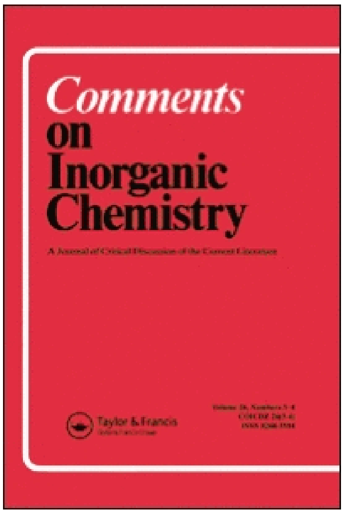

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Tris(Pyrazolyl)Methane Ligands: The Neutral Analogs of Tris(Pyrazolyl)Borate Ligands

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Tris(Pyrazolyl)Methane Ligands: the Neutral Analogs of Tris(Pyrazolyl)Borate Ligands

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Despite the widespread use of tris(pyrazolyl)borate ligands, their isoelectronic, neutral analogs, tris(pyrazolyl)methane ligands, have not been extensively studied. By use of appropriate starting materials, such as $[Cu(NCMe)_4]PF_6$ or $[Cd_2(thf)_5](BF_4)_4$, stable cationic complexes of the ligands $HC(3,5\text{-}Me_2pz)_3$, $HC(3\text{-}Phpz)_3$ and $HC(3\text{-}Bu^tpz)_3$ can be prepared with the metals copper(I), silver(I), cadmium(II), lead(II) and thallium(I). In many cases isoelectronic groups of complexes, such as $[HB(3,5\text{-}Me_2pz)_3]_2Cd$, $\{[HC(3,5\text{-}Me_2pz)_3]Cd[HB(3,5\text{-}Me_2pz)_3]\}^+$, and $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$, have been prepared and shown to have very similar structures. The ^{113}Cd NMR chemical shifts of the three complexes are also very similar. The isoelectronic complexes $\{[HC(pz)_3]_2Pb\}^{2+}$ and $[HB(pz)_3]_2Pb$ have similar distorted six-coordinate structures. The isoelectronic pair $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$ and $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ have very similar octahedral structures in which the lone pair on the lead(II) is stereochemically inactive. Thus, for most cases the tris(pyrazolyl)methane and tris(pyrazolyl)borate ligands bond to these metals in a similar fashion.

Keywords: *tris(pyrazolyl)methane ligands, tris(pyrazolyl)borate ligands, cationic metal complexes, copper(I), silver(I), cadmium(II), lead(II), thallium(I), stereochemically inactive lone pair,* ^{113}Cd *NMR*

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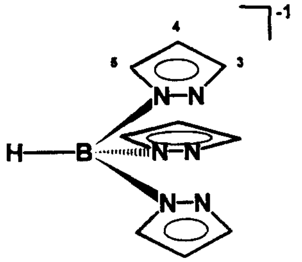
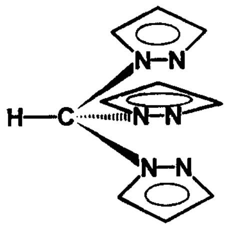
INTRODUCTION

Metal complexes of the tris(pyrazolyl)borate ligand system, first prepared in the late 1960's by Trofimenko, are one of the most extensively studied classes of coordination compounds in inorganic chemistry.[1] This area received substantial impetus in 1986 with the introduction, again by Trofimenko, of "second generation" ligands in which the pyrazolyl rings contain bulky substituents, especially at the 3-position.[2] Much of the recent interest in these ligands centers on the preparation of model complexes for metalloproteins.[2b,c]



Tris(1-pyrazolyl)borate



Tris(1-pyrazolyl)methane

In contrast, the tris(pyrazolyl)methane ligands have received much less attention. These neutral ligands are the isoelectronic analogs to the anionic tris(pyrazolyl)borate ligands, and are formally derived from them by replacing the central boron anion with a carbon atom. An early account of the syntheses of several tris(pyrazolyl)methane ligands was reported by Trofimenko.[3] Trofimenko demonstrated that as with the tris(pyrazolyl)borate analogs, these neutral ligands bind both early (Cr, Mo, W and Mn) and late transition metals (Co, Ni, and Pd).[3], Later, Elguero *et al.* developed an improved procedure for the syntheses of these ligands.[4]

Canty and co-workers have published a series of papers using the tris(pyrazolyl)methane and related ligands to develop the chemistry of the heavier metals in Groups 10 and 11.[5] For example, $\{[HC(pz)_3]AuMe_2\}^+$ has been prepared and found to have square planar geometry in the solid state. The $HC(pz)_3$ ligand is bidentate with the third pz group interacting weakly with the gold atom, causing it to be 0.048 Å above the plane of the *cis*-AuC_2N_2 unit.[5b] The complexes $[HC(pz)_3MMe_3]^+$ (M = Pd, Pt) are isomorphous, with the metal centers in a nearly octahedral geometry.[5c,d] Analogous chemistry of platinum was developed by Clark, who also prepared $[PtMe(HC(pz)_3)L]^+$(L = CO, $H_2C{=}CH_2$, alkynes) derivatives.[6] Meyer has studied the redox properties of ruthenium complexes of the $HC(pz)_3$ ligand.[7] There are also a number of other reports of the use of the tris(pyrazolyl)methane ligand to support interesting transition metal chemistry.[8]

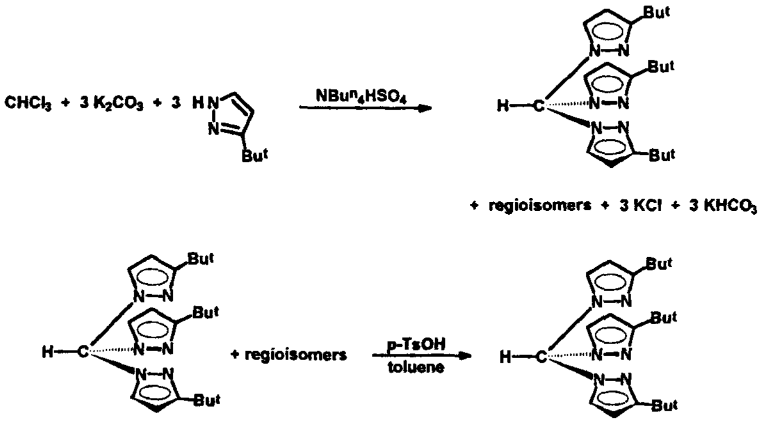
Recently, Enemark has published an account of several molybdenum complexes prepared from the $HC(3,5\text{-}Me_2pz)_3$ ligand.[9] The first solid-state structures of complexes containing this ligand, such as $[HC(3,5\text{-}Me_2pz)_3]MoI_3$, were described. In comparing the chemistry of complexes of the $HC(3,5\text{-}Me_2pz)_3$ ligand with similar complexes of tris(pyrazolyl)borate ligands, it was found that the $HC(3,5\text{-}Me_2pz)_3$ ligand is "much more labile."

Following on our studies using tris(pyrazolyl)borate ligands to prepare neutral complexes of cadmium,[10] gallium,[11] indium,[11] tin[12] and lead,[13] we became interested in studying analogous *cationic* complexes using the tris(pyrazolyl)methane ligands. At the time, only a few reports using tris(pyrazolyl)methane ligands with these metals, the syntheses of the group 12 metal complexes $\{[HC(pz)_3]_2M\}^{2+}$ (M = Zn, Cd, Hg), had been published.[8b,14] Particularly surprising was the fact that the syntheses of "second generation" tris(pyrazolyl)methane ligands, such as $HC(3\text{-}Bu^tpz)_3$, had not been reported.

Reviewed in this article are the syntheses and characterizations of cationic complexes of copper(I), silver(I), cadmium(II), lead(II) and thallium(I) using the ligands $HC(3,5\text{-}Me_2pz)_3$, $HC(3\text{-}Phpz)_3$ and $HC(3\text{-}Bu^tpz)_3$. The chemistry of these cationic complexes will be compared to that of analogous neutral complexes of the same metals containing tris(pyrazolyl)borate ligands. Cationic complexes containing *both* tris(pyrazolyl)methane and tris(pyrazolyl)borate ligands will also be discussed. A particular effort has been made to use the tris(pyrazolyl)methane ligands to prepare cationic complexes that are isoelectronic to known neutral tris(pyrazolyl)borate complexes, or new types of complexes that cannot be prepared with tris(pyrazolyl)borate ligands.

Ligand Preparations

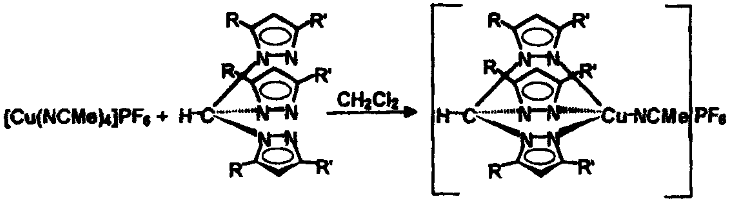
The ligand HC(3-Bu^{t}pz)$_3$ was prepared analogously to the method used to prepare HC(3,5-Me$_2$pz)$_3$,[4] but a mixture of products forms in which the *tert*-butyl group is in either the 3- or 5-position. While it is possible to isolate the desired ligand from this mixture in pure form, this isomer problem was solved by Jameson and Castellano in the preparation of HC(3-Phpz)$_3$.[15] They showed that stirring the isomer mixture in toluene containing a catalytic amount of predried *p*-toluenesulfonic acid causes it to isomerize completely to the desired 3-isomer. This method also works for the mixture of HC(Bu^{t}pz)$_3$ isomers.[16]



Thus, all three ligands needed for these studies are readily prepared. At about the same time as these syntheses were developed, a low yield synthesis of HC(3-Bu^t, 5-Mepz)$_3$ as well as higher yield syntheses of a variety of related "second generation" ligands were reported by Vehrenkamp.[17]

Syntheses and Structures

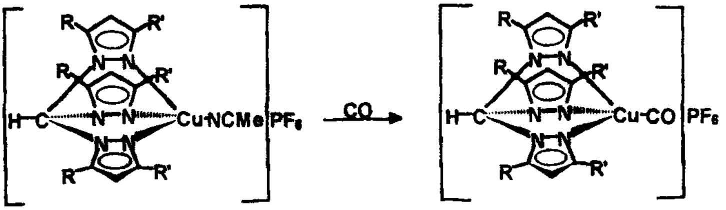
The reaction of [Cu(NCMe)$_4$]PF$_6$ with equimolar amounts of each of the three ligands in CH$_2$Cl$_2$ yields the respective {[tris(pyrazolyl)methane]Cu(NCMe)}PF$_6$ salts.[18]



R = R' = Me
R = H, R' = Ph
R = H, R' = Bu^t

All three compounds are moderately air stable even as solutions. Bubbling dioxygen into CH_2Cl_2 solutions at −78°C provides no color change, though a faint green solution results upon warming to room temperature.

The acetonitrile in the three copper(I) cations can be readily substituted with carbon monoxide under mild conditions.



R = R' = Me
R = H, R' = Ph
R = H, R' = But

These complexes are moderately air stable in solution. The carbon monoxide ligand is not removed under vacuum and remains associated with the copper(I) complexes in the FAB mass spectral analyses.

The solid state structures of $\{[HC(3\text{-}Bu^tpz)_3]Cu(NCMe)\}PF_6$ and $\{[HC(3\text{-}Bu^tpz)_3]Cu(CO)\}PF_6$ (Fig. 1) were determined by X-ray crystallography.[18] It is particularly interesting to compare the carbonyl structure to tris(pyrazolyl)borate analogs because the first stable carbonyl complex of copper was $[HB(pz)_3]CuCO$.[19]Although the structure of $[HB(3\text{-}Bu^tpz)_3]Cu(CO)$[20] has not been reported, selected bond distances and angles of three related structures (assuming a numbering scheme parallel to that in Fig. 1), along with those for $\{[HC(3\text{-}Bu^tpz)_3]Cu(CO)\}^+$, are given in Table I.

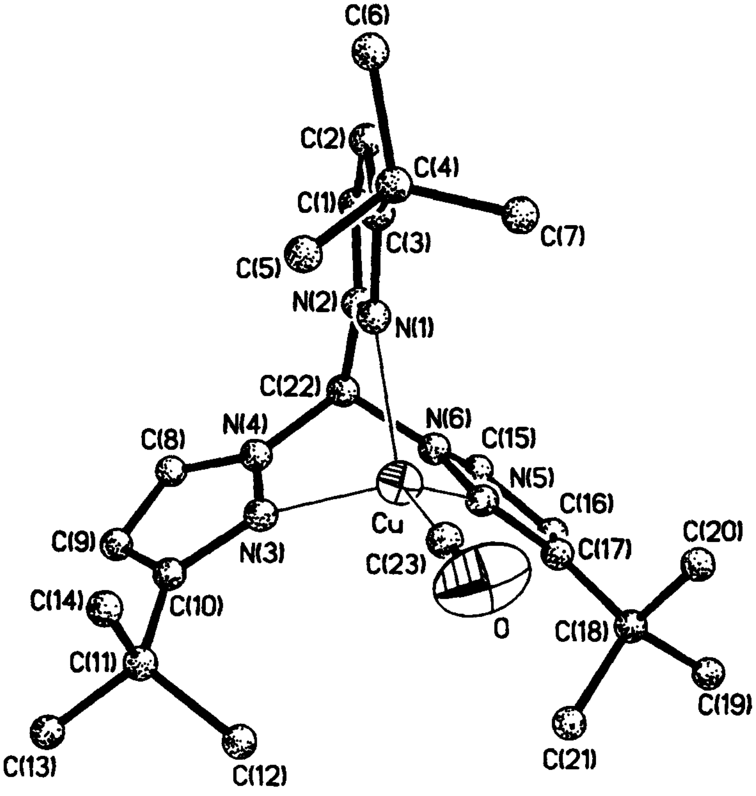


FIGURE 1 ORTEP diagram of $\{[HC(3\text{-}Bu^tpz)_3]Cu(CO)\}^+$

The metrical parameters of the four structures are very similar, especially given that the tris(pyrazolyl)methane complex is cationic, and the substituents on the pyrazolyl rings in the three tris(pyrazolyl)borate structures range from strongly electron donating to strongly electron withdrawing. The only major difference is the C(22)-N distance is 0.1 Å shorter than the B-N distances. This shorter distance is expected given the smaller covalent radius of carbon versus boron.[23]

TABLE I Selected Bond Distances (Å) and Angles (deg) for $\{[HC(3\text{-}Bu^tpz)_3]Cu(CO)\}^+$ (A), $[HB(pz)_3]CuCO$[19b] (B), $[HB(3,5\text{-}Pr^i{}_2pz)_3]CuCO$[21] (C) and $[HB(3,5\text{-}(CF_3)_2pz)_3]CuCO$[22] (D)

Distances	*A*	*B*	*C*	*D*
Cu-N(ave)	2.079	2.048(4)	2.018	2.052
Cu-C(23)	1.778(10)	1.755(11)	1.769(8)	1.808(4)
C(23)-O	1.133(9)	1.120(13)	1.118(10)	1.110(5)
C(22) or B-N(ave)	1.442	1.542(5)	1.547	1.568
Angles				
Cu-C(23)-O	176.8(9)	180		179.8(4)
C(23)-Cu-N(ave)	126.0	124.4(1)	124.7	125.3
N-Cu-N(ave)	89.0	91.3(2)	90.8	90.0
N-C(22)-N or N-B-N(ave)	111.0	108.3(4)	109.0	108.3

Infrared CO Stretching Frequencies

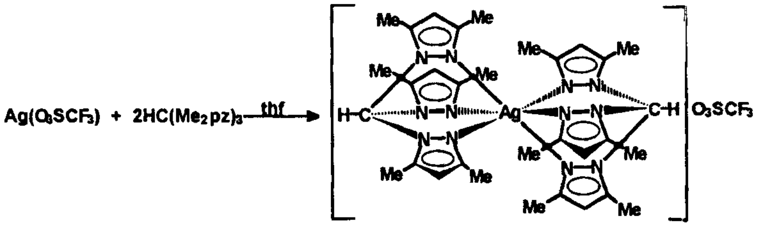
Table II shows the carbonyl stretching frequencies of the new cationic complexes and selected tris(pyrazolyl)borate analogs. As expected, in comparing complexes with similar substitution on the pyrazolyl rings, the values for the cationic complexes are higher, indicating weaker pi backbonding with the CO ligand. A similar increase in stretching frequency was noted previously for the comparison of analogous neutral tris(pyrazolyl)borate and cationic tris(imidazolyl)phosphine complexes.[24] It is interesting to note that the neutral complex $[HB(3,5\text{-}(CF_3)_2pz)_3]CuCO$, containing strongly electron withdrawing CF_3 groups, has a higher stretching frequency than the cationic tris(pyrazolyl)methane complexes.

TABLE II Carbonyl Stretching Frequencies for Tris(pyrazolyl)methane and Tris(pyrazolyl)borate Copper(I) Carbonyl Complexes

Complex	ν *CO(cm⁻¹)*	*Complex*	ν *CO (cm⁻¹)*
$\{[HC(3,5\text{-}Me_2pz)_3]CuCO\}^+$	2113	$[HB(3,5\text{-}Me_2pz)_3]CuCO$[19a]	2066
$\{[HC(3\text{-}Phpz)_3]CuCO\}^+$	2104	$[HB(3,5\text{-}Ph_2pz)_3]CuCO$[21]	2086
$\{[HC(3\text{-}Bu^tpz)_3]CuCO\}^+$	2100	$[HB(3\text{-}Bu^tpz)_3]CuCO$[20]	2069
		$[HB(3,5\text{-}(CF_3)_2pz)_3]CuCO$[22]	2137

The syntheses of stable cationic copper(I) carbonyls indicated the possible preparation of analogous silver(I) complexes with tris(pyrazolyl)methane ligands. Bruce has prepared a variety of silver(I) complexes employing anionic polypyrazolylborate ligands,[25] and very recently Dias reported the isolation and structural characterization of rare silver(I) carbonyl and silver(I) isonitrile complexes employing the highly fluorinated tris(pyrazolyl)borate ligand $[HB(3,5\text{-}(CF_3)_2pz)_3]^-$.[26]

The reaction of $Ag(O_3SCF_3)$ with two molar equivalents of $HC(3,5\text{-}Me_2pz)_3$ in thf results in the immediate precipitation of $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}(O_3SCF_3)$.[27] The same product is obtained in reactions using a 1/1, metal/ligand ratio.



A six coordinate trigonally distorted octahedral geometry about the silver(I) ion is observed in the structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}(O_3SCF_3)$, Fig. 2.[27] The intraligand Ag-N bond distances vary with two similar (2.461(7), 2.487(7) Å) and one longer (2.596(7) Å) distance (average = 2.51 Å). The intraligand N-Ag-N bond angles are restricted to an average of 77° by the chelate rings, causing correspondingly larger interligand N-Ag-N bond angles (average = 103°). The two planes formed by the three nitrogen donor atoms of each ligand are parallel, a consequence of the silver ion residing on a crystallographic center of inversion.

The pyrazolyl rings are significantly tilted with respect to the C_3 axis formed by the metal and the two methyne carbon atoms (a propeller-like distortion). Ideally, for maximum overlap with the lone pair on the donor nitrogen atoms, the metal would lie in the plane of each pyrazole ring. Any deviation where the metal lies out of this planarity can be measured by the AgN(n1)-N(n2)C(n3) (where n denotes the ring

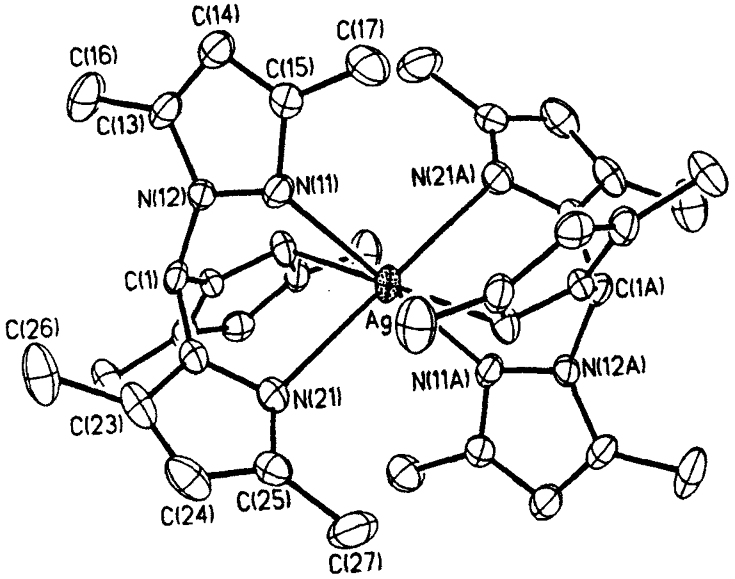
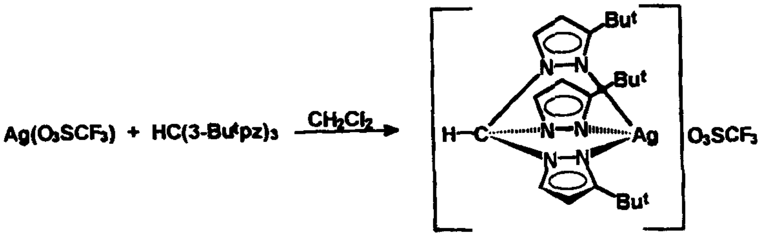


FIGURE 2 ORTEP diagram of $\{[HC(3,5\text{-}Me_2pz)_3]_2Ag\}^+$

number) torsion angle, an angle that is ideally 180° for these planar rings. The measured torsion angles range from 126.5° to 145.9° (average = 137°).

There are no analogous silver compounds with tris(pyrazolyl)borate ligands. In fact, it appears that there are no six coordinate $[poly(pyrazolyl)borate)_2M]^-$ complexes.[1,2a] In all cases, metals with a + 1 charge form neutral (poly(pyrazolyl)borate)M complexes. As outlined below, the ability to form octahedral $[(tris(pyrazolyl)methane)_2M]^+$ complexes with a variety of metals (Ag^+, Tl^+, Li^+, Na^+) is a unique feature of tris(pyrazolyl)methane ligands when compared to tris(pyrazolyl)borate ligands.

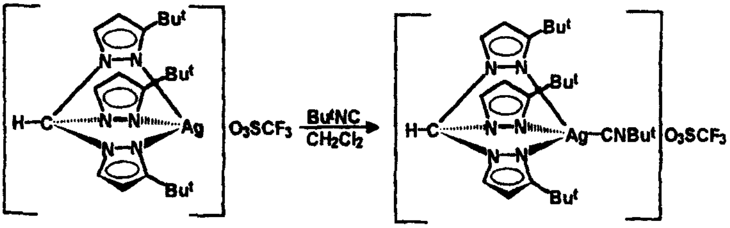
A 1/1 ligand to metal product could be obtained with the bulky $HC(3\text{-}Bu^tpz)_3$ ligand.[27] As expected, the bulky *tert*-butyl substituents in the 3-positions of the rings block the formation of the product with a ligand to metal ratio of 2/1. These aliphatic substituents also enhance the solubility of $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$ in common polar organic and halogenated solvents.



In the structure of $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$, the coordination geometry about the silver atom is pseudo-tetrahedral.[27] The three Ag-N bond distances vary from 2.343(6) to 2.410(6) Å (average = 2.38 Å). A bonding interaction exists with an oxygen atom from the triflate anion, yet the anion is disordered, which precludes an accurate determination of the Ag-O bonding distance. Intraligand N-Ag-N bond angles are restrained by the chelate rings to an average of 80°. Tilting of the pyrazolyl rings in this structure is minimal (average AgN-NC torsion angle = 178°).

Stirring a CH_2Cl_2 solution of $\{[HC(3;Bu^tpz)_3]Ag\}(O_3SCF_3)$ under an atmosphere of carbon monoxide does not produce any indication of a CO complex. In contrast, under the same conditions $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(BF_4)$, prepared from mixing $AgBF_4$ and $HC(3\text{-}Bu^tpz)_3$ in CH_2Cl_2, leads to the formation of a carbon monoxide complex.[27] A new band in the IR spectrum of this solution is observed at 2154 cm^{-1}, a band that is not observed in carbon monoxide saturated solutions that contain only $AgBF_4$. Also, a solid state IR analysis (nujol) of the solid formed by addition of hexanes to the CO saturated CH_2Cl_2 solution shows a CO stretching frequency at 2160 cm^{-1}. This solid readily loses carbon monoxide upon standing or when redissolved in CH_2Cl_2. Unfortunately, crystals suitable for an X-ray structural determination or an analytical sample could not be obtained due to this lability of the CO ligand. The first isolated carbonyl complex of silver supported by a tris(pyrazolyl)borate ligand, $[HB(3,5\text{-}(CF_3)_2pz)_3]AgCO$, has a CO stretching frequency of 2162 cm^{-1} in hexane and 2178 cm^{-1} in the solid.[26]

The more basic ligand *tert*-butylisocyanide readily reacts with $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$.[27] The CN stretching frequency is at 2202 cm^{-1}, compared to a value of 2214 cm^{-1} for



$[HB(3,5\text{-}(CF_3)_2pz)_3]AgCNBu^t$. As observed in the CO complexes, the higher stretching frequencies indicate that the CF_3 groups make the silver in the $[HB(3,5\text{-}(CF_3)_2pz)_3]Ag$ group more acidic than in cationic $\{[HC(3\text{-}Bu^tpz)_3]Ag\}^+$.

The silver atom in the structure of $\{[HC(3\text{-}Bu^tpz)_3]Ag(CNBu^t)\}(O_3SCF_3)$ is four coordinate with a pseudo-tetrahedral geometry. The Ag-N bond distances vary greatly, from 2.301(6) to 2.449(6) Å, yet the average distance (Table III) is comparable to that observed in the structures of $\{[HC(3\text{-}Bu^tpz)_3]Ag\}(O_3SCF_3)$[27] and $[HB(3,5\text{-}(CF_3)_2pz)_3]AgCNBu^t$.[26] As observed with the copper complexes, the structures of $\{[HC(3\text{-}Bu^tpz)_3]Ag(CNBu^t)\}^+$ and $[HB(3,5\text{-}(CF_3)_2pz)_3]AgCNBu^t$ are very similar, with the only difference being the expected shorter C-N bond distance in the backbone of the $HC(3\text{-}Bu^tpz)_3$ ligand compared to the B-N distance in $[HB(3,5\text{-}(CF_3)_2pz)_3]^-$.

TABLE III Selected Bond Distances (Å) and Angles (deg) for $\{[HC(3\text{-}Bu^tpz)_3]Ag(CNBu^t)\}^+$ and $[HB(3,5\text{-}(CF_3)_2pz)_3]AgCNBu^t$

Distances	$\{[HC(3\text{-}Bu^tpz)_3]Ag(CNBu^t)\}^+$	$[HB(3,5\text{-}(CF_3)_2pz)_3]AgCNBu^t$
Cu-N(ave)	2.37	2.37
Cu-C	2.053(7)	2.059(4)
C-N	1.150(7)	1.139(5)
C(22) or B-N(ave)	1.44	1.59
Angles		
Cu-C-N	168.2(6)	173.7 (4)
C-Cu-N(ave)	131	132
N-Cu-N(ave)	81	80

CADMIUM CHEMISTRY

The chemistry of cadmium(II) using poly(pyrazolyl)borate ligands has been extensively studied.[10,28] The desire to prepare model complexes for zinc metalloprotein sites is the main driving force for the syntheses of monomeric cadmium(II) compounds in which the coordination sphere about the cadmium atom can be carefully controlled. A main impetus for the development of this chemistry is the fact that cadmium has two important isotopes that are NMR active with spins = 1/2. A number of research groups have been using ^{113}Cd NMR as a "spin spy" in the study of zinc-containing proteins.[29] The strategy here is to replace the zinc, a metal with few good spectroscopic handles, with cadmium and use NMR to explore the properties of the proteins. By changing from tris(pyrazolyl)borate to tris(pyrazolyl)methane ligands, complexes of the general formula $(ligand)_2Cd$ change from being neutral to having a 2+ charge. The effect of this change in charge on the solid state structures and the ^{113}Cd NMR shifts was of particular interest, as was the comparison of the bonding properties of the two ligand types in very similar complexes.

Syntheses of Complexes

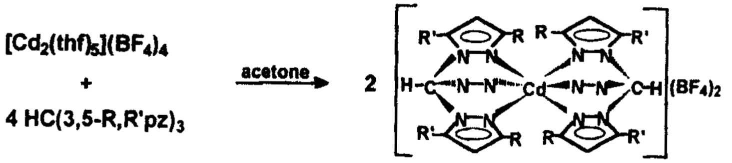
Although $[poly(pyrazolyl)borate]_2Cd$ complexes are readily prepared from the ligand salts and either $CdCl_2$ or $Cd(NO_3)_2$, these cadmium starting materials did not react with tris(pyrazolyl)methane ligands. To overcome this problem, $[Cd_2(thf)_5](BF_4)_4$ was prepared by treating a thf suspension of $Cd(acac)_2$ with $HBF_4 \cdot Et_2O$.[30]

$$2Cd(acac)_2 + 4HBF_4 \cdot Et_2O \xrightarrow{thf} [Cd_2(thf)_5](BF_4)_4 + 4\,Hacac$$

This cadmium dimer is insoluble in thf. If more soluble derivatives are desired, a $B[3,5\text{-}(CF_3)_2C_6H_3]_4{}^+$ salt can be prepared.[31]

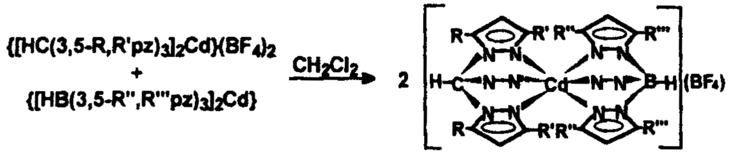
$$[Cd_2(thf)_5](BF_4)_4 + 4Na\{B[3,5-(CF_3)_2C_6H_3]_4\} \xrightarrow{thf/CH_2Cl_2} 2[Cd(thf)_3]\{B[3,5-(CF_3)_2C_6H_3]_4\}_2 + 4NaBF_4$$

Reactions of $[Cd_2(thf)_5](BF_4)_4$ with tris(pyrazolyl)methane ligands in acetone result in the immediate precipitation of the respective dications. Mixed monocationic tris(pyrazolyl)borate/tris(pyrazolyl)methane complexes of cadmium(II) are prepared by the conproportionation reactions



R = R' = Me
R = Ph, R' = H

of the dicationic tris(pyrazolyl)methane complexes with neutral tris(pyrazolyl)borate complexes in refluxing CH_2Cl_2.



R = R' = R'' = R''' = Me
R = R' = Me, R'' = Ph, R''' = H
R = H, R' = Ph, R'' = R''' = Me
R = H, R' = Ph, R'' = Ph, R''' = H

These complexes exchange tris(pyrazolyl)methane ligands on the chemical time scale, but not rapidly on the NMR time scale. Mixing $\{[HC(3\text{-}Phpz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^+$ with $HC(3,5\text{-}Me_2pz)_3$ leads to exchange of the $HC(3\text{-}Phpz)_3$ ligand and formation of $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^+$. The NMR spectrum of a mixture of $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^+$ and $HC(3\text{-}Phpz)_3$ shows both compounds with no exchange products observed. A mixture of $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^+$and $HC(3,5\text{-}Me_2pz)_3$ shows separate ^1H NMR signals for the free and coordinated $HC(3,5\text{-}Me_2pz)_3$. Also, the ^{113}Cd NMR resonance observed for this mixture is the same as for the pure complex (vide infra).

Preferential bonding of the $HC(3,5\text{-}Me_2pz)_3$ ligand is also shown with the dications. The ^1H NMR spectrum of a mixture of $HC(3\text{-}Phpz)_3$ and $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$ shows the spectra of the individual two compounds, and the ^{113}Cd NMR spectrum shows the resonance for pure

$\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$. The same spectra are observed for a mixture of $\{[HC(3\text{-}Phpz)_3]_2Cd\}^{2+}$ and $HC(3,5\text{-}Me_2pz)_3$ showing that the $HC(3,5\text{-}Me_2pz)_3$ ligand completely displaced the $HC(3\text{-}Phpz)_3$ leading to the formation of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$ and free $HC(3\text{-}Phpz)_3$.

Solid State Structures

The solid state structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$ was determined by X-ray crystallography (Fig. 3). Selected bond distances and angles are reported in Table IV, along with the comparable information for $[HB(3,5\text{-}Me_2pz)_3]_2Cd$.[10a] The space group is $R\overline{3}$, in both structures.

TABLE IV Selected Bond Distances (Å) and Angles (deg) for $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$ (A), $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^{+}$(B) and $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ (C)

Distances	*A*	*B*[a]	*C*
Cd-N(methane)	2.321(10)	2.38	
Cd-N(borate)		2.29	2.348(5)
C(methyne)-N	1.439(7)	1.44	
B-N		1.54	1.533(6)
Angles			
N-Cd-N(methane intraligand)	80.0(4)	80	
N-Cd-N(borate intraligand)		84	82.7(7)
N-Cd-N(*trans*-interligand)	180.0(1)	173	180.0(1)
N-Cd-N(*cis*-interligand)	100.0(4)	99	97.3(1)
N-C(methyne)-N	109.6(4)	112	
N-B-N		110	110.6(4)

[a] Average values.

The structure of the analogous mixed-ligand complex $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}(BF_4)$ was also determined by X-ray, but the tris(pyrazolyl)methane and tris(pyrazolyl)borate ligands were disordered. In contrast, there was no disorder in the structure of

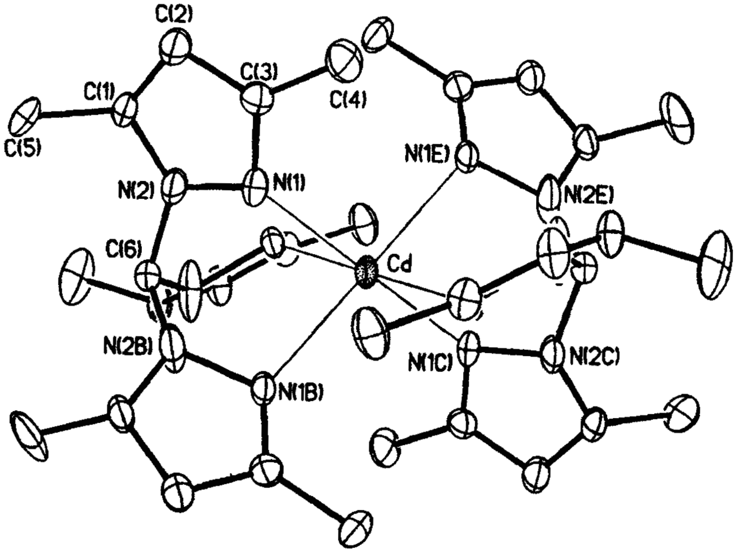


FIGURE 3 ORTEP diagram of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$

$\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$.[32] The metrical parameters are outlined in Table IV.

The three structures are very similar. The Cd-N bonds are only 0.09 Å shorter in $([HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^+$ for $[HB(3,5\text{-}Me_2pz)_3]^-$ than for $HC(3,5\text{-}Me_2pz)_3$. The average C-N distance (2.33 Å) is nearly the same as in the two homoleptic structures. As expected,[23] the C(methyne)-N distances are 0.1 Å shorter than the B-N distance. All of the bond angles are also similar. *The tris(pyrazolyl)borate and tris(pyrazolyl)methane ligands bond to cadmium(II) in a very similar fashion.*

^{113}Cd NMR

Table V list the solution ^{113}Cd NMR shifts of the tris(pyrazolyl)methane complexes along with the analogous tris(pyrazolyl)borate complexes. The chemical shifts for the three complexes containing only 3,5-Me$_2$

substitution on the pyrazolyl rings are very close (the ^{113}Cd chemical shift range is over 900 ppm[29]), even though the charge changes from 2+ to neutral. In all cases, introduction of ligands containing 3-Ph substitution, on either the tris(pyrazolyl)methane or tris(pyrazolyl)borate ligands, has a much greater effect, causing a shift of about 50 ppm per ligand. This difference was shown for $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ and $[HB(3\text{-}Phpz)_3]_2Cd$ to be the result of longer Cd-N bond distances in the latter structure.[10c]

TABLE V Cadmium-113 Chemical Shifts

Compound	*Chemical Shift*
$[HB(3,5\text{-}Me_2pz)_3]_2Cd$	202
$\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^+$	211
$\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$	207
$[HB(3,5\text{-}Me_2pz)_3][HB(3\text{-}Phpz)_3]Cd$	148
$\{[HC(3,5\text{-}Me_2pz)_3][HB(3\text{-}Phpz)_3]Cd\}^+$	140
$\{[HC(3\text{-}Phpz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^+$	168
$[HB(3\text{-}Phpz)_3]_2Cd$	94
$\{[HC(3\text{-}Phpz)_3][HB(3\text{-}Phpz)_3]Cd\}^+$	110
$\{[HC(3\text{-}Phpz)_3]_2Cd\}^{2+}$	116

Thus, *only small differences in the ^{113}Cd chemical shifts are observed with the charge differences caused by changing from tris(pyrazolyl)borate to tris(pyrazolyl)methane ligands, if the substitution on the pyrazolyl rings is not varied.* This result is readily explained by the similar structural parameters for the three complexes shown in Table IV. An interesting conclusion from these structural studies and ^{113}Cd chemical shift data is that the charge in poly(pyrazolyl)borate ligands is highly localized on the boron atom. For cadmium, the bonding properties of tris(pyrazolyl)methane ligands are very similar to tris(pyrazolyl)borate ligands.

Zinc Chemistry

Analogous chemistry with zinc(II) has not been as successful. Vahrenkamp has reported an extensive effort designed mainly to prepare tris(pyrazolyl)methaneZnX complexes, in which X was hoped to be water or an OH^- group, in order to model zinc-containing enzymes.[17] Although a number of compounds of these ligands were prepared, the "tris(pyrazolyl)methanes were not reliably tridentate and not reliably stable when exposed to zinc salts in the presence of ligating anions, aqua ligands, or alcohol solvents." The complex $\{[HC(3,4,5\text{-}Me_3pz)_3]_2Zn\}(ClO_4)_2$ was prepared and characterized structurally. It is six-coordinate, with a structure similar to $[HC(3,5\text{-}Me_2pz)_3]_2Cd(BF_4)_2$, given the smaller size of zinc.

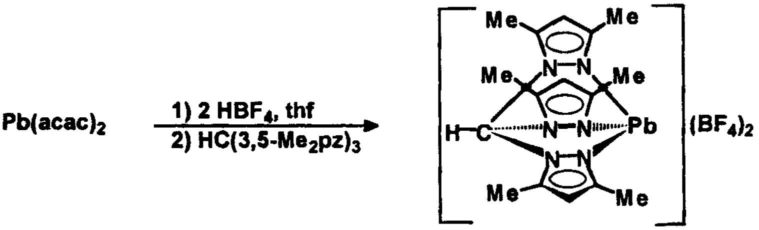
A frequent problem in these studies was decomposition of the ligand, leading to free pyrazole.[17] Analogous results have been observed in attempts to prepare zinc complexes of the $HC(3\text{-}Bu^tpz)_3$ ligand using the synthetic methods that were successful with cadmium.[33] Zinc(II) seems to be unusual in its ability to decompose tris(pyrazolyl)methane ligands, especially those with bulky substituents on the pyrazolyl rings.

LEAD CHEMISTRY

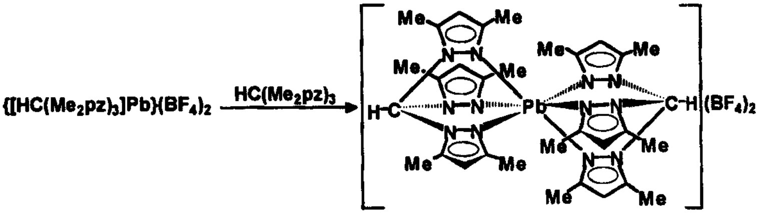
The chemistry of lead(II) is of particular interest to compare with cadmium(II) because lead(II) has a valence shell lone pair not present on cadmium(II). Using poly(pyrazolyl)borate ligands, a variety of structures were observed.[13] The potentially tridentate ligands in $[B(pz)_4]_2Pb$ are only bidentate leading to a distorted four-coordinate structure. The complex $[HB(pz)_3]_2Pb$ is six-coordinate, but has a highly distorted structure. Both of these structures appear to be strongly influenced by the lone pair on lead. In contrast, $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ has a trigonally distorted octahedral structure *with a stereochemically inactive lone pair.*

Syntheses of Complexes

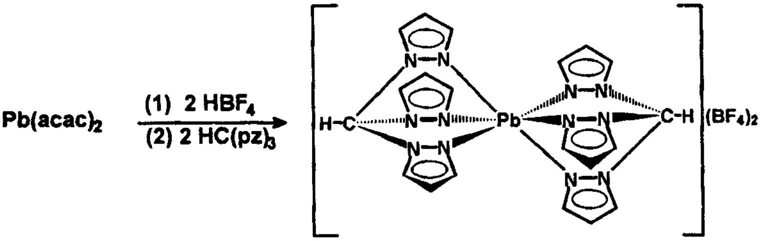
As observed with cadmium, reactions of $HC(3,5\text{-}Me_2pz)_3$ and $PbCl_2$ or $Pb(NO_3)_2$ in thf were not successful. Protonation of a thf suspension of $Pb(acac)_2$ with $HBF_4{\bullet}Et_2O$ generates a soluble Pb^{+2} ion that reacts with $HC(3,5\text{-}Me_2pz)_3$ to precipitate $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ in high yield.[34] 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.



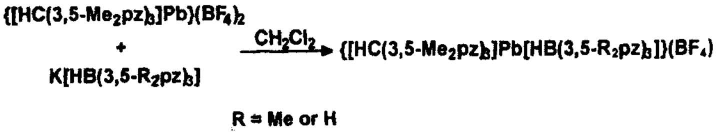
The complex $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$, with a ligand to metal ratio of 2/1, is prepared by layering a saturated acetone solution of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ that also contains a five-fold excess of $HC(3,5\text{-}Me_2pz)_3$ with hexanes.[34] This complex cannot be prepared directly from the "$Pb(BF_4)_2$" intermediate and excess ligand because of the precipitation of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$.



Reaction of two equivalents of $HC(pz)_3$ with the "$Pb(BF_4)_2$" intermediate yields $\{[HC(pz)_3]_2Pb\}(BF_4)_2$ directly.



The reactions of $\{[HC(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)_2$ with one equivalent of $K[HB(3,5\text{-}Me_2pz)_3]$ or $K[HB(pz)_3]$ yield 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.[34]



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 extraction of the neutral ligand and formation of $\{[HB(3,5\text{-}Me_2pz)_3]Pb\}(BF_4)$ or $\{[HB(pz)_3]Pb\}(BF_4)$, respectively. 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 an X-ray structural analysis were grown by addition of five equivalents 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.

Solid State Structures

Figure 4 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 shown in Table VI. The structure of the cation is a trigonally distorted octahedron.[34] 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 causing the trigonal distortion. *The lone pair on the lead(II) is clearly stereochemically inactive.*

The structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$ is very similar to that of $[HB(3,5\text{-}Me_2pz)_3]_2Pb$[13a] (Table VI). As observed in the above comparisons of analogous tris(pyrazolyl)methane and tris(pyrazolyl)borate structures, the intraligand N-Pb-N angle is slightly smaller in

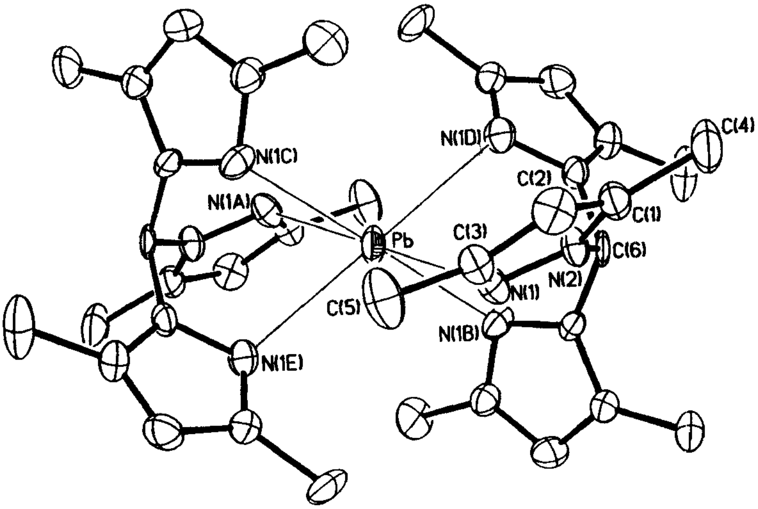


FIGURE 4 ORTEP diagram of $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$

$\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$, a consequence of the shorter C-N bond compared to the B-N bond.

TABLE VI Selected Bond Distances (Å) and Bond Angles (deg) for $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$ and $[HB(3,5\text{-}Me_2pz)_3]_2Pb$

Distance	$\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$	$[HB(3,5\text{-}Me_2pz)_3]_2Pb$
Pb-N(1)	2.635(7)	2.610(5)
C(6)-N(2)	1.451(9)	
B-N		1.553(4)
Angle		
N(1)-Pb-N(1A)	180.0	180.0
N(1)-Pb-N(1B)	72.4(3)	75.2(1)
N(1)-Pb-N(1C)	107.6(3)	104.8(1)
N(2)-C(6)-N(2B)	111.4(6)	
N-B-N		110.6(4)

Figure 5 shows the ORTEP diagram of the cation in $\{[HC(pz)_3]_2Pb\}(BF_4)_2$. 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)°, 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.

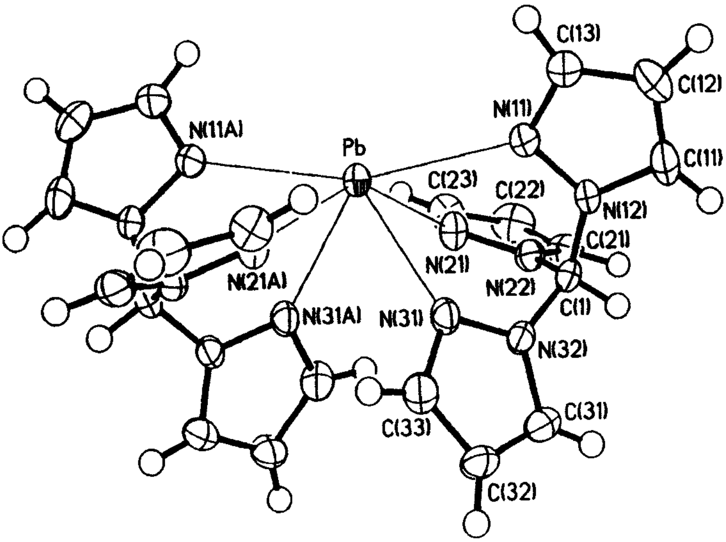


FIGURE 5 ORTEP diagram of $\{[HC(pz)_3]_2Pb\}^{2+}$

This structure of $\{[HC(pz)_3]_2Pb\}^{2+}$ is similar to that of its isoelectronic analog $[HB(pz)_3]_2Pb$ in that both are highly distorted from a regular six-coordinate geometry.[13a] 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 observed in the structure of $\{[HC(pz)_3]_2Pb\}^{2+}$, although the average of 2.61 Å is similar. 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.[35] In both of these lead structures the "open" space correlates with longer adjacent bond distances.

It might have been predicted, based solely on charge considerations, that the neutral tris(pyrazolyl)methane ligands will not bond as tightly to the metal as the anionic tris(pyrazolyl)borate ligands. This bonding difference is *not* evident in the structures of these two homoleptic pairs of isoelectronic complexes of lead(II). As observed in the cadmium(II) structures, these lead(II) structures indicate that the bonding properties of tris(pyrazolyl)methane and tris(pyrazolyl)borate ligands are very similar.

This same conclusion was made above from the structure of the mixed-ligand, cadmium(II) complex $\{[HC(3,5\text{-}Me_2pz)_3]Cd[HB(3,5\text{-}Me_2pz)_3]\}^+$.[30] Both ligands are tridentate in this complex. In contrast, the structure of $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}(BF_4)$ is very asymmetric, Fig. 6. The lead(II) ion is five-coordinate bonded to 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 remaining nitrogen donor atom N(21) from the tridentate $[HB(3,5\text{-}Me_2pz)_3]^-$ lying at the apex. The three Pb-N bonding distances from the tridentate $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand are short (average 2.43 Å), while both Pb-N bonding distances from $HC(3,5\text{-}Me_2pz)_3$ are much longer (2.745(7) Å and 2.827(7) Å). Presumably, the lone pair of electrons on the lead(II) ion occupies the open face of the square pyramid base.

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. This structure could indicate stronger bonding for the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand versus $HC(3,5\text{-}Me_2pz)_3$, but analogous five-coordinate structures are observed for both $[HB(3,5\text{-}Me_2pz)_3]_2Sn$[36] and $[HB(pz)_3]_2Sn$,[12] complexes containing only tris(pyrazolyl)borate ligands.

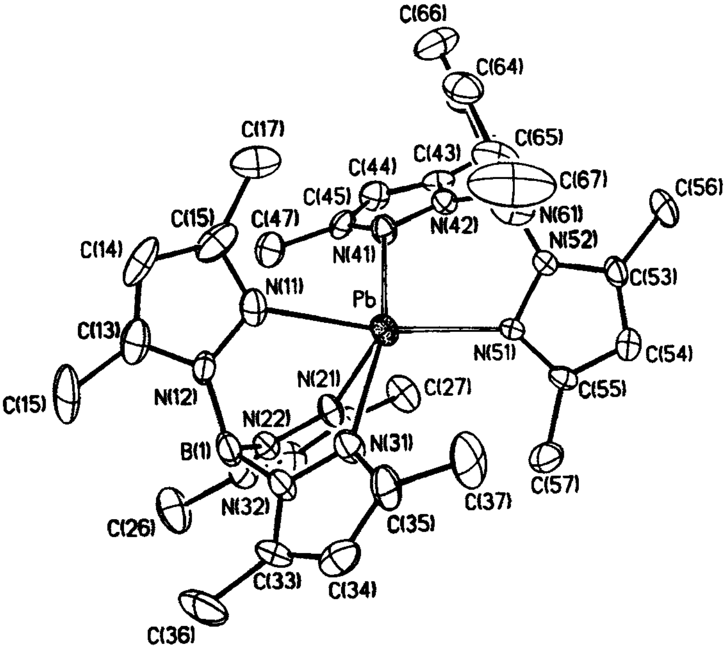
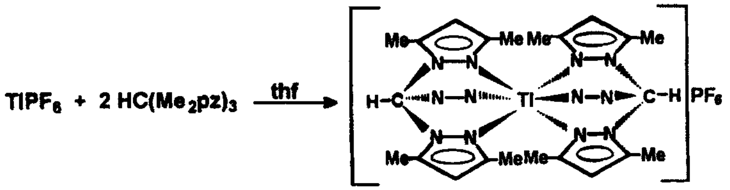


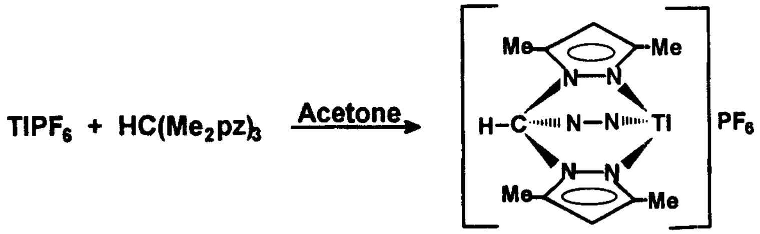
FIGURE 6 ORTEP diagram of $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}^+$

THALLIUM CHEMISTRY

Addition of $HC(3,5\text{-}Me_2pz)_3$ to a thf solution of $TlPF_6$ results in the immediate precipitation of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$. This complex also forms in a reaction of 2/1 stoichiometry, ligand/Tl^+, in acetone.[38]



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.



Acetone is required in this preparation because a reaction using 1/1 stoichiometry in THF yields insoluble $\{[HC(3,5\text{-}Me_2pz))_3]_2Tl\}PF_6$.

The structures of both complexes have been determined crystallographically.[38] The cation in $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}PF_6$ is best described as a trigonally distorted octahedron, Fig. 7. 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°). 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) (average = 2.92) Å. An interesting feature of the structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}^+$ is a substantial tilting of the rings away from an ideal C_{3v} type arrangement. The pyrazolyl rings remain nearly planar, but 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°.

As mentioned above in the silver chemistry section, there are no analogous thallium(I) compounds to $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}^+$ with tris(pyrazolyl)borate ligands. Numerous [poly(pyrazolyl)borate]Tl compounds are known.[39] This ability to form 2/1 complexes with metals in the +1 oxidation state is a unique feature of tris(pyrazolyl)methane ligands when compared to tris(pyrazolyl)borate ligands. Analogous complexes of Li^+ and Na^+ have also been prepared.[37, 40]

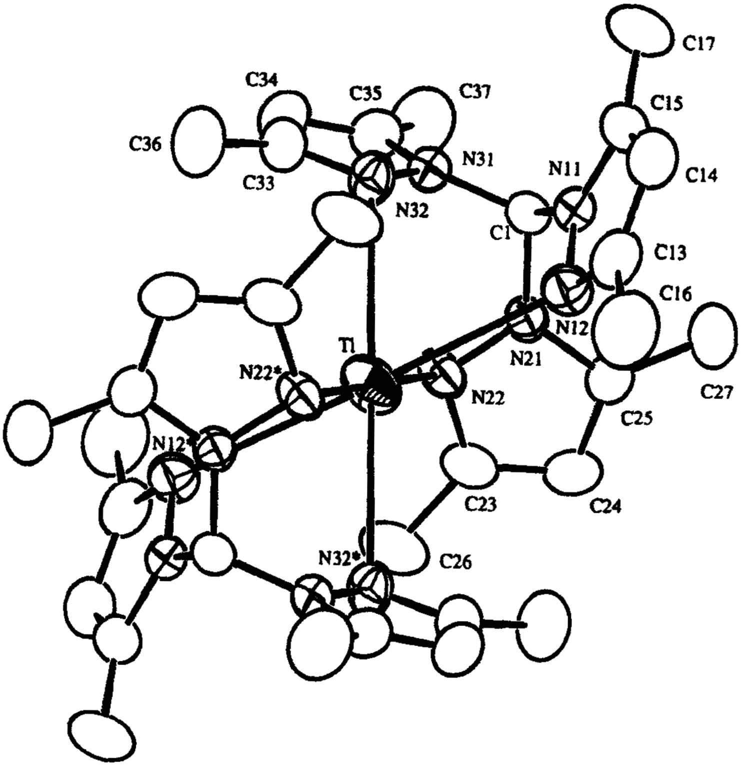


FIGURE 7 ORTEP diagram of $\{[HC(3,5\text{-}Me_2pz)_3]_2Tl\}^+$

CONCLUSION

Stable cationic complexes with many metals can be prepared with tris(pyrazolyl)methane ligands. For most cases, the tris(pyrazolyl)methane ligands bond strongly to the metals, even in mixed tris(pyrazolyl)methane/tris(pyrazolyl)borate complexes. The structures of the isoelectronic complexes $[HB(3,5\text{-}Me_2pz)_3]_2Cd$, $\{[HC(3,5\text{-}Me_2pz)_3]Cd[HB(3,5\text{-}Me_2pz)_3]\}^+$ and $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$ are very similar, even though the tris(pyrazolyl)methane complexes are cationic. Also, the ^{113}Cd NMR shifts of these three complexes are very similar. The isoelectronic complexes $\{[HC(pz)_3]_2Pb\}^{2+}$ and $[HB(pz)_3]_2Pb$ have similar distorted six-coordinate structures and the pair $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$ and $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ have very similar octahedral structures in which the lone pair on the lead(II) is stereochemically inactive. Only for $\{[HC(3,5\text{-}Me_2pz)_3]Pb[HB(3,5\text{-}Me_2pz)_3]\}^+$ does the tris(pyrazolyl)borate ligand bond more strongly. In zinc chemistry decomposition of the tris(pyrazolyl)methane ligands has hindered the syntheses of new complexes. Importantly, the charge of a complex and the geometry about the metals can be controlled by careful variations of these versatile tris(pyrazolyl)methane/poly(pyrazolyl)borate ligands.

Acknowledgments

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