P(1)−Ag(1)−P(2) 125.26(3), N(1)−Ag(1)−H(1A) 69.67(8), P(1)−Ag(1)−H(1A) 123.56(3), P(2)−Ag(1)−H(1A) 101.04(3), N(3)−Ag(2)−P(3) 121.93(8), N(3)−Ag(2)−P(4) 106.58(8), P(3)−Ag(2)−P(4) 124.42(3), N(3)−Ag(2)−H(2A) 69.3(13), P(3)−Ag(2)−H(2A) 117.2(12), P(4)−Ag(2)−H(2A) 103.4(12).

Calcd for $C_{40}H_{35}AgBF_3N_2P_2$: C, 61.49; H, 4.52; N, 3.59. Found: C, 61.28; H, 4.44; N, 3.43.

$\{[H_3B(5\text{-}(CF_3)pz)]Ag[P(p\text{-}C_6H_4CH_3)_3]_2\}$ (3). **3** was prepared analogously to **2** using $AgNO_3$ (0.085 g, 0.5 mmol), tri(*p*-tolyl)phosphine, $P(p\text{-}C_6H_4CH_3)_3$ (0.304 g, 1.0 mmol), and $Na[H_3B(5\text{-}(CF_3)pz)]$ (0.86 g, 0.5 mmol). The product was recrystallized from diethyl ether/*n*-hexane (1:3), affording derivative **3** in 76% yield. Crude **3** was dissolved in CH_2Cl_2/*n*-hexane solution, and a single crystal suitable for X-ray diffraction analysis was obtained. Mp. 140−141 °C. ^{1}H NMR (DMSO-d_6, 293K): δ 2.29 (s, 18H, C*H*$_3$), 6.47 (d, 1H, 4-C*H*), 7.09−7.13 (m, 24H, C_6H_4), 7.33 (d, 1H, 3-C*H*). ^{1}H NMR ($CDCl_3$, 293K): δ 2.33 (s, 18H, C*H*$_3$), 6.45 (d, 1H, 4-C*H*), 7.06−7.25 (m, 24H, C_6H_4), 7.55 (d, 1H, 3-C*H*). ^{19}F NMR (DMSO-d_6, 293K): δ −58.40 (s). ^{31}P NMR (DMSO-d_6, 293K): δ 6.31 (s). ^{31}P NMR ($CDCl_3$, 293K): δ 6.66 (s). ^{31}P NMR ($CDCl_3$, 223K): δ 7.17 (dd, $J(^{31}P\text{-}^{107}Ag) = 414$ Hz, $J(^{31}P\text{-}^{109}Ag) = 435$ Hz). IR (nujol, cm^{-1}): 3180w (CH); 2384m, 2303m (BH); 1524m (C═C + C═N); 657w, 646m, 631s, 612m, 564w, 553w; 516s, 509s, 501s (PR_3); 460w, 449w, 430m, 420w, 413w, 377w, 227w. ESI-MS (major negative-ions, CH_3OH), *m*/*z* (%): 135 (30) $[5\text{-}(CF_3)pz]^-$, 149 (100) $[H_3B(5\text{-}(CF_3)pz)]^-$. ESI-MS (major positive-ions, CH_3OH), *m*/*z* (%): 717 (100) $\{Ag[P(p\text{-}C_6H_4CH_3)_3]_2\}^+$. Anal. Calcd for $C_{46}H_{47}AgBF_3N_2P_2$: C, 63.83; H, 5.47; N, 3.24. Found: C, 63.67; H, 5.64; N, 3.27.

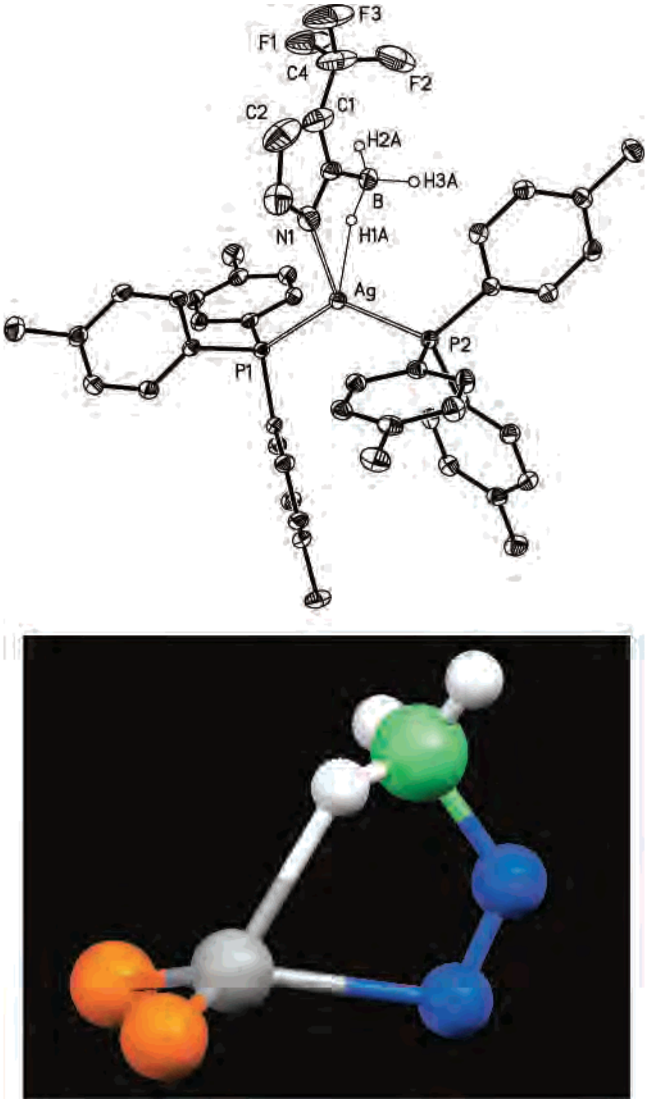


Figure 3. (a) (top) Molecular structure of $\{[H_3B(5\text{-}(CF_3)pz)]Ag[P(p\text{-}C_6H_4\text{-}CH_3)_3]_2\}$ (**3**) showing the atom numbering scheme at 35% probability level. All of the hydrogen atoms except those on boron have been omitted for clarity. (b) (bottom) A view of $\{[H_3B(5\text{-}(CF_3)pz)]Ag[P(p\text{-}C_6H_4CH_3)_3]_2\}$ showing coordination geometry at silver (only selected atoms are included). Selected bond distances (Å) and angles (°): Ag−N(1) 2.336(3), Ag−P(1) 2.4246(6), Ag−P(2) 2.4425(6), Ag−H(1A) 2.17(3), B−N(2) 1.600(4); N(1)−Ag−P(1) 115.77(6), N(1)−Ag−P(2) 106.46(7), P(1)−Ag−P(2) 130.11(2), N(1)−Ag−H(1A) 68.9(9), P(1)−Ag−H(1A) 106.9(9), P(2)−Ag−H(1A) 112.4(9).

Table 1. Crystal Data and Summary of Data Collection and Refinement

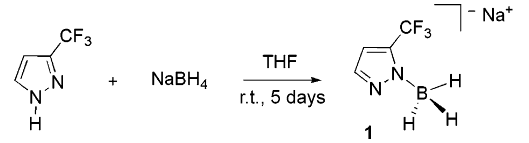
compound	**2**	**3**
empirical formula	C40 H35 Ag B F3 N2 P2	C46 H47 Ag B F3 N2 P2
fw	781.32	865.48
T	100(2) K	100(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimensions	$a = 13.0475(8)$ Å	$a = 12.0954(5)$ Å
	$b = 14.8880(9)$ Å	$b = 12.4403(6)$ Å
	$c = 20.4489(13)$ Å	$c = 14.3438(6)$ Å
	$\alpha = 106.897(1)°$	$\alpha = 81.045(1)°$
	$\beta = 104.392(1)°$	$\beta = 86.313(1)°$
	$\gamma = 95.097(1)°$	$\gamma = 89.387(1)°$
vol	3625.4(4) Å^3	2127.60(16) Å^3
Z	4	2
D_{calcd}	1.431 mg/m^3	1.351 mg/m^3
reflns collected	26 648	15 221
independent reflns	13 329 [R(int) = 0.0295]	8133 [R(int) = 0.0137]
GOF on F^2	1.070	1.062
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0571, wR2 = 0.1504	R1 = 0.0348, wR2 = 0.0901
R indices (all data)	R1 = 0.0691, wR2 = 0.1627	R1 = 0.0386, wR2 = 0.0937

{[H$_3$B(5-(CF$_3$)pz)]Ag[P(*m*-C$_6$H$_4$CH$_3$)$_3$]$_2$} (4). 4 was prepared analogously to **2** by using AgNO$_3$ (0.085 g, 0.5 mmol), tri(*m*-tolyl)phosphine, P(*m*-C$_6$H$_4$CH$_3$)$_3$ (0.304 g, 1.0 mmol), and Na[H$_3$B(5-(CF$_3$)pz)] (0.86 g, 0.5 mmol). The product was recrystallized from CH$_2$Cl$_2$/*n*-hexane (1:2), affording derivative **4** in 72% yield. ^{1}H NMR (DMSO-*d*$_6$, 293K): δ 2.34 (s, 18H, C*H*$_3$), 6.61 (d, 1H, 4-C*H*), 6.90−7.50 (m, 24H, C$_6$*H*$_4$), 7.74 (d, 1H, 3-C*H*). ^{1}H NMR (CDCl$_3$, 293K): δ 2.45 (s, 18H, C*H*$_3$), 6.56 (d, 1H, 4-C*H*), 6.77−7.40 (m, 24H, C$_6$*H*$_4$), 7.46 (d, 1H, 3-C*H*). ^{19}F NMR (DMSO-*d*$_6$, 293K): δ −59.25 (sbr). ^{31}P NMR (CDCl$_3$, 293K): 10.32 (s). ^{31}P NMR (CDCl$_3$, 223K): δ 11.16 (d, $J(^{31}P-Ag) = 328$ Hz). IR (nujol, cm^{-1}): 3100w (CH); 2429br (BH); 1509m (C=C + C=N); 617s, 564s, 555s; 518m, 461sbr (PR$_3$); 441w, 386w, 270w, 255w, 227m, 215m, 204w. ESI-MS (major negative-ions, CH$_3$OH), *m*/*z* (%): 135 (90) [5-(CF$_3$)pz]$^-$, 149 (100) [H$_3$B(5-(CF$_3$)pz)]$^-$. ESI-MS (major positive-ions, CH$_3$OH), *m*/*z* (%): 717 (100) {Ag[P(*m*-C$_6$H$_4$-CH$_3$)$_3$]$_2$}$^+$. Anal. Calcd for C$_{46}$H$_{47}$AgBF$_3$N$_2$P$_2$: C, 63.83; H, 5.47; N, 3.24. Found: C, 63.74; H, 5.58; N, 3.11.

{[H$_3$B(5-(CF$_3$)pz)]Ag[P(*o*-C$_6$H$_4$CH$_3$)$_3$]$_2$} (5). 5 was prepared analogously to **2** using AgNO$_3$ (0.085 g, 0.5 mmol), tri(*o*-tolyl)phosphine, P(*o*-C$_6$H$_4$CH$_3$)$_3$ (0.304 g, 1.0 mmol), and Na[H$_3$B(5-(CF$_3$)pz)] (0.86 g, 0.5 mmol). The product was recrystallized from diethyl ether/*n*-hexane (1:1), affording derivative **5** in 61% yield. ^{1}H NMR (DMSO-*d*$_6$, 293K): δ 2.31 (s, 18H, C*H*$_3$), 6.63 (d, 1H, 4-C*H*), 6.95−7.45 (m, 24H, C$_6$*H*$_4$), 7.81 (d, 1H, 3-C*H*). ^{1}H NMR (CDCl$_3$, 293K): δ 2.36 (s, 18H, C*H*$_3$), 6.53 (d, 1H, 4-C*H*), 7.05−7.35 (m, 24H, C$_6$*H*$_4$), 7.54 (d, 1H, 5-C*H*). ^{19}F NMR (DMSO-*d*$_6$, 293K): δ −59.74 (sbr). ^{31}P NMR (CDCl$_3$, 293K): δ 9.81 (s). ^{31}P NMR (CDCl$_3$, 223K): δ 11.18 (d, $J(^{31}P-Ag) = 331$ Hz). IR (nujol, cm^{-1}): 3070w (CH); 2401br (BH); 1548m (C=C + C=N); 568m, 552s; 519m, 473w, 458m (PR$_3$); 419w, 398w, 376m, 352m, 335w, 325m, 303m, 289w, 280s, 254s, 247s, 227s, 208s. ESI-MS (major negative-ions, CH$_3$OH), *m*/*z* (%): 149 (100) [H$_3$B(5-(CF$_3$)pz)]$^-$. ESI-MS (major positive-ions, CH$_3$OH), *m*/*z* (%): 717 (100) {Ag-[P(*o*-C$_6$H$_4$CH$_3$)$_3$]$_2$}$^+$. Anal. Calcd for C$_{46}$H$_{47}$AgBF$_3$N$_2$P$_2$: C, 63.83; H, 5.47; N, 3.24. Found: C, 63.72; H, 5.55; N, 3.16.

X-ray Data Collection and Structure Determinations. A suitable crystal of each sample covered with a layer of hydrocarbon oil was selected and mounted with Paratone-N oil on a cryo-loop and immediately placed in the low-temperature nitrogen stream. The X-ray intensity data of [H$_3$B(5-(CF$_3$)pz)]Ag[P(C$_6$H$_5$)$_3$]$_2$ and [H$_3$B(5-(CF$_3$)pz)]Ag[P(*p*-C$_6$H$_4$CH$_3$)$_3$]$_2$ were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with a Oxford Cryosystems 700 Series Cryostream cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube ($\lambda = 0.710\,73$ Å). The data frames were integrated with the Bruker *SAINT-Plus* software package. Data were corrected for absorption effects using the multiscan technique (*SADABS*). Structures were solved and refined using Bruker *SHELXTL* (Version 6.14) software package. Details of the data collection and refinement are in the cif files.

Scheme 2



[H$_3$B(5-(CF$_3$)pz)]Ag[P(C$_6$H$_5$)$_3$]$_2$ crystallizes in the triclinic crystal system and the $P\bar{1}$ space group. The structure was solved using Direct methods. The structure solution and refinement proceeded smoothly. There are two chemically similar but crystallographically different molecules in the asymmetric unit. Hydrogen atoms on the boron atoms were located from the difference map and included and refined isotropically. Other hydrogens were placed at calculated positions and refined using a riding model. All of the non-hydrogen atoms were refined anisotropically. The final full-matrix least-squares refinement on F^2 with 901 variables converged at R1 = 5.71% and wR2 = 15.04% for observed data with $I > 2\sigma(I)$. The GOF was 1.070.

[H$_3$B(5-(CF$_3$)pz)]Ag[P(*p*-C$_6$H$_4$CH$_3$)$_3$]$_2$ crystallizes in the triclinic crystal system and $P\bar{1}$ space group. The structure was solved using Direct methods. The structure solution and refinement proceeded smoothly. Hydrogen atoms on the boron atom were located from the difference map and included and refined isotropically. Other hydrogens were placed at calculated positions and refined using a riding model. All non-hydrogen atoms were refined anisotropically. The final full-matrix least-squares refinement on F^2 with 514 variables converged at R1 = 3.48% and wR2 = 9.01% for observed data with $I > 2\sigma(I)$. The GOF was 1.062.

Results and Discussion

The sodium salt of the trihydro(5-CF$_3$-pyrazol-1-yl)borate ligand, Na[H$_3$B(5-(CF$_3$)pz)], **1**, has been synthesized by treating a THF solution of 3-(trifluoromethyl)-1H-pyrazole with NaBH$_4$ in 1:1 molar ratio at room temperature for 5 days (Scheme 2). Na[H$_3$B(5-(CF$_3$)pz)] was purified by recrystallization from CH$_2$Cl$_2$/*n*-hexane and obtained in a 87% isolated yield. Notably, this method yielded only the trihydro(pyrazolyl)borate species with the −CF$_3$ substituent in the 5-position, in which the boron was bonded to the more-hindered nitrogen species, reminiscent of dipole-stabilized[31,32] organometallic intermediates.

The authenticity of Na[H$_3$B(5-(CF$_3$)pz)] was confirmed by ^{1}H, ^{13}C, ^{19}F NMR, elemental analysis, IR, and ESI-MS spectroscopy. The novel ligand **1** is a white, microcrystalline solid, soluble in common organic solvents and in methanol.

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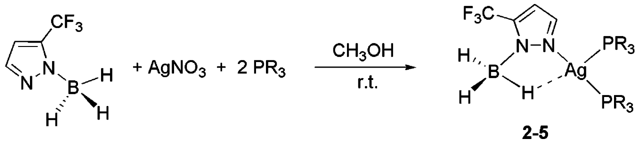
Scheme 3



Significantly, it can be kept in methanol aqueous solution without significant hydrolysis to boronic acids. The hydrolytic stability is a desirable feature for wider ligand utility and further applications.

The infrared spectrum of the ligand **1** showed a weak absorption at 3180 cm^{-1} due to the pz ring C−H stretching and a medium absorption at 1529 cm^{-1} related to ring breathing vibrations. The presence of the BH_3 moiety is detected by intense, broad absorptions at 2357, 2318, and 2271 cm^{-1} due to the B−H stretching vibrations. The ^{1}H NMR chemical shifts of 4-C*H* and 3-C*H* protons (in DMSO-d_6 solution) are at δ 6.30, and 7.17 respectively; the B−H protons for **1** appear as a broad quartet centered at 2.10 ppm, with a coupling constant *J*(B−H) between the boron and the hydrides of 89−90 Hz.[33] Generally, the 3- and 5-trifluoromethylpyrazole regioisomers can be distinguished on the basis of ^{19}F chemical shift.[34] The ^{19}F NMR spectrum of Na[$H_3B(5\text{-}(CF_3)pz)$], in DMSO-d_6 solution, exhibits just a singlet at −57.45 ppm, being in the expected region of 5-trifluoromethylpyrazole.[35]

The ^{13}C chemical shifts of 4-*C*H, 5-*C*CF$_3$ and 3-*C*H carbons (in DMSO-d_6 solution) are at δ 104.28, 133.79, and 135.85 respectively. For comparison, the ^{13}C chemical shift of 3-*C*CF$_3$ carbons is in the range 139.53−141.31 ppm in polyfluorinated scorpionate ligands,[35−38] whereas the ^{13}C chemical shift of 5-*C*CF$_3$ carbon is at 136.32 ppm in the [$HB(3,5\text{-}(CF_3)_2pz)_3$]Na ligand.[35] The ^1J(C,F) = 267.0 Hz due to the *C*F$_3$ moiety and the ^2J(C,F) = 35.8 Hz due to the *C*CF$_3$ group are in accordance with the values reported for other polyfluorinated scorpionate ligands.[35] The ESI-MS negative-ion spectrum of **1** in methanol is dominated by the free anionic ligand [$H_3B(5\text{-}(CF_3)pz)$]$^-$ at *m*/*z* 149 (100%).

The sodium salt of [$H_3B(5\text{-}(CF_3)pz)$]$^-$ was used in the preparation of the silver(I) complexes {[$H_3B(5\text{-}(CF_3)pz)$]Ag(PR_3)$_2$} ($PR_3 = P(C_6H_5)_3$ (**2**), P(*p*-$C_6H_4CH_3)_3$ (**3**), P(*m*-$C_6H_4CH_3)_3$ (**4**), and P(*o*-$C_6H_4CH_3)_3$ (**5**), as depicted in Scheme 3.

The treatment of Na[$H_3B(5\text{-}(CF_3)pz)$] with $AgNO_3$ in the presence of phosphane coligands led to **2**−**5** in good yield. In the absence of phosphane coligands, the reaction between **1** and $AgNO_3$ resulted in the silver reduction. The stoichiometry of these compounds was not affected by increasing (>2 equiv) the amount of the relevant phosphane. In the presence of stechiometric amounts of phosphane coligands, the reaction resulted in the silver reduction. **2**−**5** are soluble in $CHCl_3$, methanol, acetone, and DMSO, and they are insoluble in water, diethyl ether, and aliphatic or aromatic hydrocarbon solvents.

The infrared spectra of **2**−**5** show all of the bands required by the presence of the trihydro(5-CF$_3$-pyrazol-1-yl)borate and the phosphane coligands: weak absorptions in the range 3180−3190 cm^{-1} due to the pz ring C−H stretching and medium absorptions in the range 1550−1560 cm^{-1} related to ring breathing vibrations. Coordination of B−H bonds to metal ions characteristically leads to higher B−H stretching frequencies.[39] For example, derivatives **2**−**5** {[$H_3B(5\text{-}(CF_3)pz)$]Ag[PR_3]$_2$} exhibit B−H stretchings in the range 2302−2429 cm^{-1}, in according with a κ^2-N,H chelating coordination of the ligand. In the far-IR spectra, we have assigned the broad absorptions from 450 to 550 cm^{-1} to the phenyl quadrant out-of-plane bending and in plane-bending vibrations on the basis of previous reports on free phosphanes[40] and phosphane silver(I) complexes.[41]

The room-temperature ^{1}H NMR spectra of **2**−**5**, in DMSO-d_6 solution, show only one set of resonances for H(4) and H(3) protons, in the ranges 6.45−7.81 ppm. The phosphane coligands show a characteristic series of resonances in the aromatic region. The absence of distinct resonances for the terminal B−H and bridging B−H−M hydrides clearly implies a fluxional process in solution, as is often observed for complexes bound to borohydrides.[42] The ^{19}F NMR signals in the range of −58.40 to −59.64 ppm for **2**−**5**, in DMSO-d_6 solution, could be assigned to the trifluoromethyl groups at pyrazole ring 5-positions.

In the ^{31}P NMR spectrum of derivative {[$H_3B(5\text{-}(CF_3)pz)$]Ag[$P(C_6H_5)_3$]$_2$}, **2**, in $CDCl_3$ solution, a single broad signal is observed at 8.25 ppm at 293 K and a doublet at 9.31 ppm at 223 K, with coupling constants ^1J(Ag-^{31}P) at 417 Hz typical of diphosphane species,[43,44] in accordance with the crystallographic data. In the ^{31}P NMR spectrum of derivative {[$H_3B(5\text{-}(CF_3)pz)$]Ag[P(*p*-$C_6H_4CH_3)_3$]$_2$}, **3**, in $CDCl_3$ solution, a double doublet is observed at 223 K at 7.17 ppm with coupling constants ^1J(^{107}Ag-^{31}P) of 414 Hz and ^1J(^{109}Ag-^{31}P) of 435 Hz, all typical of a P_2Ag system.[43,44] In the spectra of derivatives **4** and **5**, {[$H_3B(5\text{-}(CF_3)pz)$]Ag[PR_3]$_2$} (R = *m*-$C_6H_4CH_3$ or *o*-$C_6H_4CH_3$), a single broad signal is observed at 293 K at 10.32 and 9.81 ppm, respectively, and a doublet is observed at 11.16 and 11.18 ppm, at 223K, with coupling constants ^1J(Ag-^{31}P) in the range 328−331 Hz typical of triphosphane species.[45]

Electrospray ionization mass spectroscopy was used to probe the existence of aggregates of the scorpionate ligand

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with Ag(I) and phosphane coligand in solution. Both positive-ion and negative-ion spectra of ligand **1** and of **2**−**5**, dissolved in methanol were recorded at low voltage (3.5−4.0 kV); under these experimental conditions, the dissociation is minimal, and most of the analyte is transported to the mass spectrometer as the intact molecular species.[46] In methanol solution, the negative-ion spectra of **1**−**5** were dominated by the fragment at *m*/*z* 149 (100%) due to the free scorpionate ligand, $[H_3B(5\text{-}(CF_3)pz)]^-$ together with a minor peak at *m*/*z* 135, due to the species $[5\text{-}(CF_3)pz]^-$. The positive-ion spectra of all of the triorganophosphane derivatives **2**−**5** were dominated by the fragment $[Ag(PR_3)_2]^+$, indicating individual species with a metal to ligand ratio of 1:2 also in solution.

X-ray quality crystals of **2** and **3** were obtained from a $CHCl_3$/diethyl ether (1:2) solution and CH_2Cl_2/diethyl ether solution, respectively. There are two molecules of **2** in the asymmetric unit. Both **2** and **3** have three-coordinate, pseudotetrahedral silver atoms. The $[H_3B(5\text{-}(CF_3)pz)]^-$ ligand coordinates to silver in κ^2-N,H fashion. The Ag•••H contacts are strong enough to pyramidalize the silver centers (the sum of the angles of the $NAgP_2$ core of **2** and **3** are 350 (av) and 352°, respectively).

The Ag−H distances in **2** and **3** (av. 2.07(5) and 2.17(3) Å, respectively) are shorter than those observed for the analogous systems containing the B−H•••Ag motif, such as the trimer $[Ag_3(Tp^{An})_2][ClO_4]$ (Tp^{An} is tris[3-(2-methoxyphenyl)pyrazol-1-yl]hydroborate), where the Ag•••H separations are in the range 2.5−2.8 Å[47] and the dimer $[Ag(Tm)]_2$ (Tm is hydrotris(3-methyl-1-imidazolyl-2-thione)borate) with Ag•••H separations of 2.83(5) and 2.45(5) Å.[48] For comparison, the sum of the van der Waals radii of silver and hydrogen is 2.92 Å, whereas the sum of the covalent radii of silver and hydrogen is 1.70 Å.[49,50] The Ag•••B (av. 2.941 and 2.952 Å) distances in **2** and **3** are similar to the Cu•••B distances observed in the analogous copper complex $[H_2B(3,5\text{-}(CF_3)_2pz)_2]Cu(PPh_3)_2$ (Cu•••B = 2.891 Å)[22] and in the hydrogen-bridged dimer $\{[H_2B(3,5\text{-}(CF_3)_2pz)_2]CuCNBu^t\}_2$ (Cu•••B = 3.050 Å).[21] Both the κ^2-N,H coordination mode in a poly(pyrazolyl)borate and Ag•••H−B bonds are rare. The P−Ag−P angle in **3** (which contains two $P(p\text{-}C_6H_4CH_3)_3$) coligands is about 5° larger than the corresponding angles observed for **2**. Other key metric parameters such as Ag−N and Ag−P distances are very similar between the two adducts.

Summary and Conclusion

Overall, we describe the synthesis and isolation of a mono(pyrazolyl)borate and its silver chemistry. Furthermore, $[H_3B(5\text{-}(CF_3)pz)]^-$ represents the first 5-substituted trihydro(azolyl)borate system. Despite the presence of fairly reducing borohydride moieties, the silver(I) adducts of $[H_3B(5\text{-}(CF_3)pz)]^-$ could be isolated using phosphane auxiliary ligands. Crystal structures of $[H_3B(5\text{-}(CF_3)pz)]Ag[P(C_6H_5)_3]_2$ and $[H_3B(5\text{-}(CF_3)pz)]Ag[P(p\text{-}C_6H_4CH_3)_3]_2$ revealed κ^2-N,H coordination modes in a poly(pyrazolyl)borate and weak Ag•••H−B bonds.

Acknowledgment. This work was supported by University of Camerino (FAR) and the Robert A. Welch Foundation (Y-1289 for HVRD).

Supporting Information Available: Crystallographic information files (CIF) of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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