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A Six-Coordinate Tris(3,5-dimethyl-1-pyrazolyl)methane−Thallium(I) Complex with a Stereochemically Inactive Lone Pair: Syntheses and Solid State Structures of {[HC(3,5-Me$_2$pz)$_3$]$_2$Tl}PF$_6$ and {[HC(3,5-Me$_2$pz)$_3$]Tl}PF$_6$ (pz = Pyrazolyl)

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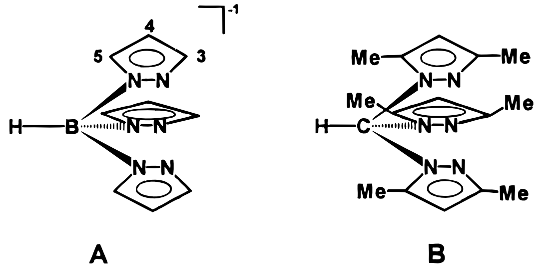
The addition of the tris(pyrazolyl)methane ligand HC(3,5-Me$_2$pz)$_3$ (pz = pyrazolyl ring) to a THF solution of TlPF$_6$ results in the immediate precipitation of {[HC(3,5-Me$_2$pz)$_3$]$_2$Tl}PF$_6$. The structure has been determined crystallographically. The arrangement of the nitrogen donor atoms about the thallium is best described as a trigonally distorted octahedron. The thallium atom sits on a crystallographic center of inversion; thus the planes formed by the three nitrogen donor atoms of each ligand are parallel. The Tl−N bond distances range from 2.891(5) to 2.929(5) Å (average = 2.92) Å. The lone pair on thallium is clearly stereochemically inactive and does not appear to influence the structure. The pyrazolyl rings are planar, but are tilted with respect to the thallium atom so as to open up the N···N intraligand bite distances. The thallium(I) complex with a ligand to metal ratio of 1/1, {[HC(3,5-Me$_2$pz)$_3$]Tl}PF$_6$, is prepared in acetone by the reaction of equimolar amounts of HC(3,5-Me$_2$pz)$_3$ and TlPF$_6$. The structure of the cation is a trigonal pyramid, with Tl−N bond distances that range from 2.64(1) to 2.70(1) Å (average = 2.67) Å. Pyrazolyl ring tilting is also observed in this complex, but the degree of tilting is smaller. Crystal data for {[HC(3,5-Me$_2$pz)$_3$]$_2$Tl}PF$_6$: monoclinic, $P2_1/c$, $a = 9.210(6)$ Å, $b = 13.36(1)$ Å, $c = 16.067(8)$ Å, $\beta = 92.48(5)°$, $V = 1975(2)$ Å^3, $Z = 2$, $R = 0.029$. For {[HC(3,5-Me$_2$pz)$_3$]Tl}PF$_6$: monoclinic, P2$_1$/n, $a = 10.685(2)$ Å, $b = 16.200(5)$ Å, $c = 13.028(3)$ Å, $\beta = 94.02(2)°$, $V = 2249.6(8)$ Å^3, $Z = 4$, $R = 0.042$.

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. As part of this effort, we have initiated an investigation into the preparation and structural characterization of complexes of these metals using the unique properties of the poly(pyrazolyl)borate ligand system (**A**, Chart 1).[1] These ligands are extremely versatile because substitution on the pyrazolyl rings, especially at the 3-position, can have a profound effect on the properties of the ligand. One initial goal of the research was the syntheses of complexes of thallium(I), indium(I), tin(II), and lead(II) in which the lone pair on the metal was stereochemically inactive. This question was investigated in the mid-1980s by Zuckerman for tin(II) and lead(II) using metallocene complexes.[2] With decaphenylstannocene,[2] he was able to synthesize the first molecular, main-group complex in which the lone pair is stereochemically inert. We[3] and others[4] have failed to produce poly(pyrazolyl)borate compounds of tin(II) with an inactive lone pair, but we have been successful in lead(II) chemistry.[5] The six-coordinate structure of [HB(3,5-Me$_2$pz)$_3$]$_2$Pb (pz = pyrazolyl ring) has the lead atom sitting on a center of inversion and the planes formed by the three nitrogen donor atoms of each ligand are parallel. The lone pair on lead is clearly *stereochemically inactive*. In our search for other ligands that could produce additional complexes of this type, we have initiated a study of the main group chemistry of the tris(3,5-dimethyl-1-pyrazolyl)methane ligand (**B**, Chart 1), HC(3,5-Me$_2$pz)$_3$, the neutral analog of the anionic [HB(3,5-Me$_2$pz)$_3$]$^-$ ligand. The HC(3,5-Me$_2$pz)$_3$ ligand and a couple of its transition metal complexes were reported by Trofimenko in 1970,[6] but the first complexes of it to be structurally characterized, complexes of molybdenum, have just appeared.[7] A number of papers using the HC(pz)$_3$ ligand with transition metals have appeared[8] as have the syntheses of the group 12 metal complexes {[HC(pz)$_3$]$_2$M}$^{2+}$ (M = Zn, Cd, Hg).[8b,9]

Chart 1



A **B**

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We are particularly interested in the chemistry of indium(I) and thallium(I) with these ligands (our studies with tin(II) and lead(II) will be reported elsewhere). Poly(pyrazolyl)borate complexes of thallium(I) are well-known,[10] and there are recent reports of indium(I) complexes.[11] In all cases, the neutral [poly(pyrazolyl)borate]M complexes forms. Reported here are reactions of the neutral $HC(3,5\text{-}Me_2pz)_3$ ligand with $TlPF_6$. We have prepared *both* the 2/1 and 1/1, ligand/metal, complexes of thallium(I), $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ and $\{[HC(3,5\text{-}Me_2pz)_3]Tl\}PF_6$. Both of these complexes have been characterized in the solid state by X-ray crystallography. The $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ complex has an octahedral structure with a *stereochemically inactive lone pair*, the first complex of thallium(I) of this type to be structurally characterized.[12] We also analyzed an interesting bonding feature of these complexes that results in a tilting of the pyrazolyl rings.

Experimental Section

All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or in a Vacuum Atmospheres HE-493 dry box. All solvents were dried, degassed, and distilled prior to use. ^1H and ^{13}C NMR chemical shifts are reported in ppm vs TMS. $TlPF_6$ was purchased from Strem Chemicals and used as received. $HC(3,5\text{-}Me_2pz)_3$ was prepared according to a literature procedure.[13] Elemental analyses were performed by National Chemical Consulting, Inc.

Caution! Thallium(I) compounds are extremely toxic and care should be used when handling them.

$\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$. A THF (8 mL) solution of $HC(3,5\text{-}Me_2pz)_3$ (0.22 g; 0.74 mmol) was added to a THF (6 mL) solution of $TlPF_6$ (0.13 g; 0.37 mmol). A white solid precipitated immediately. The reaction mixture was cannula filtered after stirring overnight. The remaining white solid was washed with hexanes (5 mL) and dried under vacuum (0.23 g; 0.24 mmol; 66%). Crystals suitable for an X-ray structural analysis were grown by layering a saturated acetone solution with hexanes and allowing slow diffusion of the two layers, mp = 281−284 °C. This complex also forms in a reaction of this stoichiometry in acetone. ^1H NMR (acetone-d_6): δ 8.20 (1; s; $HC(Me_2pz)_3$); 6.03 (3; s; 4-H pz); 2.29, 2.18 (9, 9; s, s; 3,5-Me pz). ^{13}C NMR (acetone-d_6): 149.5, 141.2 (3,5-C pz); 107.4 (4-C pz); 75.7 ($HC(Me_2pz)_3$); 12.6, 9.9 (3,5-Me pz). Anal. Calcd for $C_{32}H_{44}F_6N_{12}PTl$: C, 40.62; H, 4.69. Found: C, 40.94; H, 4.75.

$\{[HC(3,5\text{-}Me_2pz)_3]Tl\}PF_6$. An acetone (8 mL) solution of $HC(3,5\text{-}Me_2pz)_3$ (0.47 g; 1.6 mmol) was added to an acetone (7 mL) solution of $TlPF_6$ (0.55 g; 1.6 mmol). The reaction solution was stirred overnight before cannula filtering through a plug of Celite. The filtrate was concentrated to dryness under vacuum. The remaining pale yellow material was washed with toluene (5 mL) and the resultant white solid was dried under vacuum (0.79 g; 1.2 mmol; 77%). Crystals suitable for an X-ray structural analysis were grown by layering a saturated acetone solution with hexanes and allowing slow diffusion of the two layers, mp = 258−264 °C. ^1H NMR (acetone-d_6): δ 8.18 (1; s; $HC(Me_2pz)_3$); 6.15 (3; s; 4-H pz); 2.55, 2.27 (9, 9; s, s; 3,5-Me pz). ^{13}C NMR (acetone-d_6): 150.9, 141.6 (3,5-C pz); 107.6 (4-C pz); 72.2 ($HC(Me_2pz)_3$); 12.5, 9.9 (3,5-Me pz). Anal. Calcd for $C_{16}H_{22}F_6N_6PTl$: C, 29.67; H, 3.42. Found: C, 30.06; H, 3.28.

Table 1. Crystallographic Data for the Structural Analyses

chem formula	$TlC_{32}H_{44}F_6N_{12}P$	$TlC_{16}H_{22}F_6N_6P$
fw	946.11	647.72
crys sys	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	9.210(6)	10.685(2)
b (Å)	13.36(1)	16.200(5)
c (Å)	16.067(8)	13.028(3)
β (deg)	92.48(5)	94.02(2)
V (Å^3)	1975(2)	2249.6(8)
Z	2	4
ρ_{calcd} (g cm^{-1})	1.60	1.91
μ(Mo Kα) (cm^{-1})	42.16	73.04
range of 2θ (deg)	0−48	0−45
temp (°C)	20	20
no. of observns. ($I > 3\sigma$)	1891	2050
goodness of fit	1.71	2.44
abs cor	empirical	empirical
largest peak in final diff map (e/Å^3)	0.43	1.21
residuals: R;[a] R_w[b]	0.029; 0.029	0.042; 0.044

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

Crystallographic Analyses. The crystals used for intensity measurements were mounted in thin-walled glass capillaries. Unit cells were determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing was performed on a Digital Equipment Corp. VAX station 3520 computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Lorentz-polarization and absorption corrections were applied to the data in each analysis. Neutral atom scattering factors were calculated by the standard procedures.[14a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[14b] Full matrix least-squares refinements were carried out for reflections with $I > 3\sigma(I)$ where $\sigma(I)$ was derived from counting statistics. In each analysis, the intensities of three standard reflections were measured every 150 reflections. These showed no significant deviations during the data collection process. The space groups were established from the patterns of systematic absences observed during the collection of intensity data. Each structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms for each structure were calculated by assuming idealized geometries at the carbon atoms, C−H = 0.95 Å. The hydrogen atoms were included in the structure factor calculations but they were not refined.

Results

Addition of $HC(3,5\text{-}Me_2pz)_3$ to a THF solution of $TlPF_6$ results in the immediate precipitation of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ (eq 1). This complex also forms in a reaction of 2/1 stoichiometry, ligand/Tl^+, in acetone. It was fully characterized by ^1H and ^{13}C NMR as well as elemental analysis. No coupling was observed to ^{205}Tl in the ^1H or ^{13}C NMR spectra.

The thallium(I) complex with a ligand to metal ratio of 1/1 was prepared in acetone by the reaction of $HC(3,5\text{-}Me_2pz)_3$ and $TlPF_6$ in a 1:1 ratio (eq 2). Acetone is required in this

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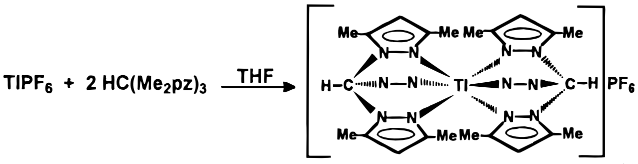

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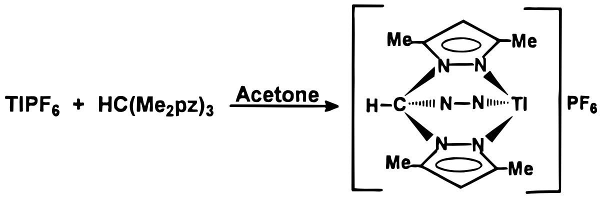

(2)

preparation because a reaction using 1/1 stoichiometry in THF yields insoluble $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$. The ^1H and ^{13}C NMR spectra of $\{[HC(3,5\text{-}Me_2pz)_3]Tl\}PF_6$ are clearly different from $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$, and again no coupling was observed to ^{205}Tl. The NMR of a mixture of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ and $\{[HC(3,5\text{-}Me_2pz)_3]Tl\}PF_6$ in acetone-d_6 show individual spectra for each complex, indicating that the ligands do not exchange fast on the NMR time scale. FAB mass spectra of both compounds yield only the ion of appropriate mass for $\{[HC(3,5\text{-}Me_2pz)_3]Tl\}^+$. Both compounds are soluble in acetone and methylene chloride, and are air stable.

Solid State Structures. $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$. An ORTEP diagram of the cation in $[HC(3,5\text{-}Me_2pz)_3]_2Tl]PF_6$ is shown in Figure 1 and Table 2 lists selected bond distances and angles. The structure of the cation is best described as a trigonally distorted octahedron. The thallium atom sits on a crystallographic center of inversion, thus the planes formed by the three nitrogen donor atoms of each ligand are parallel. Intraligand N−Tl−N bond angles are restrained to less than 90° by the chelate rings and vary from 66.0(1) to 70.2(1)° (average = 67.5°). On the other hand, the *cis* interligand N−Tl−N bond angles are greater than 90° and range from 109.8(1) to 114.0(1)°. All *trans* N−Tl−N angles are 180°, as required by the symmetry. The lone pair on thallium is clearly stereochemically inactive.

The Tl−N bond distances are very similar and range from 2.891(5) to 2.929(5) Å (average = 2.92) Å. An interesting feature of the structure is a substantial tilting of the rings away from an ideal C_{3v} type arrangement. The pyrazolyl rings remain nearly planar, with an average mean deviation from the plane of 0.0077 Å and the largest deviation of 0.0156 Å. The thallium atom lies out of these planes with TlN(n2)−N(n1)C(n5) (n = ring number) torsion angles of 135.6° (n = 1), 111.3° (n = 2), and 122.6° (n = 3) with an average of 123.2°. These angles would be 180° in the absence of the tilting. The N−C1−N angles, which also influence the way the ligands bond the metal, are all very similar and average 111.2°. These bond angles and distances produce intraligand N···N "bite" distances of N12···N22 = 3.375(7), N12···N32 = 3.172(7) and N22···N32 = 3.183(7) Å (average 3.24) Å.

$\{[HC(3,5\text{-}Me_2pz)_3]Tl\}PF_6$. An ORTEP diagram of the cation in $\{[HC(3,5\text{-}Me_2pz)_3]Tl]\}PF_6$ is shown in Figure 2. Table 2 lists selected bond distances and angles. The structure of the cation is a trigonal pyramid. The N−Tl−N bond angles vary from 68.1(3)° to 69.9(3) (average = 69.2°). The Tl−N bond distances are similar and range from 2.64(1) to 2.70(1) Å (average = 2.67) Å. As observed in the structure of $[HC(3,5\text{-}Me_2pz)_3]_2Tl]^+$, ring tilting is also present in this complex, but the degree of tilting is much less. The pyrazolyl rings remain planar, with an average mean deviation from the plane of 0.0038 Å. TlN(n2)−N(n1)C(n5) torsion angles are 157.1° (n = 1), 150.0° (n = 2), and 159.5° (n = 3) with an average of 155.5°. The N−C1−N angles are very similar and average 112.6°. The intraligand N···N "bite" distances are N12···N22 = 3.04(1), N12···N32 = 3.01(1) and N22···N32 = 3.05(1) Å (average 3.03 Å).

A packing diagram of the unit cell is shown in Figure 3. Each thallium is weakly bonded to two fluorine atoms in a PF_6^- counterion, with Tl−F distances of 3.02(1) and 3.14(1) Å. Given the regular arrangement of the N_3Tl central core, these interactions do not greatly impact on the overall structure.

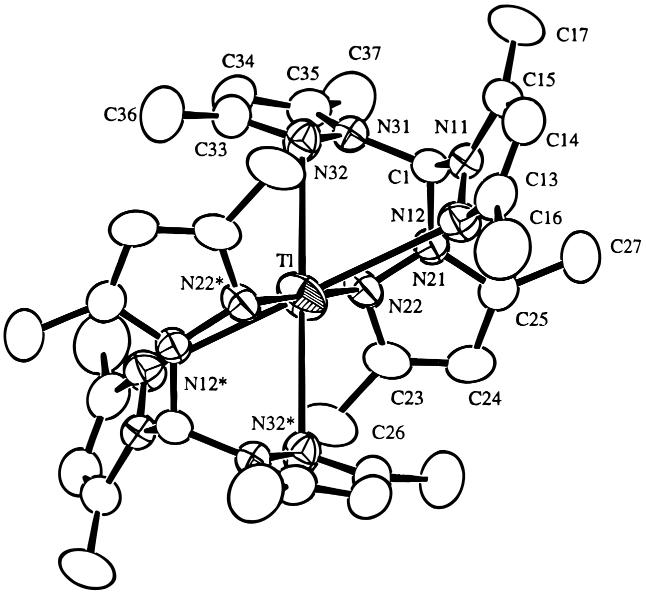

Figure 1. ORTEP diagram of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}^+$.

Table 2. Selected Bond Distances and Bond Angles

Bond Distances in Å

bond	$\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}$-$(PF_6)$	$\{[HC(3,5\text{-}Me_2pz)_3]Tl\}$-$(PF_6)$
Tl−N12	2.929(5)	2.678(9)
Tl−N22	2.938(5)	2.64(1)
Tl−N32	2.891(5)	2.70(1)
N11−C1	1.477(6)	1.43(1)
N21−C1	1.458(7)	1.45(1)
N31−C1	1.443(8)	1.46(1)

Bond Angles in deg

angle	$\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}$-$(PF_6)$	$\{[HC(3,5\text{-}Me_2pz)_3]Tl\}$-$(PF_6)$
N12−Tl−N22	70.2(1)	69.9(3)
N12−Tl−N32	66.0(1)	68.1(3)
N22−Tl−N32	66.2(1)	69.7(3)
N12−Tl−N12*	180.00	
N12−Tl−N22*	109.8(1)	
N12−Tl−N32*	114.0(1)	
N22−Tl−N22*	180.00	
N22−Tl−N32*	113.8(1)	
N32−Tl−N32*	180.00	
N11−C1−N21	110.7(5)	113.8(9)
N11−C1−N31	111.8(5)	112(1)
N21−C1−N31	111.2(4)	112(1)

Discussion

Although a number of six-coordinate thallium(I) complexes are known,[15] as well as an eight-coordinate structure with a fairly regular geometry about thallium(I),[16] the complex $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ appears to be the first example of a coordina-

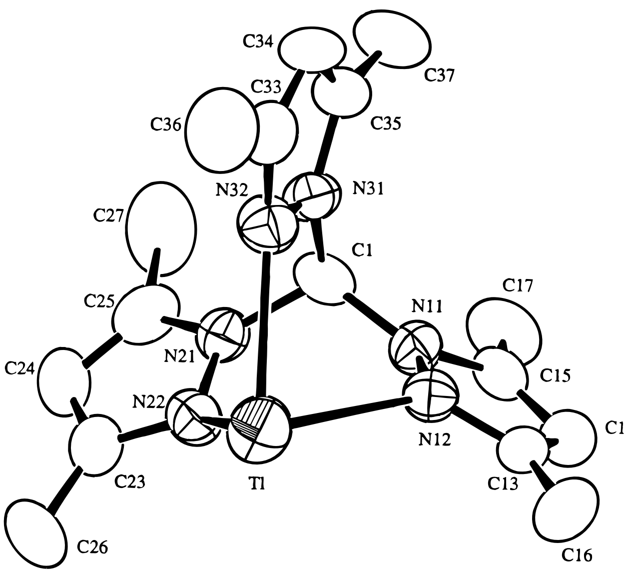

Figure 2. ORTEP diagram of $\{[HC(3,5\text{-}Me_2pz)_3]Tl\}^+$.

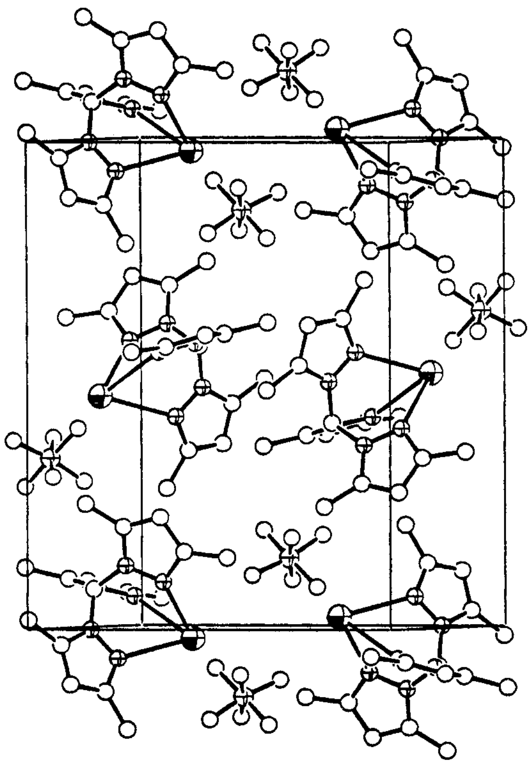

Figure 3. Packing diagram of the unit cell of $\{[HC(3,5\text{-}Me_2pz)_3]Tl\}$-$PF_6$ showing the contacts between the cations and the anions.

tion compound of thallium(I) having a six-coordinate, octahedral geometry to be characterized crystallographically. The symmetry of the complex clearly indicates that the lone pair on thallium does not distort the geometry about the metal atom. The observed trigonal distortion of the octahedron can be explained by the linking of the pyrazolyl rings within the ligand. The structure is very similar to that of $[HB(3,5\text{-}Me_2pz)_3]_2Pb$,[5a] another six-coordinate complex with an inactive lone pair. In fact, the average M−N distances in the two structures differ by 0.31 Å, exactly the amount that the ionic radius of six-coordinate thallium(I) is larger than lead(II).[17] Although the Tl−N distances are long, they are as expected given the large size of six-coordinate thallium(I).

Should one expect any effect of the lone pair from thallium(I) on the geometry? On the basis of a large number of group 2 and 14 metallocene structures, Hanusa has argued[18] that "the lone pair of electrons in the group 14 metallocenes is stereochemically inactive." The basis for the argument is the similarity of the structures of group 2 and 14 metallocenes when the ligand and size of the metal are held constant. Most of the structures are "bent" and this bending can be attributed to van der Waals interligand attractive forces. Certainly the bending in the structures of the group 2 complexes cannot be attributed to lone pair effects.

In addition to $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ (a complex that could be described as having a structure analogous to a metallocene with parallel intraligand N_3 planes), we have also structurally characterized $[HB(pz)_3]_2Pb$.[5a] In this six-coordinate complex, the planes formed by the three nitrogen donor atoms of each ligand are not parallel, analogous to a bent metallocene. Despite the significant differences in the structures, the average Pb−N bond distances in the two [hydrotris(pyrazolyl)borate]$_2$Pb structures are the same. The bonding schemes in both molecules must be similar, with little or no influence from an "active" lone pair in $[HB(pz)_3]_2Pb$. An additional piece of evidence for the lack of influence of lone pairs on these structures that we have noted previously[19] comes from the structure of $[HB(3,5\text{-}Me_2pz)_3]_2Cd$, a molecule that is isomorphous with $[HB(3,5\text{-}Me_2pz)_3]_2Pb$, but lacks a lone pair on the metal. Despite the lack of a lone pair on the metal, the Cd−N bond distances in this molecule differ from the Pb−N distances in the above two structures and the Tl−N distances in $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}$-$PF_6$ by the difference in the ionic radii of the metal atoms.

Given these arguments, *the regular structures of* $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}^+$ *and* $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ *are expected for complexes with bulky ligands*. The most stable arrangement of the ligands dominates the structures. Another example of lead(II) in an octahedral O_6 environment with bulky groups about the lead has been observed for the central lead atom in $[Pb_3(\mu\text{-}O\text{-}t\text{-}Bu)_6]$.[20]

The isolation of a pair of complexes containing one and two polydentate ligands per metal is unusual and allows interesting comparisons. The unexpected compound of the pair is $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$. Numerous [poly(pyrazolyl)borate]Tl compounds are known,[10] and the neutral ligand 1,4,7-triazacyclononane (cycloN$_3$), which has a N_3 donor grouping, also forms the 1/1 complex $[cycloN_3Tl]PF_6$.[21] A 2/1 complex, $[(\eta^5\text{-}C_5H_5)_2Tl]^-$, has also been characterized in metallocene chemistry, and has a bent structure.[22]

The structure most similar to $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ is the recently published thallium(I) structure of the hydrotris(3-(2-pyridyl)-pyrazolyl)borate ligand, $[HB(3\text{-}pypz)_3]Tl$ (py = pyridyl ring).[23] In this structure, the pyrazolyl ring Tl−N

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Table 3. Average M−N Bond Distances (Å), Average MN−NC Torsion Angles (deg) and Average Intraligand N···N Distances (Å) of Selected Complexes

compound	MN−NC torsion angle	M−N dist	av N···N dist	ref
$\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}(PF_6)$	123.2	2.92	3.24	this work
$\{[HC(3,5\text{-}Me_2pz)_3]Tl\}(PF_6)$	155.5	2.67	3.03	this work
$[HC(3,5\text{-}Me_2pz)_3]MoI_3$	177.3	2.20	2.92	7
$[HB(3,5\text{-}Me_2pz)_3]_2Pb$	159.4	2.61	3.18	5a
$[HB(3,5\text{-}Me_2pz)_3]_2Cd$	158.6	2.35	3.10	19
$[HB(3,5\text{-}Me_2pz)_3]_2Zn$	174.6	2.17	2.98	24

distances average 2.67 Å and the nitrogen atoms on the three pyridyl groups also point toward the metal with Tl−N distances much longer at an average 3.18 Å. Interestingly, the average Tl−N distances in this structure of 2.92 Å is the same as for $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$.

The bond distances in six-coordinate $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ are considerably longer than in three-coordinate $\{[HC(3,5\text{-}Me_2pz)_3]Tl\}PF_6$. The average Tl−N distances in $\{[HC(3,5\text{-}Me_2pz)_3]Tl\}PF_6$ (average 2.67 Å) are slightly longer than those reported in most [poly(pyrazolyl)borate]Tl structures (range 2.50−2.61 Å[10a−e,g]) and in the cationic $[cycloN_3Tl]^+$ complex (average 2.61 Å[21]). An average distance of 2.68 Å is observed for [tris(3-anthryl)pyrazolyl)borate]Tl.[10f] Given these similar bond distances and the correlation in bond distances between $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ and $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ with changes in ionic radii, there appear to be only small differences in observed bond distances of analogous tris(pyrazolyl)borate and tris(pyrazolyl)methane complexes, even though there is a change in the overall charge of the complexes. The major change in bond distances is the considerable lengthening observed with the higher coordination number complexes compared to those with lower coordination numbers.

Finally, an interesting structural feature that is clearly evident in the ORTEP diagrams of the two thallium complexes is the tilting of the pyrazolyl rings away from alignment with the metal (a "propeller-like" distortion), especially in the structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$. A discussion of this type of distortion has been noted previously in the analysis of the structures of [HB(Menthpz)$_3$]Tl and [HB(Mementhpz)$_3$]Tl[10d] and also for $[HB(3,5\text{-}Bu^t_2pz)_3]M$ complexes where M is a variety of main group metals.[10g] For the [HB(Menthpz)$_3$]Tl and [HB(Mementhpz)$_3$]Tl pair, the former is not distorted, having almost perfect C_{3v} symmetry, but unfavorable nonbonding interactions caused by bulky substituents on the pyrazolyl rings in the latter complex cause this type of distortion. For complexes such as $[HB(3,5\text{-}Bu^t_2pz)_3]Tl$, the distortion is attributed to the bulky substituent at the 5-position. A result of the tilting is that the lone pairs of electrons on the ligands do not point directly at the thallium atom.

This tilting distortion is evident in complexes of large metal ions with poly(pyrazolyl)borate and poly(pyrazolyl)methane ligands that do *not* contain bulky substituents. Table 3 shows average MN(donor)-N(nondonor)C(pyrazolyl ring) torsion angles for six complexes, all with 3,5-Me$_2$-substitution on the pyrazolyl ring. For complexes with planar pyrazolyl rings, as observed with these complexes, the deviation of this angle from 180° defines the degree of tilting of the rings. Also shown are the average M−N bond distances and the N···N intraligand distances. In the two structures with shorter M−N distances (2.20 Å or less), the torsion angles are near the ideal C_{3v} value of 180°. In the three structures with M−N bond distances in the range of 2.348−2.673 Å, the distortions are moderate. Only in the structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$, the case with very long M−N bond distances, are the distortions pronounced. It has been noted previously with complexes of the $[HB(Mementhpz)_3]^-$ ligand[25] that the size of the metal was important in the tilting distortion, and the size of the metal atom clearly correlates with this tilting distortion for the $[HB(3,5\text{-}Bu^t_2pz)_3]M$ complexes.[10g]

The bite size of either of these ligand types in a C_{3v} arrangement is fixed by the size of the pyrazolyl ring, the B−N or C−N bond distances, and the N−B−N or N−C−N bond angles. In the structure of the free ligand, $HC(3,5\text{-}Me_2pz)_3$,[26] the C−N bond distances (average 1.45 Å) and N−C−N bond angles (average 111°) are essentially the same as in both thallium complexes, indicating that these values cannot change greatly to accommodate different types of metal atoms. The analogous distances and angles in poly(pyrazolyl)borate ligands are also very similar to those in the $HC(3,5\text{-}Me_2pz)_3$ ligand and its complexes. With these values fixed, the only way for the ligand to increase its bite size, as measured by the intraligand N···N distances, is the tilting distortion noted in the structures of both types of ligands with large metals. The severe distortions for $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ open up these N···N distances to an average of 3.24 Å, by far the largest in the table. Even with these distortions in the structure, $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ is an air stable compound with a high melting point. The pyrazolyl rings in these tripodal ligands can tilt away from ideal C_{3v} symmetry to accommodate larger metal atoms or to overcome unfavorable nonbonding interactions from bulky pyrazolyl ring substitution *and still form very stable complexes*. This ability to tilt the pyrazolyl rings is a further demonstration of the versatility of poly(pyrazolyl)borate and poly(pyrazolyl)methane ligands and suggests that they have an even greater potential for ligation than previously recognized.

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Supporting Information Available: Tables of complete data collection information, bond distances, bond angles, positional parameters, and anisotropic thermal parameters (14 pages). Ordering information is given on any current masthead page.

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