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Syntheses of Cationic Lead(II) and Tin(II) Complexes Containing Tris(pyrazolyl)methane Ligands. Control of Stereochemistry by Variation in Ligand Substitution

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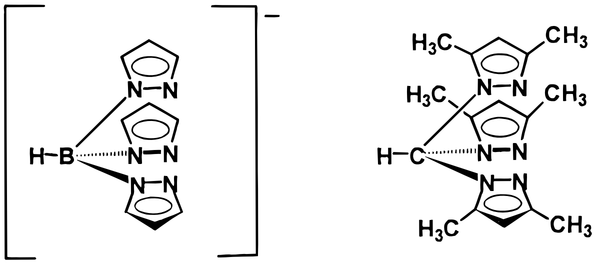
The addition of 2 equiv of $HBF_4 \cdot Et_2O$ to a THF suspension of $Pb(acac)_2$ (acac = acetylacetonate) followed by addition of 1 molar equiv of the tris(pyrazolyl)methane ligand $HC(3,5\text{-}Me_2pz)_3$ (pz = pyrazolyl ring) results in the immediate precipitation of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ (**1**). The complex $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$ (**2**) was prepared by precipitation from an acetone solution of **1** containing an excess of $HC(3,5\text{-}Me_2pz)_3$. Both $\{[HC(pz)_3]_2Pb\}(BF_4)_2$ (**3**) and $\{[HC(pz)_3]Pb\}(BF_4)_2$ (**4**) are prepared by the addition of the respective equivalent amounts of $HC(pz)_3$ to the $HBF_4 \cdot Et_2O{-}Pb(acac)_2$ THF solution. The lead ion in **1** is three coordinate with normal Pb−N distances ranging from 2.379(14) to 2.434(16) Å (average = 2.41 Å). The six-coordinate lead ion in **2** is in a trigonally distorted octahedral environment with equivalent Pb−N bond distances (2.635(7) Å). The lone pair on lead is *stereochemically inactive* and does not appear to influence the structure. The lead ion in **3** is in an asymmetric six-coordinate environment with disparate Pb−N bond distances ranging from 2.609(5) to 2.789(5) Å (average = 2.69 Å) and very different interligand N−Pb−N bond angles. Reactions of equal molar amounts of **1** with either $K[HB(3,5\text{-}Me_2pz)_3]$ or $K[HB(pz)_3]$ yield $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ (**5**) and $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(pz)_3]\}(BF_4)$ (**6**). The highly asymmetric structure of **5** is best described as a distorted square base pyramid. The $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand is tridentate with Pb−N distances ranging from 2.375(7) to 2.475(8) Å (average = 2.43 Å), whereas the $HC(3,5\text{-}Me_2pz)_3$ ligand is bidentate with long Pb−N distances of 2.745(7) and 2.827(7) Å. Reaction of $Sn(O_3SCF_3)_2$ with 1 molar equiv of $HC(3,5\text{-}Me_2pz)_3$ in THF yields the complex $\{[HC(3,5\text{-}Me_2pz)_3]Sn\}(O_3SCF_3)_2$ (**7**).

Introduction

We are interested in the preparation of coordination complexes of the post-transition metals in which the environment about the metal can be carefully controlled by choice of ligand. Employing the versatile poly(pyrazolyl)borate ligand set (**A**, Chart 1), we and others have shown that a number of lead(II) and tin(II) complexes can be prepared.[1] A variety of different coordination geometries have been observed in these complexes, including an octahedral coordination complex of lead(II), $[HB(3,5\text{-}Me_2pz)_3]_2Pb$, with a stereochemically inactive lone pair.[1a,b] The complex $[HB(pz)_3]_2Pb$ is also six coordinate but has a highly distorted structure.[1a] In contrast, $[B(pz)_4]_2Pb$ is four coordinate.[1a] In tin(II) chemistry, Cowley has prepared and structurally characterized the five-coordinate complex $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ and the four-coordinate complex $[HB(3,5\text{-}Me_2pz)_3]SnCl$.[1c] We have prepared and structurally characterized a five-coordinate complex $[HB(pz)_3]_2Sn$,[1d] a four-coordinate complex $[B(pz)_4]_2Sn$,[1e] and a three-coordinate complex $[H_2B(pz)_2]SnCl$.[1e] In the five-coordinate structures of $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ and $[HB(pz)_3]_2Sn$, one of the tris(pyrazolyl)borate ligands is tridentate and the other is bidentate.

Chart 1



A **B**

Recently we have become interested in the coordination chemistry of the neutral tris(pyrazolyl)methane ligands, such as $HC(3,5\text{-}Me_2pz)_3$ (**B**, Chart 1), which are formally derived from poly(pyrazolyl)borate ligands by replacing a boron anion with a carbon atom and are thus isoelectronic to them.[2] The synthesis of tris(pyrazolyl)methane ligands was first reported

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by Trofimenko in 1970, and the preparations were later modified by Elguero.[3] A variety of [tris(pyrazolyl)methane]$_2$M complexes of the post-transition metals have been prepared,[2,4] and $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$,[2a] $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$,[2b] and $\{[HC(3,4,5\text{-}Me_3pz)_3]_2Zn\}(ClO_4)_2$[4a] have been structurally characterized. As in the lead structure discussed above, the thallium(I) ion in the structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ resides at the inversion center of a trigonally distorted octahedron and the lone pair is stereochemically inactive. In cadmium(II) chemistry, mixed-ligand tris(pyrazolyl)methane/tris(pyrazolyl)borate complexes, such as $\{[HC(3,5\text{-}Me_2pz)_3]Cd[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$, were also prepared.[2b] This mixed-ligand complex was also structurally characterized and was shown to be six coordinate.[2e] The complex $\{[HC(3,5\text{-}Me_2pz)_3]Tl\}PF_6$,[2a] with a ligand to metal ratio of 1:1, has also been prepared and structurally characterized.

Reported herein is the investigation of tin(II) and mainly lead(II) complexes using the ligands $HC(3,5\text{-}Me_2pz)_3$ and $HC(pz)_3$. The syntheses and solid state structures of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$, $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$, $\{[HC(pz)_3]_2Pb\}(BF_4)_2$, and the mixed tris(pyrazolyl)borate/tris(pyrazolyl)methane complex $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ are presented. The structures of these complexes are very different. The cation in $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$ is another example of an octahedral complex of these heavy metals in which the lead(II) lone pair is *stereochemically inactive*, whereas the lone pair appears to influence the structures of the other complexes.

Experimental Section

General Procedures. All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Proton and ^{13}C NMR chemical shifts are reported in parts per million versus TMS, and the ^{119}Sn NMR chemical shift is reported in parts per million versus $SnMe_4$. Tetrafluoroboric acid/diethyl ether complex (85%) was purchased from Aldrich and used as received. The chemicals lead(II) acetylacetonate and tin(II) trifluoromethanesulfonate were purchased from Strem Chemicals, Inc. $HC(3,5\text{-}Me_2pz)_3$,[3] $HC(pz)_3$,[3] $K[HB(3,5\text{-}Me_2pz)_3]$,[5a] and $K[HB(pz)_3]$[5b] were prepared according to literature procedures. Elemental analyses were performed by National Chemical Consulting, Inc.

$\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ (1). $Pb(acac)_2$ (1.22 g, 3.01 mmol) was suspended in THF (15 mL). This mixture was treated with 85% $HBF_4\cdot Et_2O$ (0.94 mL, 6.0 mmol) and was allowed to stir for 30 min. The addition of a THF (10 mL) solution of $HC(3,5\text{-}Me_2pz)_3$ (0.90 g, 3.0 mmol) by cannula transfer resulted in the precipitation of a white solid. The reaction mixture was allowed to stir 2 days before cannula filtering. The remaining white solid was washed with hexanes (3 × 10 mL) and was collected after drying (1.62 g, 2.39 mmol, 79%). This solid was purified by repeated precipitation from an acetone/hexanes solvent mixture. Crystals suitable for X-ray structural analysis and the analytical sample were grown by slow diffusion of hexanes into a saturated acetone solution; mp = 296−298 °C (dec). ^1H NMR (acetone-d_6): δ 8.29 (1, s, $HC(Me_2pz)_3$), 6.37 (3, s, 4-*H*), 2.81 (9, s, 3,5-$(CH_3)_2$), 2.41 (9, s, 3,5-$(CH_3)_2$). ^{13}C NMR (acetone-d_6): δ 153.9 (3-*C*), 144.2 (5-*C*), 108.9 (4-*C*), 71.2 ($HC(Me_2pz)_3$), 12.7, 10.8 ($(CH_3)_2$). Anal. Calcd for $C_{16}H_{22}B_2F_8N_6Pb$: C, 28.29; H, 3.26; N, 12.37. Found: C, 28.46; H, 3.34; N, 12.42.

$\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$ (2). A portion of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ and a 5-fold excess amount of $HC(3,5\text{-}Me_2pz)_3$ was dissolved in acetone, and the mixture was filtered through a plug of Celite. The filtrate was layered with an equal volume of hexanes, and the mixture was set aside to allow for slow diffusion of the two layers. Crystals suitable for X-ray structural analysis and the analytical sample were obtained after several days; mp = 292−295 °C. ^1H NMR (acetone-d_6): δ 8.24 (1, s, $HC(Me_2pz)_3$), 6.15 (3, br, 4-*H*), 2.86 (9, s, 3,5-$(CH_3)_2$), 2.24 (9, br, 3,5-$(CH_3)_2$). Anal. Calcd for $C_{32}H_{44}B_2F_8N_{12}Pb$: C, 39.32; H, 4.54. Found: C, 39.49; H, 4.47.

$\{[HC(pz)_3]_2Pb\}(BF_4)_2$ (3). $Pb(acac)_2$ (0.40 g, 0.99 mmol) was suspended in THF (10 mL). This mixture was treated with 85% $HBF_4\cdot Et_2O$ (0.31 mL, 1.97 mmol) and was allowed to stir for 30 min. Addition of a THF (5 mL) solution of $HC(pz)_3$ (0.42 g, 1.96 mmol) by cannula transfer resulted in precipitation of a white solid. The reaction mixture was allowed to stir for 18 h before cannula filtering. The remaining white solid was washed with hexanes and dried under vacuum (0.58 g, 0.72 mmol, 72%). Crystals suitable for X-ray structural analysis and the analytical sample were grown by slow diffusion of hexanes into a saturated acetone solution; mp = 285−290 °C (dec). ^1H NMR (acetone-d_6): δ 9.4 (2, s, $HC(pz)_3$), 8.36 (6, d, J_{HH} = 2.5 Hz, 3-*H*), 7.82 (6, d, J_{HH} = 2.1 Hz, 5-*H*), 6.56 (6, dd, J_{HH} = 2.5, 2.1 Hz, 4-*H*). Mass spectrum (FAB): (*m/z*) 509 ($\{[HC(pz)_3]Pb\}(BF_4)^+$), 655 ($\{[HC(pz)_3]_2Pb\}F^+$), 723 ($\{[HC(pz)_3]_2Pb\}(BF_4)^+$). Anal. Calcd for $C_{20}H_{20}B_2F_8N_{12}Pb$: C, 29.68; H, 2.49. Found: C, 29.36; H, 2.17.

$\{[HC(pz)_3]Pb\}(BF_4)_2$ (4). This complex was prepared as above for **3** using 0.25 g (0.62 mmol) of $Pb(acac)_2$, 0.19 mL (1.20 mmol) of 85% $HBF_4\cdot Et_2O$, and 0.13 g (0.61 mmol) of $HC(pz)_3$ (0.30 g, 0.50 mmol, 82%); mp = 245−250 °C. ^1H NMR (acetone-d_6): δ 9.62 (1, s, $HC(pz)_3$), 8.57 (3, d, J_{HH} = 2.6 Hz, 3-*H*), 8.20 (3, d, J_{HH} = 2.1 Hz, 5-*H*), 6.68 (3, dd, J_{HH} = 2.6, Hz, 2.2 Hz, 4-*H*). Anal. Calcd for $C_{10}H_{10}B_2F_8N_6Pb$: C, 20.19; H, 1.69. Found: C, 19.90; H, 1.66.

$\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ (5). The solid $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ (0.15 g, 0.22 mmol) was suspended in THF (5 mL), and the mixture was cooled to −78 °C before treating dropwise by cannula transfer with a THF (10 mL) solution of $K[HB(3,5\text{-}Me_2pz)_3]$ (0.07 g, 0.2 mmol). The reaction mixture was stirred for 4 h and then cannula filtered through a plug of Celite. The gold-colored filtrate was evaporated to dryness providing a white powder (0.17 g, 0.19 mmol, 71%); mp = 240−242 °C. Crystals suitable for elemental analysis and X-ray structural determination were grown by layering a CH_2Cl_2 solution of the complex, that also contained a 5-fold excess of $HC(3,5\text{-}Me_2pz)_3$, with hexanes. ^1H NMR ($CDCl_3$): δ 8.09 (1, s, $HC(Me_2pz)_3$), 5.91 (3, s, 4-*H*), 5.87 (3, s, 4-*H*), 2.37 (9, s, 3,5-$(CH_3)_2$), 2.37 (9, s, 3,5-$(CH_3)_2$), 2.12 (9, s, 3,5-$(CH_3)_2$), 2.06 (9, s, 3,5-$(CH_3)_2$). ^{13}C NMR (acetone-d_6): δ 150.7, 149.5, 147.0, 141.6 (3-*C*, 5-*C*); δ 108.1, 107.5 (4-*C*), 71.0 ($HC(Me_2pz)_3$), 14.1 (3,5-$(CH_3)_2$), 13.2 (3,5-$(CH_3)_2$), 13.1 (3,5-$CH_3)_2$), 11.2 (3,5-$(CH_3)_2$). Anal. Calcd for $C_{31}H_{44}B_2F_4N_{12}Pb$: C, 41.86; H, 4.99. Found: C, 42.11; H, 5.24.

$\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(pz)_3]\}(BF_4)$ (6). The solid $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ (0.20 g, 0.29 mmol) was suspended in THF (5 mL), and the mixture was cooled to −78 °C. This mixture was treated dropwise by cannula transfer with a THF (5 mL) solution of $K[HB(pz)_3]$ (0.070 g, 0.28 mmol). This reaction mixture was allowed to stir overnight before cannula filtering through a plug of Celite. The filtrate was evaporated to dryness providing a yellow powder (0.12 g, 0.15 mmol, 50%); mp = 200−204 °C. Crystals suitable for an analytical sample were grown by layering a CH_2Cl_2 solution of the complex and a 5-fold excess of $HC(3,5\text{-}Me_2pz)_3$ with hexanes. ^1H NMR ($CDCl_3$): δ 8.16 (1, s, $HC(Me_2pz)_3$), 7.79 (3, d, J_{HH} = 2.1 Hz, 3-H), 7.58 (3, s, 5-*H* in pz), 6.26 (3, t, J_{HH} = 2.1 Hz, 4-*H* in pz), 5.92 (3, s, 4-*H* in Me_2pz), 2.23 (9, s, 3,5-$(CH_3)_2$), 1.86 (9, s, 3,5-$(CH_3)_2$). ^{13}C NMR (acetone-d_6): δ 149.3 (3-*C* in Me_2pz), 141.6 (5-*C* in Me_2pz), 141.5 (3-*C* in pz), 137.1 (5-*C* in pz), 107.8 (4-*C*), 105.8 (4-*C*), 78.7 ($HC(Me_2pz)_3$), 13.0 (3,5-$(CH_3)_2$ in Me_2pz), 10.4 (3,5-$(CH_3)_2$ in Me_2pz). A high-resolution fast atom bombardment mass spectrum shows M^+ (*m/e*): calcd for $C_{25}H_{32}{}^{11}BN_{12}{}^{208}Pb$ 719.2732; found 719.2735. Anal. Calcd for $C_{25}H_{32}B_2F_4N_{12}Pb$: C, 37.28; H, 4.00; N, 20.87. Found: C, 37.49; H, 4.00; N, 20.67.

$\{[HC(3,5\text{-}Me_2pz)_3]Sn\}(O_3SCF_3)_2$ (7). A THF (10 mL) solution of $Sn(O_3SCF_3)_2$ (2.19 g, 5.26 mmol) was treated dropwise by cannula transfer with a THF (10 mL) solution of $HC(Me_2pz)_3$ (1.57 g, 5.26 mmol). A white solid precipitated after stirring several minutes. The reaction mixture was allowed to stir 2 days before cannula filtering. The white solid was washed with hexanes (3 × 10 mL) and dried (3.27 g, 4.57 mmol, 86.7%). This solid was purified by repeated precipitation from an acetone/hexanes solvent mixture; mp = 236−243 °C. ^1H NMR (acetone-d_6): δ 8.37 (1, s, $HC(Me_2pz)_3$), 6.38 (3, s, 4-*H*); 2.85 (9, s,

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Table 1. Crystallographic Data for the Structural Analyses of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ (**1**), $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$ (**2**), $\{[HC(pz)_3]_2Pb\}(BF_4)_2$ (**3**), and $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ (**5**)

	1	**2**	**3**	**5**
formula	$C_{16}H_{22}B_2F_8N_6Pb$	$C_{32}H_{44}B_2F_8N_{12}Pb$	$C_{20}H_{20}B_2F_8N_{12}Pb$	$C_{31}H_{44}B_2F_4N_{12}Pb$
formula weight	679.20	977.60	809.29	889.59
space group	$P2_1/c$	$R\bar{3}c$	$C2/c$	$P2_1/c$
a, Å	12.707(2)	12.290(3)	14.372(5)	10.399(1)
b, Å	10.347(3)	12.290(3)	12.489(3)	13.149(1)
c, Å	18.357(2)	44.960(2)	15.661(4)	27.930(3)
β, deg	108.874(13)		99.87(3)	96.946(8)
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
V, Å^3	2283.93(5)	5874(3)	2770(1)	3790.8(7)
Z	4	6	4	4
cryst color	colorless	colorless	colorless	colorless
ρ (calcd), g cm^{-3}	1.9363	1.660	1.941	1.559
μ (Mo Kα), cm^{-1}	12.84	43.93	61.82	45.09
temp, °C	25	25	25	25
$R(F)$,[a] $R_w(F)$[b], $R_w(F^2)$[c]	0.0609, 0.0584, −	0.0424, −, 0.1022	0.0368, −, 0.0790	0.0370, −, 0.0795

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

3,5-(CH_3)$_2$), 2.50 (9, s, 3,5-(CH_3)$_2$). ^{13}C NMR (acetone-d_6): δ 155.1 (3-*C*), 145.1 (5-*C*), 121.2 (q, CF_3, J_{CF} = 318 Hz), 108.7 (4-*C*), 69.1 (H*C*(Me$_2$pz)$_3$), 13.2 ((CH_3)$_2$), 10.8 ((CH_3)$_2$). ^{119}Sn NMR (acetone-d$_6$): δ −802.1. Anal. Calcd for $C_{18}H_{22}F_6N_6O_6S_2Sn$: C, 30.23; H, 3.10; N, 11.75. Found: C, 30.28; H, 3.17; N, 11.74.

Crystallographic Studies. Crystal, data collection, and refinement parameters are given in Table 1. A single crystal of **1** was mounted inside a thin wall capillary tube. Suitable crystals of **2**, **3**, and **5** for single-crystal X-ray diffraction were sectioned and mounted with epoxy cement on thin glass fibers. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° ≤ 2θ ≤ 25°).

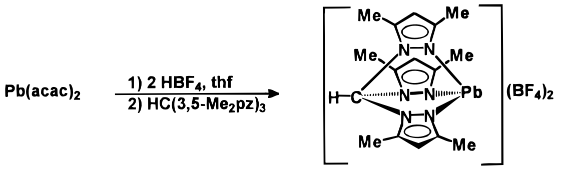
The unit-cell parameters, photographic data, systematic absences and occurrences of equivalent reflections are consistent with the space group $P2_1/c$ for **1** and **5**, $R\bar{3}c$ or $R3c$ for **2**, and $C2/c$ or Cc for **3**. The presence of an inversion center in **2** indicated the centrosymmetric space group. E-statistics and the presence of a 2-fold axis of symmetry suggested the centrosymmetric option for **3**. These solutions gave chemically reasonable and computationally stable results of refinement.

The structure of **1** was solved by the Patterson heavy atom method, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. The structures of **2**, **3**, and **5** were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. A lamina semi-empirical absorption correction was applied to **5** with a minimum glancing angle of 4°, as indexed on the prominent [001] crystal face, and semi-empirical ellipsoid absorption corrections were applied to **1**, **2**, and **3**.

The lead atom in **2** is located on a 3-fold axis of symmetry and an inversion center while a boron atom and one of the fluorine atoms of the counteranion are located on a 3-fold axis of symmetry. The lead atom in **3** is located on a 2-fold axis of symmetry. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms in **3** were located from the difference map and refined with average carbon−hydrogen bond distances. The remaining hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors for **1** are contained in the SHELXTL-76 program libraries (G. Sheldrick, Siemens XRD, Madison, WI). All software and sources of the scattering factors for **2**, **3**, and **5** are contained in the SHELXTL (5.3) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

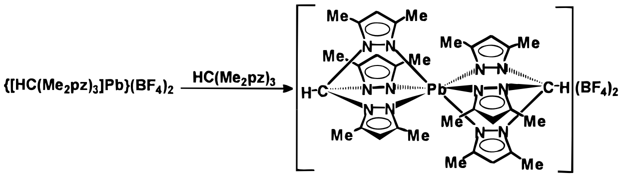
Results

Syntheses. Protonation of a THF suspension of Pb(acac)$_2$ with $HBF_4{\cdot}Et_2O$ generates a soluble Pb^{+2} ion that reacts with HC(3,5-Me$_2$pz)$_3$ to precipitate $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ in high yield (eq 1). No attempts to isolate or characterize the Pb(BF$_4$)$_2$ intermediate in the preparation were made, but this route was necessary to prepare the complex. Similar reactions of HC(3,5-Me$_2$pz)$_3$ and PbCl$_2$ or Pb(NO$_3$)$_2$ in THF were not successful, and it was not possible to prepare the complex under aqueous conditions.



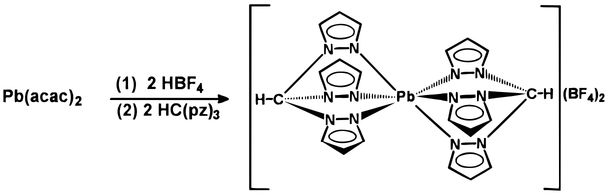
(1)

The complex $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$, with a ligand to metal ratio of 2:1, is prepared by layering a saturated acetone solution of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ that also contains a 5-fold excess of HC(3,5-Me$_2$pz)$_3$ with hexanes (eq 2). This complex cannot be prepared directly from the Pb(BF$_4$)$_2$ intermediate and excess ligand because of the precipitation of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$.



(2)

Reactions using either 2 or 1 molar equiv of HC(pz)$_3$ with the Pb(BF$_4$)$_2$ intermediate yield $\{[HC(pz)_3]_2Pb\}(BF_4)_2$ (eq 3) and $\{[HC(pz)_3]Pb\}(BF_4)_2$, respectively.



(3)

The reaction of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ with 1 equiv of K[HB(3,5-Me$_2$pz)$_3$] or K[HB(pz)$_3$] yields the mixed-ligand tris(pyrazolyl)methane/tris(pyrazolyl)borate products $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ and $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(pz)_3]\}(BF_4)$, respectively (eq 4).

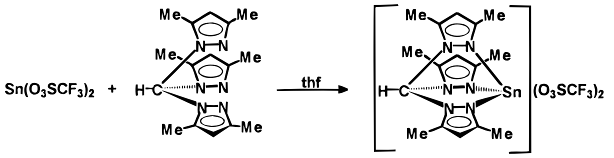
$$\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2 + K[HB(3,5\text{-}R_2pz)_3] \xrightarrow{CH_2Cl_2} \{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}R_2pz)_3]\}(BF_4) \quad (4)$$

$$R = Me \text{ or } H$$

Purification of these two mixed ligand complexes proved difficult due to the lability of the neutral ligand $HC(3,5\text{-}Me_2pz)_3$. Simply washing either product with hexanes results in the extraction of the neutral ligand and formation of $\{[HB(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)$ or $\{[HB(pz)_3]Pb\}(BF_4)$. Similarly, addition of hexanes to a CH_2Cl_2 solution of $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ results in the precipitation of $\{[HB(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)$. Crystals of $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ suitable for X-ray structural analysis were grown by addition of 5 equiv of $HC(3,5\text{-}Me_2pz)_3$ to a saturated CH_2Cl_2 solution of $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$, followed by slow diffusion of hexanes into this homogeneous mixture. Both mixed-ligand complexes were obtained analytically pure by this method. They are air stable solids, as are all the complexes reported here, and are soluble in THF, CH_2Cl_2, and acetone.

The pyrazolyl rings of each ligand are equivalent in the ^1H and ^{13}C NMR spectra for both complexes indicating a dynamic behavior (the rings in $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ are nonequivalent in the solid state, vide infra). Spectra of a mixture of $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ and added neutral ligand $HC(3,5\text{-}Me_2pz)_3$ also show only one set of resonances for each ligand (the resonances for $HC(3,5\text{-}Me_2pz)_3$ are between those observed for the free ligand and the complex), indicating that the free and coordinated $HC(3,5\text{-}Me_2pz)_3$ exchange fast on the NMR time scale.

Addition of $HC(3,5\text{-}Me_2pz)_3$ to a THF solution of $Sn(O_3SCF_3)_2$ results in the precipitation of $\{[HC(3,5\text{-}Me_2pz)_3]Sn\}(O_3SCF_3)_2$ in high yield (eq 5). This complex is partially soluble in acetone or CH_2Cl_2. No products with a 2:1 ligand to metal ratio have been prepared. In reactions of $\{[HC(3,5\text{-}Me_2pz)_3]Sn\}(O_3SCF_3)_2$ with $K[HB(3,5\text{-}Me_2pz)_3]$ or $K[HB(pz)_3]$, the anionic tris(pyrazolyl)borate ligands completely displace the neutral tris(pyrazolyl)methane ligand, forming substitution products $\{[HB(3,5\text{-}Me_2pz)_3]Sn\}(O_3SCF_3)$ and $\{[HB(pz)_3]Sn\}(O_3SCF_3)$, respectively.



(5)

Solid State Structures. The structures of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$, $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$, $\{[HC(pz)_3]_2Pb\}(BF_4)_2$, and $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ have been determined crystallographically. Crystallographic data are provided in Table 1.

$\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$. Figure 1 shows the ORTEP diagram of the cation in $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$, and selected bond distances and angles are given in Table 2. The lead ion is in a three-coordinate, trigonal pyramidal arrangement. The three Pb−N bonding distances are similar and vary from 2.379(14) to 2.434(16) Å (average = 2.41 Å). Weak Pb−F interactions are present from two fluorine atoms of two different BF_4^- anions (Pb−F distances of 2.685(10) and 2.875(26) Å). An even weaker interaction with a third fluorine atom exists at a distance of 3.032 Å. Given the regular arrangement of the N_3Pb core, these interactions do not impact greatly on the overall structure. Intraligand N−Pb−N bond angles are restrained by the chelate bite of the ligand to an average of 75°.

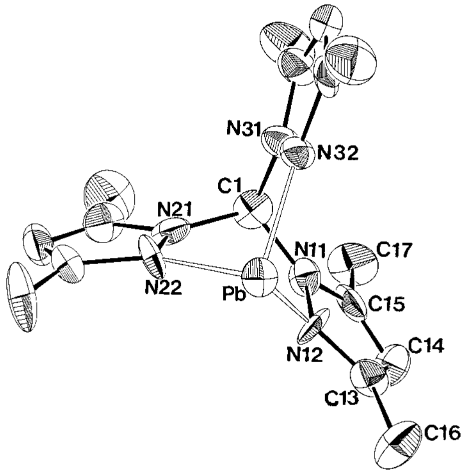


Figure 1. ORTEP diagram of the cation $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}^{2+}$.

Table 2. Selected Bond Distances and Angles for $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$

Bond Distances (Å)			
Pb−N(12)	2.424(14)	Pb-F(2)	2.875(26)
Pb−N(22)	2.434(16)	Pb-F(5)	2.685(10)
Pb−N(32)	2.379(14)		
Selected Bond Angles (deg)			
N(12)-Pb−N(22)	73.1(4)	F(2)-Pb−N(32)	73.8(6)
N(12)-Pb−N(32)	76.3(4)	F(5)-Pb−N(12)	144.8(4)
N(22)-Pb−N(32)	74.9(4)	F(5)-Pb−N(22)	77.3(4)
F(2)-Pb−N(12)	71.4(7)	F(5)-Pb−N(32)	77.8(4)
F(2)-Pb−N(22)	137.0(6)	F(2)-Pb-F(5)	122.9(6)

The structure of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}^{2+}$ is very similar to that of $\{[HC(3,5\text{-}Me_2pz)_3]Tl\}^+$,[2a] with which it is isoelectronic. The average Pb−N bonding distances are 0.26 Å shorter than the corresponding Tl−N bond distances, but this difference is expected given the difference in the ionic radii between the two metals (0.31 Å).[6]

A notable difference in the two structures is the degree of tilting of the pyrazolyl rings away from alignment with the metal. Tilting of the pyrazolyl rings away from perfect C_{3v} symmetry is minimal in the present structure, as indicated by the average PbN(n2)−N(n1)C(n5) (where n denotes the ring number) torsion angle of 172°, whereas substantial tilting was observed in the structure of $\{[HC(3,5\text{-}Me_2pz)_3]Tl\}PF_6$ (TlN−NC torsion angle = 155.5°). In the absence of tilting, angles of 180° would be expected and the metal atom would reside in the planes defined by the pyrazolyl ring. The cause of this distortion in the thallium structure was attributed to the size of the metal atom being large in comparison to the intrinsic "bite" of the ligand. In the present structure, only a minimal distortion is necessary because of the smaller size of lead(II) compared with that of thallium(I).

Wieghardt has previously reported the syntheses and X-ray crystal structures of two lead(II) compounds that are similar to the structure of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ presented here.[7] These include the complexes $LPb(ClO_4)_2$ and $LPb(NO_3)_2$ where L is triazacyclononane ($C_6H_{15}N_3$). In both structures, the average Pb−N bond lengths (2.44 Å) as well as the average intraligand N−Pb−N bond angles (71°) are comparable to those observed in $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ (2.41 Å, 75°) and there are interactions with oxygen atoms from the counteranions. We have previously noted the similarity between the ligands $HC(3,5\text{-}Me_2pz)_3$ and triazacyclononane.[2d] Both are neutral tridentate N_3 donor ligands that readily coordinate a metal ion.

$\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$. Figure 2 shows the ORTEP diagram of the cation in $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$, and selected bond distances and angles are given in Table 3. The

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(6) Shannon, R. D. *Acta Crystallogr., Sect A* **1976**, *A32,* 751.

(7) Wieghardt, K.; Kleine-Boymann, M.; Nuber, B.; Weiss, J.; Zsolnai, L.; Huttner, G. *Inorg. Chem.* **1986**, *25,* 1647.

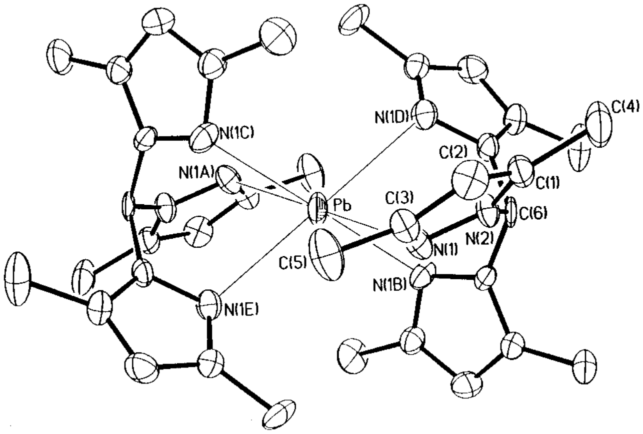

Figure 2. ORTEP diagram of the cation $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$.

Table 3. Selected Bond Distances and Bond Angles for $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$ (**2**) and $\{[HC(pz)_3]_2Pb\}(BF_4)_2$ (**3**)

2		3	
	Bond Distances (Å)		
Pb−N(1)	2.635(7)	Pb−N(11)	2.789(5)
		Pb−N(21)	2.660(5)
		Pb−N(31)	2.609(5)
C(6)−N(2)	1.451(9)	C(1)−N(12)	1.439(8)
		C(1)−N(22)	1.462(8)
		C(1)−N(32)	1.445(8)
	Selected Bond Angles (deg)		
N(1)−Pb−N(1A)	180.0	N(11)−Pb−N(21)	67.8(2)
N(1)−Pb−N(1B)	72.4(3)	N(11)−Pb−N(31)	65.5(2)
N(1)−Pb−N(1C)	107.6(3)	N(21)−Pb−N(31)	69.8(2)
		N(11)−Pb−N(11A)	161.4(2)
		N(11)−Pb−N(21A)	119.0(2)
		N(11)−Pb−N(31A)	132.5(2)
		N(21)−Pb−N(21A)	140.9(2)
		N(21)−Pb−N(31A)	78.7(2)
		N(31)−Pb−N(31A)	72.0(2)

structure of the cation is a trigonally distorted octahedron. The lead ion sits on a crystallographic center of inversion; thus, the planes formed by the three nitrogen donor atoms of each ligand are parallel. Intraligand N−Pb−N bond angles are restrained to 72.4(3)° by the chelate rings with *cis* interligand N−Pb−N bond angles of 107.6(3)°. All *trans* N−Pb−N angles are 180°, as required by the symmetry. *The lone pair on lead(II) is clearly stereochemically inactive.*

The structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$ is closely related to the structures previously reported for the isoelectronic cation $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}^{+}$ [2a] and the neutral tris(pyrazolyl)borate analog $[HB(3,5\text{-}Me_2pz)_3]_2Pb$.[1a] Notably, in each structure, the lone pair of electrons is stereochemically inactive. The Pb−N bond distances in the two lead structures are nearly identical at 2.610(5) Å for $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ and 2.635(7) Å for $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$.

One difference between the structures of $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ and $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$ is that the tilting of the pyrazolyl rings is much greater in the cation with a PbN−NC torsion angle of 130.1° versus the 159° angle in the neutral complex. The greater tilting in the cation is likely a result of the smaller covalent radius of carbon versus boron, which is reflected in the C(6)−N(2) bond length of 1.451(9) Å being 0.1 Å shorter than the B−N bond distance in $[HB(3,5\text{-}Me_2pz)_3]_2Pb$. This shortening coupled with comparable N−C(6)−N and N−B−N bond angles causes the intrinsic bite of the $HC(3,5\text{-}Me_2pz)_3$ ligand to be smaller than that of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand. The smaller bite forces a larger distortion of the $HC(3,5\text{-}Me_2pz)_3$ ligand when it bonds with the large, six-coordinate lead(II) ion. In contrast, the tilt angles in $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ and $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$ are both 159°, a consequence of the smaller size of cadmium(II). An even greater tilting of 123° is observed in the structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}^{+}$, where the thallium(I) ion is even larger (average Tl−N bond distance of 2.92 Å) than lead(II).[6] The greater tilting in $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$ compared to $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}^{2+}$ is also mainly attributed to the longer Pb−N bond distances in the six-coordinate complex, but the coordination geometry may also have an influence.

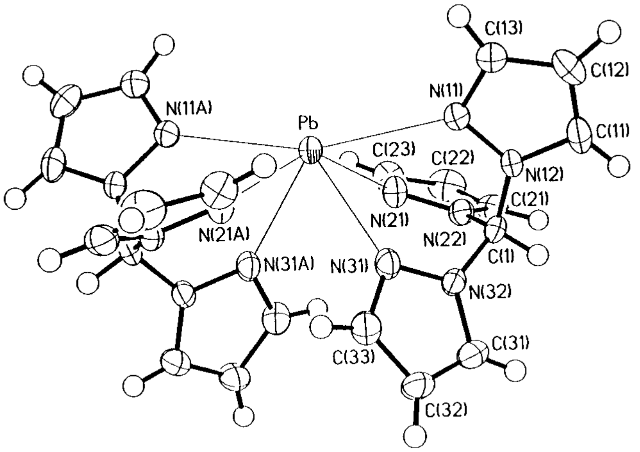

Figure 3. ORTEP diagram of the cation $\{[HC(pz)_3]_2Pb\}^{2+}$.

$\{[HC(pz)_3]_2Pb\}(BF_4)_2$. Figure 3 shows the ORTEP diagram of the cation in $\{[HC(pz)_3]_2Pb\}(BF_4)_2$ (**3**), and selected bond distances and angles are given in Table 3. The lead is six coordinate, but the arrangement of the nitrogen donor atoms is highly asymmetric with three pairs of Pb−N bonding distances of 2.609(5), 2.660(5), and 2.789(5) Å (average = 2.69 Å). The intraligand bond angles are fairly similar ranging from 65.5(2)° to 69.8(2)° (average = 67.7°); however the interligand bond angles between equivalent nitrogen atoms vary from 72.0(2)° to 140.9(2)° and all the way to 161.4(2)° for the N(11)−Pb−N(11A) angle. These interligand bond angles correlate with the bond distances in that the longer bond distances are associated with the larger angles.

This structure of **3** is somewhat similar to that of its isoelectronic analog $[HB(pz)_3]_2Pb$ in that both are highly distorted from a regular six-coordinate geometry.[1a] For $[HB(pz)_3]_2Pb$, the Pb−N bond distances range from 2.462(13) to 2.806(13) Å, an even greater range than that observed in the structure of **3**, although the average of 2.61 Å is close to that observed in **3**. The distortions in these two structures can be attributed to a stereoactive lone pair on the lead(II) center. In general, it is well-known that in higher coordinate lead structures, bonds adjacent to the presumed location of the lead(II) lone pair are generally longer than bonds remote from the lone pair.[8] In both of these lead structures, the "open" space in the structures correlates with longer adjacent bond distances.

$\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$. Figure 4 shows the ORTEP diagram of the cation in $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$, and selected bond distances and angles are given in Table 4. The lead(II) ion is five coordinate with a tridentate $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand and a bidentate $HC(3,5\text{-}Me_2pz)_3$ ligand. The geometry for this five-coordinate cation can be best described as a distorted square base pyramid with two nitrogen donor atoms from each ligand (N(11), N(31), N(41), and N(51)) occupying the basal positions and the

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(8) (a) Harrison, P. G. In *Comprehensive Coordination Chemistry;* Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Permagon: Oxford, 1987; Vol. 3, p 183. (b) Lawton, S. L; Kokotailo, G. T. *Inorg. Chem.* **1972**, *11*, 363.

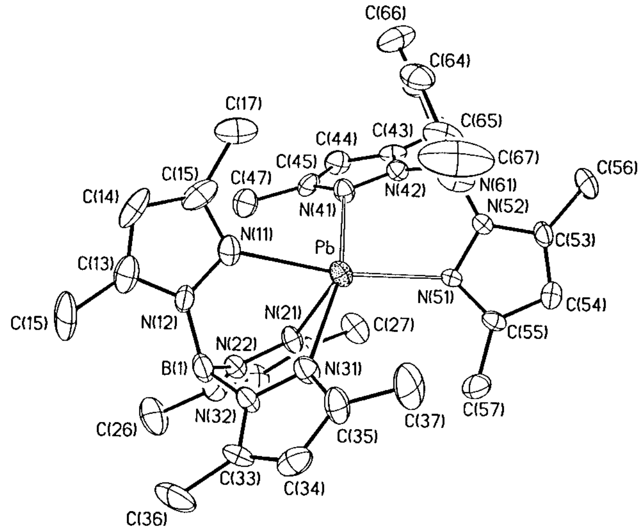

Figure 4. ORTEP diagram of the cation $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}^+$.

Table 4. Selected Bond Distances and Bond Angles for $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$

	Bond Distances (Å)		
Pb−N(11)	2.430(7)	Pb−N(41)	2.745(7)
Pb−N(21)	2.375(7)	Pb−N(51)	2.827(7)
Pb−N(31)	2.475(8)	Pb−N(61)	3.19
	Bond Angles (deg)		
N(11)−Pb−N(21)	78.6(3)	N(21)−Pb−N(41)	86.1(2)
N(11)−Pb−N(31)	77.5(3)	N(21)−Pb−N(51)	92.8(2)
N(11)−Pb−N(41)	91.4(2)	N(31)−Pb−N(41)	160.8(2)
N(11)−Pb−N(51)	158.7(2)	N(31)−Pb−N(51)	119.7(2)
N(21)−Pb−N(31)	76.4(2)	N(41)−Pb−N(51)	68.4(2)

remaining nitrogen donor atom (N21) from the tridentate $[HB(3,5\text{-}Me_2pz)_3]^-$ lying at the apex. Presumably, the lone pair of electrons on the lead(II) ion occupies the open face of the square pyramid base.

Metrical parameters in the structure of $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ are highly asymmetric. The three short Pb−N bonding distances from the tridentate $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand vary over a range from 2.375(7) to 2.475(8) Å (average 2.43 Å), while both Pb−N bonding distances from $HC(3,5\text{-}Me_2pz)_3$ are much longer (2.745(7) and 2.827(7) Å). Among the five Pb−N bonding distances, the shortest is associated with the nitrogen donor atom (N21) that is in the apical position of the square base pyramid or *trans* to the presumed site of the lone pair.

Intraligand N−Pb−N bond angles in the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand are restricted by the chelate bite to an average of 78°, while the sole intraligand N−Pb−N bond angle from the bidentate $HC(3,5\text{-}Me_2pz)_3$ ligand is even smaller (68.4(2)°). As a result of these restrained angles, three of the four *cis* N−Pb−N bond angles in the basal plane are highly irregular, yet the average of these four bond angles is 89°. Additionally, two of the four basal−apical interactions are distorted from 90° (78.6° and 76.4°) due to chelation.

The structure of $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ resembles the five-coordinate structures of $[HB(3,5\text{-}Me_2pz)_3]_2Sn$[1c] and especially $[HB(pz)_3]_2Sn$[1d] reported previously. Notably, the geometry around the metal ion in each structure is a square base pyramid. As observed in the structure of $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$, the Sn−N bond distances in $[HB(pz)_3]_2Sn$ vary substantially from 2.263(3) to 2.732(4) Å. Similarly, the shortest Sn−N bond distance is *trans* to the presumed lone pair of electrons on the tin(II) ion. Likewise, in the basal plane, there exists two short Sn−N bond distances (2.322(3) and 2.373(3) Å) and two longer distances (2.732(4) and 2.578(3) Å). Finally, the N−Sn−N bond angles in the basal plane are also highly irregular with three of these angle less than 80° and the fourth much larger at 124°. The average Sn−N bond distance (2.45 Å) is 0.12 Å shorter than the average Pb−N bond distance (2.57 Å) observed in the present structure. This value can be largely accounted for by the difference in ionic radii between the two metals.[6]

Discussion

The preparation of a series of new lead(II) complexes and one new tin(II) complex using $HC(3,5\text{-}Me_2pz)_3$ and $HC(pz)_3$ further demonstrates the utility of these tris(pyrazolyl)methane ligands in the preparation of cationic post-transition metal complexes. Determination of the coordination ability of these neutral ligands, especially in comparison to the heavily studied poly(pyrazolyl)borate ligands, is one of the main goals of our study. Investigating the chemistry of zinc(II), Vahrenkamp has very recently indicated that tris(pyrazolyl)methane ligands were not “reliably tridentate and not reliably stable when exposed to zinc salts”.[4] In the chemistry of lead(II) and tin(II) reported here, there are also some indications that the neutral tris(pyrazolyl)methane ligands do not bond as tightly to the metal as the anionic tris(pyrazolyl)borate ligands. This bonding difference might be anticipated based solely on charge considerations, but this result is *not* evident in the structures of the homoleptic pairs of isoelectronic complexes of lead(II) and cadmium(II). For the $[HB(3,5\text{-}Me_2pz)_3]_2Cd$[9] and $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$ [2b] matched pair, the structures are very similar with Cd−N bond distances in the tris(pyrazolyl)methane structure a little shorter (2.321(10) Å) than those in the tris(pyrazolyl)borate structure (2.348(5) Å). An analogous result is observed here with $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$ and $[HB(3,5\text{-}Me_2pz)_3]_2Pb$,[1a] where the tris(pyrazolyl)methane ligands have Pb−N bond distances that are 0.02 Å shorter. All four complexes are air and thermally stable. The structures of these four complexes indicate that the bonding of the tris(pyrazolyl)methane and tris(pyrazolyl)borate ligands to lead(II) and cadmium(II) is very similar.

This same conclusion is made from the chemistry and structure of the mixed-ligand, cadmium(II) complex $\{[HC(3,5\text{-}Me_2pz)_3]Cd[HB(3,5\text{-}Me_2pz)_3]\}^+$.[2e] Both ligands are tridentate in this complex. In contrast, the inability of the $HC(3,5\text{-}Me_2pz)_3$ ligand to compete with tris(pyrazolyl)borate ligands in the chemistry of tin(II) and the structure of $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ is an indication of the stronger bonding of the tris(pyrazolyl)borate ligands in these cases. In the mixed-ligand structure, the $HC(3,5\text{-}Me_2pz)_3$ ligand is only bidentate and the average Pb−N bond distances are 0.36 Å longer than those in the tridentate $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand. The reasons for the great structural difference in $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}^+$ compared to either of its isoelectronic homoleptic complexes or of the analogous mixed-ligand cadmium complex are not readily apparent, although the lone pair on the lead could be exerting an influence.

The impact of the lead(II) lone pair on the structures on the six L_2Pb complexes (L = tris(pyrazolyl)methane or poly(pyrazolyl)borate ligand) we have now prepared and structurally characterized is not consistent. In two of the structures, $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ and $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$, the lone pair seems to have no influence and is considered to be stereochemically inactive. Not only are these structures octahedral but the average Pb−N bond distances are very similar to those in the

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(9) Reger, D. L.; Mason, S. S.; Rheingold, A. L.; Ostrander, R. L. *Inorg. Chem.* **1993**, *32*, 5216.

distorted six-coordinate complexes $[HB(pz)_3]_2Pb$ and $\{[HC(pz)_3]_2Pb\}^{2+}$. In both of these distorted structures, the lone pair would be considered as stereochemically active, but an impact on the average Pb−N bond distances might have been expected.[10] Presumably, the differences in the structures of these two pairs of complexes is explained by the steric effects of the methyl groups in the former pair, forcing the octahedral geometry. In the remaining two structures in the series, $[B(pz)_4]_2Pb$ and $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}^+$, two or one, respectively, of the potentially tridentate ligands are only bidentate, and there is a clear space in the structures that can be identified as the location of the lone pair.

In a recent article, Hanusa has argued,[11] based on a large number of group 2 and 14 metallocene structures, that "the confinement of the metal valence electrons of the divalent Group 14 metals to nondirectional orbitals of high *s*-character" limits their influence on the structures of metallocene complexes. He calls for more comparative studies of this type. We are presently investigating the chemistry of the metals in groups 1 and 2 using tris(pyrazolyl)methane and mixed tris(pyrazolyl)methane/tris(pyrazolyl)borate ligand sets to further understand this chemistry.

The lone pair on lead may also be influencing the solution chemistry of $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$. The fast exchange of the tris(pyrazolyl)methane ligand observed in the ^1H and ^{13}C NMR spectra of a mixture of $HC(3,5\text{-}Me_2pz)_3$ and $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ shows the $HC(3,5\text{-}Me_2pz)_3$ ligand is labile in solution. Also, the fact that simply washing the mixed-ligand complexes with hexanes leads to extraction of $HC(3,5\text{-}Me_2pz)_3$ suggests that it is not tightly bonded to the lead. These results contrast our work with mixed tris(pyrazolyl)methane/hydrotris(pyrazolyl)borate complexes of cadmium(II), such as $\{[HC(3,5\text{-}Me_2pz)_3]Cd[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$, where the $HC(3,5\text{-}Me_2pz)_3$ ligand is tridentate and strongly bonded to the metal. For these complexes, added $HC(3,5\text{-}Me_2pz)_3$ does not exchange with the coordinated ligand fast on the NMR time scale and $HC(3,5\text{-}Me_2pz)_3$ is not extracted away by hexanes.[2b]

In conclusion, it has been shown that stable lead(II) complexes with unusual geometries can be prepared with tris(pyrazolyl)methane ligands. For most cases, the tris(pyrazolyl)methane ligands bond strongly to post-transition metals, even in mixed tris(pyrazolyl)methane/tris(pyrazolyl)borate complexes. For $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}^+$ and in tin(II) chemistry, the tris(pyrazolyl)borate ligand bonds more strongly. Importantly, the geometry about the lead and even the coordination number can be controlled by variations in the ligand charge and substitution with these versatile tris(pyrazolyl)methane/poly(pyrazolyl)borate ligands.

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Supporting Information Available: Tables of complete data collection information, bond distances, angles, positional parameters, and anisotropic thermal parameters (31 pages). Ordering information is given on any current masthead page.

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