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Tl(I)-, Cu(I)-, and Ag(I) Complexes of the Ditopic 1,3-Phenylene-Bridged Heteroscorpionate Ligand $[1,3\text{-}C_6H_4(t\text{BuBpz}_2)_2]^{2-}$

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The complexes $Tl_2[1,3\text{-}C_6H_4(t\text{BuBpz}_2)_2]$ (**1Tl**), $[Cu(PPh_3)]_2[1,3\text{-}C_6H_4(t\text{BuBpz}_2)_2]$ (**1Cu**), and $[Ag(PPh_3)]_2[1,3\text{-}C_6H_4(t\text{BuBpz}_2)_2]$ (**1Ag**) featuring a novel ditopic 1,3-phenylene-bridged heteroscorpionate ligand have been prepared and investigated by ^1H, ^{13}C, ^{11}B, and ^{31}P NMR spectroscopy (pz = pyrazolyl). X-ray crystal structure analyses revealed **1Tl** and **1Ag** to adopt a *trans* configuration with respect to the phenylene bridge in the solid state. In solution at room temperature, both scorpionate substituents are free to rotate about their B−C(phenylene) bonds. The Tl(I) coordination to two pyrazolyl nitrogen atoms as well as the Ag(I) coordination to two pyrazolyl and one PPh_3 ligand is augmented by short intramolecular contacts to the phenylene π-system.

Introduction

Bis- and tris(pyrazol-1-yl)borates ("scorpionates") are among the most versatile and most popular ligands in coordination chemistry.[1,2] However, even though their discovery dates back to 1966[3] only very few examples of ditopic scorpionates exist today[4−6] despite the fact that these ligands would be extremely useful for the preparation of (hetero)oligonuclear metal complexes. Our group has synthesized the ferrocene-based discorpionate **A** (Figure 1) and studied its reactivity toward selected metal ions (i.e., Tl(I), Mo(0), Mo(II), and Zr(IV)).[5,7] More recently, we published the 1,3- and 1,4-phenylene-bridged ditopic bis(pyrazol-1-yl)borates **B** and **C** (Figure 1), which were characterized as their Li^+ and K^+ salts.[6] The purpose of this paper is to report on complexes of **B** with the metal ions Tl(I), Cu(I), and Ag(I).

Thallium derivatives such as **1Tl** (Scheme 1) are important ligand transfer reagents in place of the oftentimes less efficient alkali metal scorpionates. Moreover, an investigation of the solid state structure of **1Tl** is of interest since the ligand $[\mathbf{1}]^{2-}$ provides only two pyrazolyl donor sites *per* Tl(I) ion. Mononuclear two-coordinated Tl(I) complexes are not abundant in the literature, and it will thus be revealing to investigate how the coordination sphere of the metal center is expanded in the solid state (e.g., via interactions with the aromatic rings[8] or supplementary Tl⋯Tl $d^{10}-d^{10}$ interactions[9,10]).

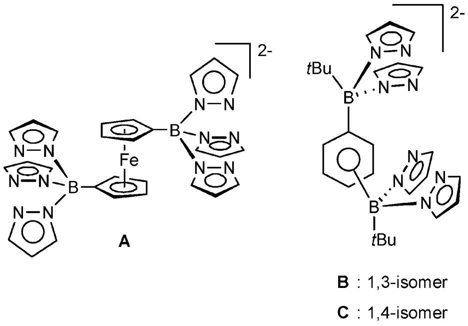

Figure 1. Ditopic poly(pyrazol-1-yl)borate ligands **A**−**C**.

The dinuclear compounds **1Cu** and **1Ag** (Scheme 1) were prepared in order to extend our studies into the field of transition metal complexes of $[\mathbf{1}]^{2-}$. The copper(I) bis(pyrazol-1-yl)borate compounds $[(H_2Bpz_2)Cu(PCy_3)]$ and $[(H_2Bpz_2)Cu(PPh_3)_2]$ have been employed as catalysts for the cyclopropanation of olefins,[11] while the complexes $[(H_2Bpz^x{}_2)M(2,4,6\text{-collidine})]$ (M = Cu(I), Ag(I); $pz^x = 3,5\text{-}(CF_3)_2pz$, pz = pyrazolyl) have been shown to exhibit bright blue phosphorescence.[12] Applications of compounds such as **1Cu** and **1Ag** both in homogeneous catalysis and in materials science can thus be anticipated and will be investigated in the future.

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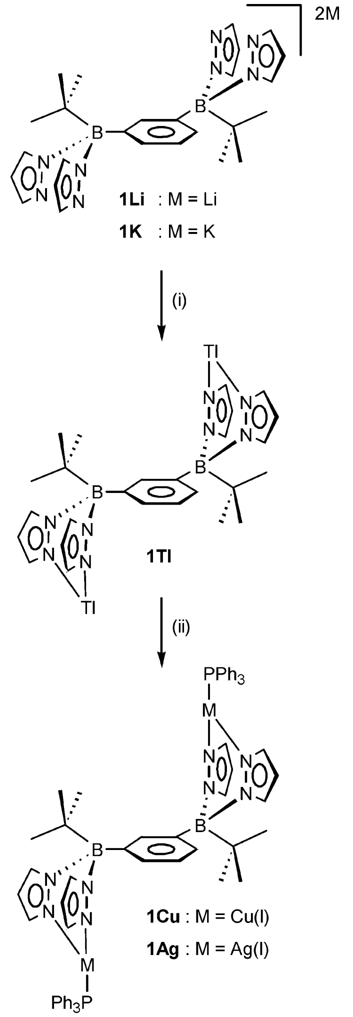
Scheme 1. Synthesis of the Tl(I) Complex 1Tl, the Cu(I) Complex 1Cu, and the Ag(I) Complex 1Ag[a]



[a] (i) **1Li** + TlOEt, toluene, −78 °C to room temperature. (ii) **1Cu**: + CuI/PPh$_3$, acetonitrile, −78 °C to room temperature; **1Ag**: + AgOTf/PPh$_3$, toluene, −78 °C to room temperature.

Results and Discussion

Syntheses and Spectroscopy. The lithium heteroscorpionate **1Li**[6] was readily transformed into the corresponding thallium complex **1Tl** using thallium(I) ethoxide (TlOEt) in toluene (Scheme 1). The reaction of **1K**[6] with TlOEt or TlNO$_3$ is less efficient for the preparation of **1Tl**. X-ray quality crystals grew from a toluene solution of **1Tl** at 4 °C. Treatment of **1Tl** in acetonitrile with 2 equiv of CuI led to a reaction product that decomposed within hours even at low temperature and under an inert gas atmosphere. As a result, the reaction mixture adopted a bluish color, thereby indicating the formation of Cu(II) ions (a similar observation has been reported by Pérez et al.[11]). This redox reaction can be suppressed by addition of 2 equiv of PPh$_3$, which leads to the formation of the stable dinuclear Cu(I) complex **1Cu** (Scheme 1). Even with excess amounts of PPh$_3$ it was not possible to introduce more than one phosphine ligand into the coordination spheres of the Cu(I) ions (NMR spectroscopic control). Treatment of silver triflate (AgOTf) with PPh$_3$ in toluene followed by addition of **1Tl** afforded the Ag(I) complex **1Ag** in moderate yield. In solution, the compound is sensitive to daylight. Crystals suitable for X-ray crystallography were obtained from toluene/hexane (1:1) at −20 °C. It is important to note that both in terms of product selectivity and in terms of yield the thallium complex **1Tl** is superior the alkali metal salts **1Li** and **1K** for the synthesis of **1Cu** and **1Ag**.

The ^{11}B NMR spectrum of **1Tl** (**1Cu**, **1Ag**) gives rise to one signal at 3.0 ppm (3.4 ppm, 3.7 ppm), thereby testifying to the presence of magnetically equivalent, tetracoordinated[13] boron atoms.

The ^{31}P NMR signal of **1Cu** appears at 6.9 ppm (293 K, d_8-THF, $h_{1/2} = 80$ Hz), 13.0 ppm downfield of the ^{31}P NMR resonance of [(HBpz$_3$)Cu(PPh$_3$)] (233 K, CDCl$_3$: $\delta(^{31}\text{P}) = -6.1$; pz = pyrazolyl),[14] which features a tetracoordinated N$_3$CuP complex core. At a temperature of 203 K, two signals of almost equal intensity at $\delta(^{31}\text{P}) = 6.2$ and $\delta(^{31}\text{P}) = 6.8$ (with a high-field shoulder) are visible in the ^{31}P NMR spectrum of **1Cu**. This finding may be explained by a restricted rotation about the B−C(ipso) bond leading to the formation of three rotamers, which do not interconvert on the NMR time scale. Even though both isotopes of copper contain NMR-active $I = 3/2$ nuclei (natural abundance: ^{63}Cu = 69.09%, ^{65}Cu = 30.91%), ^{31}P−$^{63/65}$Cu coupling is not resolved, thereby indicating a low symmetry of the Cu(I) coordination sphere.

At room temperature, the ^{31}P NMR spectrum of **1Ag** consists of a broad singlet at 16.4 ppm (293 K, d_8-THF, $h_{1/2} = 300$ Hz). Similar chemical shift values have been observed both for the three-coordinated complex [(pz$_2$-Bpz$_2$)Ag(PPh$_3$)] ($\delta(^{31}\text{P}) = 16.9$, s, br)[15] and for the tetracoordinated compound [(HBpz$_3$)Ag(PPh$_3$)] ($\delta(^{31}\text{P}) = 15.3$, br).[16] The difference $\Delta\delta(^{31}\text{P})$ between the chemical shift of **1Ag** and of the free PPh$_3$ ligand ($\delta(^{31}\text{P}) = -5.6$)[17] is greater than that observed for **1Cu**, suggesting a weaker metal−phosphorus bonding interaction in the latter (**1Cu**: $\Delta\delta(^{31}\text{P}) = 12.5$, **1Ag**: $\Delta\delta(^{31}\text{P}) = 22.0$). However, the fact that ^{31}P−$^{107/109}$Ag coupling is not resolved in the ^{31}P NMR spectrum of **1Ag** at room temperature points to a rapid phosphine association/dissociation equilibrium also in this compound. Upon cooling to 213 K, the broad ^{31}P NMR signal of **1Ag** transforms into two pairs of doublets with $\delta(^{31}\text{P}) = 15.6$ and 17.2 (intensity ratio about 1:2). As in the case of **1Cu**, decoalescence is likely due to the deceleration of intramolecular motions, leading to the formation of two rotamers in addition to the two isotopomers. The P−Ag coupling constants of **1Ag** ($^1J(^{31}\text{P}-^{107}\text{Ag}) = 598$ Hz, $^1J(^{31}\text{P}-^{109}\text{Ag}) = 690$ Hz) are in nice agreement with the values obtained for the related compounds [(pz$_2$Bpz$_2$)-Ag(PPh$_3$)] (223 K, CDCl$_3$: $\delta(^{31}\text{P}) = 16.8$, dd, $^1J(^{31}\text{P}-^{107}\text{Ag}) = 622$ Hz, $^1J(^{31}\text{P}-^{109}\text{Ag}) = 719$ Hz)[15] and [(HBpz$_3$)-Ag(PPh$_3$)] (223 K, CDCl$_3$: $\delta(^{31}\text{P}) = 17.0$, dd, $^1J(^{31}\text{P}-^{107}\text{Ag}) = 607$ Hz, $^1J(^{31}\text{P}-^{109}\text{Ag}) = 700$ Hz).[16] In contrast, silver scorpionates bearing *two* tertiary phosphine ligands were reported to possess significantly smaller

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Table 1. Crystal Data and Structure Refinement Details for 1Tl and 1Ag

	1Tl	**1Ag**
formula	$C_{26}H_{34}B_2N_8Tl_2$	$C_{62}H_{64}Ag_2B_2N_8P_2$
fw	888.97	1220.51
color, shape	colorless, block	colorless, plate
temp (K)	173(2)	173(2)
radiation	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
cryst syst	tetragonal	triclinic
space group	$P\bar{4}2_1c$	$P\bar{1}$
a (Å)	28.980(2)	12.2675(18)
b (Å)	28.980(2)	13.5058(19)
c (Å)	9.3367(8)	20.106(3)
α (deg)	90	100.432(11)
β (deg)	90	100.391(11)
γ (deg)	90	112.787(11)
V (Å^3)	7841.3(10)	2902.9(7)
Z	8	2
D_{calcd} (g cm^{-3})	1.506	1.396
F(000)	3344	1252
μ (mm^{-1})	8.232	0.776
cryst size (mm^3)	0.32 × 0.26 × 0.24	0.26 × 0.11 × 0.04
no. of reflns collected	26 177	23 965
no. of indep reflns (R_{int})	7417 (0.0966)	10 262 (0.1249)
no. of data/restraints/ params	7417/0/343	10 262/24/728
GOOF on F^2	0.871	0.785
R1, wR2 ($I > 2\sigma(I)$)	0.0560, 0.1359	0.0571, 0.0890
R1, wR2 (all data)	0.1088, 0.1786	0.1500, 0.1117
largest diff peak and hole (e Å^{-3})	1.063, −0.935	0.566, −0.829

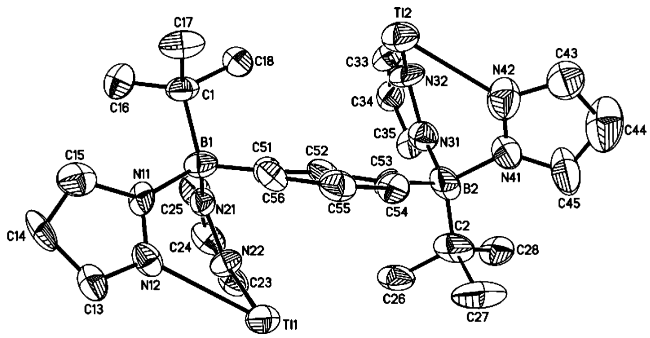

Figure 2. Structure of **1Tl** in the crystal. Selected bond lengths (Å), atom···atom distances (Å), bond angles (deg), and torsion angles (deg); H atoms omitted for clarity: Tl(1)−N(12) = 2.627(19), Tl(1)−N(22) = 2.603(16), Tl(2)−N(32) = 2.633(19), Tl(2)−N(42) = 2.47(2), B(1)−N(11) = 1.63(3), B(1)−N(21) = 1.52(3), B(2)−N(31) = 1.63(3), B(2)−N(41) = 1.57(3), B(1)−C(1) = 1.67(3), B(1)−C(51) = 1.58(3), B(2)−C(2) = 1.56(4), B(2)−C(53) = 1.65(4), Tl(1)···C(51) = 3.02, Tl(2)···C(53) = 3.03; N(12)−Tl(1)−N(22) = 70.4(5), N(32)−Tl(2)−N(42) = 72.1(7), N(11)−B(1)−N(21) = 103.8(16), N(11)−B(1)−C(51) = 108.7(16), N(21)−B(1)−C(51) = 111.2(18), C(1)−B(1)−N(11) = 109.8(18), C(1)−B(1)−N(21) = 110.6(17), C(1)−B(1)−C(51) = 112.4(16), N(31)−B(2)−N(41) = 105.3(17), N(31)−B(2)−C(53) = 104.9(19), N(41)−B(2)−C(53) = 108(2), C(2)−B(2)−N(31) = 110(2), C(2)−B(2)−N(41) = 116(2), C(2)−B(2)−C(53) = 112.2(17); C(1)−B(1)−C(51)−C(52) = −86(2), B(1)−N(11)−N(12)−Tl(1) = 7(2), B(1)−N(21)−N(22)−Tl(1) = 3(2), C(2)−B(2)−C(53)−C(52) = −86(2), B(2)−N(31)−N(32)−Tl(2) = −6(2), B(2)−N(41)−N(42)−Tl(2) = −1(3).

coupling constants (e.g., [(H_2Bpz_2)Ag(PPh_3)$_2$] (223 K, $CDCl_3$: average value $^1J(^{31}P-^{107/109}Ag)$ = 387 Hz),[18] which leads to the conclusion that the Ag(I) ions in **1Ag** are coordinated to *one* PPh_3 ligand only.

In the ^{1}H NMR spectrum of **1Tl**, one signal is found for the two *t*Bu substituents, the protons H4 and H6 of the central phenylene ring are magnetically equivalent, and the four pyrazolyl rings give rise to not more than three proton resonances. The same is true for the room-temperature proton spectra of **1Cu** and **1Ag**. This signal pattern thus clearly indicates free rotation of the B(*t*Bu)-pz_2 substituents about the B−C(phenylene) bonds in all three compounds at 293 K. Variable-temperature ^{1}H NMR spectroscopy on **1Ag**, however, reveals an extreme broadening of most signals assigned to the scorpionate ligand already at 253 K. At a temperature of 193 K, numerous new signals appear in the aliphatic as well as in the aromatic region of the spectrum. However, the low-temperature resonances are not sufficiently well resolved to allow a detailed analysis. Integration of their ^{1}H NMR spectra indicates complexes **1Cu** and **1Ag** to contain one PPh_3 ligand *per* metal atom, which is in accord both with our interpretation of the P−Ag coupling constants of **1Ag** (see above) and with its X-ray crystal structure analysis (see below).

At room temperature, the ^{13}C NMR spectra of **1Tl**, **1Cu**, and **1Ag** are rather similar and do not show any unusual features.

Crystal Structure Determinations. Crystal data and details of the structure determinations are summarized in Table 1. The Tl(I) complex **1Tl** crystallizes from toluene in the tetragonal space group $P\text{-}42_1c$ (Figure 2). The conformation of **1Tl** is similar to the conformation adopted by the ditopic scorpionate ligand in the related potassium salt **1K**[6] (Scheme 1) with both *t*Bu substituents, as well as both Tl(I) ions, being located at opposite sides of the 1,3-phenylene backbone (**1Tl**: C(1)−B(1)−C(51)−C(52) = C(2)−B(2)−C(53)−C(52) = −86(2)°; **1K**: the corresponding torsion angle possesses a value of 99.0(3)°). Contrary to crystalline **1K**, which establishes a polymeric structure with the potassium ions being coordinated by four pyrazolyl rings of two different **[1]**$^{2-}$ moieties,[6] **1Tl**, in a first approximation, consists of discrete dinuclear complexes with each Tl(I) ion being coordinated to two pyrazolyl nitrogen atoms of its scorpionate ligand (Tl(1)−N(12) = 2.627(19) Å, Tl(1)−N(22) = 2.603(16) Å, Tl(2)−N(32) = 2.633(19) Å, Tl(2)−N(42) = 2.47(2) Å; N(12)−Tl(1)−N(22) = 70.4(5)°, N(32)−Tl(2)−N(42) = 72.1(7)°). These values are consistent with the Tl−N bond lengths and N−Tl−N bond angles reported previously for some mononuclear thallium bis(pyrazol-1-yl)borate compounds.[19−24] In complexes of the type [(H_2Bpz_2)Tl], the bonding to the "two-coordinate" Tl(I) ions is usually augmented by a weak intramolecular B−H···Tl interaction.[19,20,23] In the case of **1Tl**, however, a third Tl coordination site is occupied by the respective *ipso*-carbon atom of the phenylene core (Figure 3). The corresponding distances Tl(1)···C(51) = 3.02 Å and Tl(2)···C(53) = 3.03 Å are significantly

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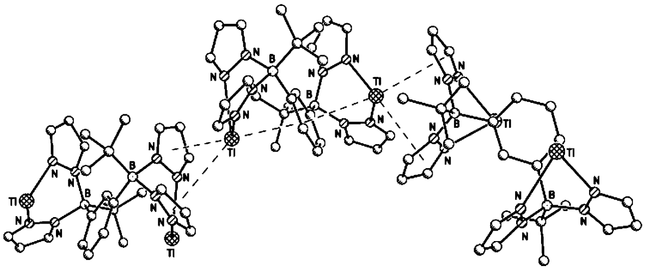

Figure 3. Packing diagram for **1Tl**; view approximately along [1−1 0].

shorter than the sum of the van der Waals radii (3.66 Å) of thallium (1.96 Å)[25] and carbon (1.70 Å)[25] and fall in the same range as in other Tl(I)-arene complexes.[19,26−29] Recently, a novel coordination geometry of thallium(I) tris(pyrazol-1-yl)borate complexes has been discovered in polymeric $[(FcBpz_3)Tl]_n$[5,30] (Fc = $(C_5H_5)Fe(C_5H_4)$), in $[(CymBpz_3)Tl]_4$[31] (Cym = $(MeC_5H_3)Mn(CO)_3$), which forms cyclic tetramers, and in the monomeric species $[(PhBpz^{tBu}{}_3)Tl]$.[22] In these three compounds the Tl(I) ion forms σ-adducts with only *two* of the scorpionate's pyrazolyl groups, while the third pyrazolyl ring is rotated by approximately 90° about the B−N bond. Nevertheless, distances smaller than the sum of the van der Waals radii (3.51 Å) of thallium (1.96 Å) and nitrogen (1.55 Å) are observed between the thallium centers and the boron-bound nitrogen atoms ($[(FcBpz_3)Tl]_n$: Tl−*N*B = 3.210 Å, $[(PhBpz^{tBu}{}_3)Tl]$: Tl−*N*B = 2.833 Å; *N*B: boron-bound nitrogen atom). The metal atom thus appears to interact with the third pyrazolyl ring via the nitrogen p-orbital component of the aromatic π-system.[22] Similar Tl−π-N(pyrazolyl) contacts may also be established *inter*molecularly between two *different* thallium scorpionate molecules as, for example, in $[(H_2Bind_2)Tl]$ (ind = indazolyl), which forms centrosymmetric dimers in the solid state (Tl−*N*B = 3.340 Å, Tl···COG = 3.267 Å; COG: center of gravity of the pyrazolyl ring).[32] In the case of **1Tl**, each Tl ion forms two π-contacts to the two pyrazolyl rings of a neighboring scorpionate ligand (Tl(1)−N(11A) = 3.437 Å, Tl(1)···COG(1) = 3.360 Å; Tl(1)−N(21A) = 3.426 Å, Tl(1)···COG(2) = 3.458 Å; Tl(2)−N(31B) = 3.482 Å, Tl(2)···COG(3) = 3.302 Å; Tl(2)−N(41B) = 3.996 Å, Tl(2)···COG(4) = 4.019 Å; Figure 3).

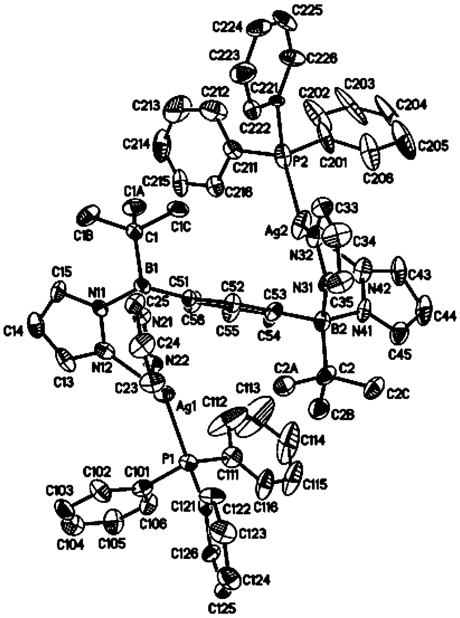

Figure 4. Structure of **1Ag** in the crystal. Selected bond lengths (Å), atom···atom distances (Å), bond angles (deg), and torsion angles (deg); H atoms omitted for clarity: Ag(1)−N(12) = 2.242(6), Ag(1)−N(22) = 2.246(5), Ag(1)−P(1) = 2.343(2), Ag(2)−N(32) = 2.288(5), Ag(2)−N(42) = 2.279(7), Ag(2)−P(2) = 2.336(3), B(1)−N(11) = 1.625(10), B(1)−N(21) = 1.608(8), B(2)−N(31) = 1.593(10), B(2)−N(41) = 1.620(11), B(1)−C(1) = 1.605(11), B(1)−C(51) = 1.596(11), B(2)−C(2) = 1.647(12), B(2)−C(53) = 1.644(10), Ag(1)···C(51) = 2.880, Ag(2)···C(53) = 2.749; N(12)−Ag(1)−N(22) = 84.9(2), N(32)−Ag(2)−N(42) = 82.9(2), N(11)−B(1)−N(21) = 103.5(6), N(11)−B(1)−C(51) = 108.3(5), N(21)−B(1)−C(51) = 106.7(5), C(1)−B(1)−N(11) = 110.9(6), C(1)−B(1)−N(21) = 112.9(5), C(1)−B(1)−C(51) = 113.9(7), N(31)−B(2)−N(41) = 104.5(6), N(31)−B(2)−C(53) = 107.0(6), N(41)−B(2)−C(53) = 108.3(5), C(2)−B(2)−N(31) = 112.8(5), C(2)−B(2)−N(41) = 110.8(6), C(2)−B(2)−C(53) = 113.0(7), N(12)−Ag(1)−P(1) = 128.8(2), N(22)−Ag(1)−P(1) = 137.4(1), N(32)−Ag(2)−P(2) = 124.6(2), N(42)−Ag(2)−P(2) = 132.5(2); C(1)−B(1)−C(51)−C(52) = 84.4(8), B(1)−N(11)−N(12)−Ag(1) = 10.4(7), B(1)−N(21)−N(22)−Ag(1) = −4.8(8), C(2)−B(2)−C(53)−C(52) = 78.2(9), B(2)−N(31)−N(32)−Ag(2) = −8.6(8), B(2)−N(41)−N(42)−Ag(2) = −2.5(8).

The Ag(I) complex **1Ag** crystallizes from toluene/hexane (1:1) in the triclinic space group $P\bar{1}$ (Figure 4). As in the case of **1K** and **1Tl**, a *trans* conformation of the discorpionate ligand is observed associated with torsion angles C(1)−B(1)−C(51)−C(52) and C(2)−B(2)−C(53)−C(52) of 84.4(8)° and 78.2(9)°, respectively. Each Ag(I) ion is coordinated by two pyrazolyl rings (Ag−N bond lengths between 2.242(6) and 2.288(5) Å) and one PPh_3 ligand in a trigonal fashion. The Ag(1)−P(1) and Ag(2)−P(2) bond lengths are 2.343(2) and 2.336(3) Å, which may be compared to the Ag−P value of 2.351(1) Å reported for $[(Ph_2Bpz_2)Ag\{P(C_6H_4Me\text{-}p)_3\}]$[33] and of 2.331(2)/2.335(2) and 2.336(3)/2.337(2) Å in $[(pz_2Bpz_2)Ag(PPh_3)]$[15] and in tetracoordinated $[(HBpz_3)Ag(PPh_3)]$[16] (two crystallographically independent molecules in the asymmetric unit). Both Ag(I) centers of **1Ag** deviate significantly from the ideal planar configuration (sum of angles around Ag(1): 351.1°, Ag(2): 340.0°), which alleviates the steric repulsion between the PPh_3 ligand and the nearby *t*Bu substituent. However, pyramidalization may also result from weak bonding interactions between the silver ions and the phenylene π-system (Ag(1)···C(51) = 2.880 Å, Ag(2)···C(53) = 2.749 Å). Noteworthily, the three-coordinate Ag(I) ions of all other complexes that may be used for comparison are rigorously planar.[15,18,33] There are, however, other degrees

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of asymmetry in some of these compounds, which are far less pronounced in **1Ag**, where the two Ag(1)−N (Ag(2)−N) bond lengths differ by as little as 0.004 Å (0.009 Å) and the maximum disparity in the N−Ag−P angles is 8.6°. The three-coordinated complex [(Ph$_2$Bpz$_2$)Ag{P(C$_6$H$_4$Me-p)$_3$}],[33] for example, albeit strictly planar, shows one very short Ag−N bond in the solid state (d(Ag−N) = 2.194(4) Å), whereas the second one is longer by 0.217 Å (d(Ag−N′) = 2.411(4) Å), which implies a rather weak interaction. Nevertheless, the N′ donor is close enough to the silver ion to distort the N−Ag−P angle from linear to bent (160.3(1)°). The elongated Ag−N′ bond in [(Ph$_2$Bpz$_2$)Ag{P(C$_6$H$_4$Me-p)$_3$}] goes along with a torsion of the respective pyrazolyl ring about the B−N bond so that the Ag(I) ion lies well out of the ring plane (1.21 Å). In the case of the other pyrazolyl ring, the magnitude of the displacement is only 0.12 Å (cf. **1Ag**: Ag(1) vs N(11)N(12)C(13)C(14)C(15): 0.448 Å, Ag(1) vs N(21)N(22)C(23)C(24)C(25): 0.032 Å, Ag(2) vs N(31)N(32)C(33)C(34)C(35): 0.243 Å, Ag(2) vs N(41)N(42)C(43)C(44)C(45): 0.132 Å).

Conclusion

The dinuclear Tl(I) complex Tl$_2$[1,3-C$_6$H$_4$(tBuBpz$_2$)$_2$] (**1Tl**) featuring a ditopic heteroscorpionate ligand was synthesized from the corresponding lithium salt Li$_2$[1,3-C$_6$H$_4$(tBuBpz$_2$)$_2$] (**1Li**) and thallium ethoxide. NMR spectroscopy on **1Tl** clearly shows that there is free rotation about the B−C(phenylene) bonds at room temperature. In the solid state, the two Tl(I) ions are located at opposite sides of the 1,3-phenylene backbone. Each Tl(I) ion is coordinated by two pyrazolyl nitrogen atoms and one phenylene *ipso*-carbon atom. The relevant atom−atom distances Tl(1)···C(51) = 3.02 Å and Tl(2)···C(53) = 3.03 Å are smaller than the lower limit of the range (3.10−3.50 Å) for Tl−C bonds in complexes with discrete arenes η^6-bonded to Tl(I).[8] When treated with CuI or AgOTf in the presence of PPh$_3$, **1Tl** acts as an excellent ligand transfer reagent for the preparation of the dinuclear M(I)PPh$_3$ complexes **1Cu** and **1Ag**. In both compounds, each metal center is coordinated to only one PPh$_3$ ligand. At room temperature, both compounds show an average ^{31}P NMR spectrum for the conformations present. Neither ^{31}P−$^{63/65}$Cu nor ^{31}P−$^{107/109}$Ag coupling is resolved. At lower temperatures, when the rate of interconversion is slowed, separate peaks are observed for different rotamers of **1Cu** and **1Ag**. Moreover, $^1J(^{31}$P−^{107}Ag) and $^1J(^{31}$P−^{109}Ag) values of 598 and 690 Hz could be determined upon cooling a sample of **1Ag** to 213 K. An X-ray crystal structure analysis of **1Ag** shows each Ag(I) ion to be coordinated to two pyrazolyl rings in a chelating manner and with equal Ag−N bond lengths. A third coordination side of the silver center is occupied by the PPh$_3$ ligand. Pyramidalization of both Ag(I) ions (sum of angles around Ag(1): 351.1°, Ag(2): 340.0°) together with short Ag···C(ipso) distances (Ag(1)···C(51) = 2.880 Å, Ag(2)···C(53) = 2.749 Å) indicate bonding interactions between the silver ions and the phenylene π-system. Further transition metal chemistry with **1Li**, **1K**, and **1Tl** is under active investigation in our laboratory.

Experimental Section

General Considerations. All reactions and manipulations of air-sensitive compounds were carried out in dry, oxygen-free argon using standard Schlenk ware. Solvents were freshly distilled under argon from Na/benzophenone (toluene) and Na/Pb alloy (hexane) prior to use. Acetonitrile and chloroform were dried over molecular sieves (4 Å). NMR: Bruker AMX 250, Bruker AMX 400, Bruker DPX 250. ^{11}B and ^{31}P NMR spectra were reported relative to external BF$_3$·Et$_2$O and H$_3$PO$_4$, respectively. Abbreviations: s = singlet, d = doublet, tr = triplet, vtr = virtual triplet, mult = multiplet, br = broad, n.r. = multiplet expected in the ^{1}H NMR spectrum but not resolved, n.o. = signal not observed, pz = pyrazolyl, Ph = phenyl, i = ipso, o = ortho, m = meta, p = para. Unless stated otherwise, NMR spectra were run at room temperature. Elemental analyses were performed by the microanalytical laboratory of the University of Frankfurt.

Synthesis of Tl$_2$[1,3-C$_6$H$_4$(tBuBpz$_2$)$_2$] (1Tl). To a stirred solution of TlOEt (0.20 g, 0.80 mmol) in toluene (5 mL) was added a solution of **1Li** (0.17 g, 0.35 mmol) in toluene (25 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. After filtration, the filtrate was concentrated to a volume of 15 mL and stored at 4 °C, whereupon colorless needlelike crystals formed. The mother liquor was evaporated to dryness and the solid remainder recrystallized from hexane/toluene (1:3) to give a second crop of **1Tl**. Yield: 0.16 g (51%). ^{11}B{^{1}H} NMR (128.4 MHz, CDCl$_3$): δ 3.0 ($h_{1/2}$ = 200 Hz). ^{1}H NMR (250.1 MHz, CDCl$_3$): δ 1.16 (s, 18H, CH$_3$), 6.15 (vtr, 4H, $^3J_{\mathrm{HH}}$ = 2.0 Hz, pzH-4), 6.50 (d, 2H, $^3J_{\mathrm{HH}}$ = 7.3 Hz, H-4,6), 6.57 (s, 1H, H-2), 7.11 (tr, 1H, $^3J_{\mathrm{HH}}$ = 7.3 Hz, H-5), 7.28, 8.04 (2 × d, 2 × 4H, $^3J_{\mathrm{HH}}$ = 1.8 Hz, 2.2 Hz, pzH-3,5). ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 31.5 (br, CH$_3$), 103.1 (pzC-4), 126.3 (C-5), 134.0 (C-4,6), 136.0, 136.9 (pzC-3,5), 146.1 (C-2), n.o. (CB). ESI-MS: m/z 890 [M$^+$]. Anal. Calcd for C$_{26}$H$_{34}$B$_2$N$_8$Tl$_2$ (888.97): C, 35.13; H, 3.85; N, 12.60. Found: C, 35.43; H, 3.90; N, 12.71.

Synthesis of [Cu(PPh$_3$)]$_2$[1,3-C$_6$H$_4$(tBuBpz$_2$)$_2$] (1Cu). To a solution of CuI (34 mg, 0.18 mmol) in acetonitrile (15 mL) was added **1Tl** (80 mg, 0.09 mmol) in acetonitrile (20 mL) at −78 °C. The reaction was allowed to warm to room temperature and stirred for 3 h, whereupon a yellow precipitate formed. After filtration, PPh$_3$ (47 mg, 0.18 mmol) in acetonitrile (5 mL) was slowly added to the colorless filtrate and the resulting solution stirred for 2 h. The solvent was evaporated in vacuo, the solid residue triturated with hexane (2 × 20 mL) and then extracted into toluene (2 × 15 mL). After the extract had been evaporated to dryness, the remaining solid material was recrystallized from hexane/CHCl$_3$ (1:1) at −20 °C. Yield: 68 mg (67%). ^{11}B{^{1}H} NMR (128.4 MHz, d_8-THF): δ 3.4 ($h_{1/2}$ = 550 Hz). ^{31}P{^{1}H} NMR (162.0 MHz, d_8-THF): δ 6.9 (s, $h_{1/2}$ = 80 Hz). ^{1}H NMR (250.1 MHz, d_8-THF): δ 0.87 (s, 18H, CH$_3$), 5.94 (br, 4H, pzH-4), 6.99 (tr, 1H, $^3J_{\mathrm{HH}}$ = 7.4 Hz, H-5), 7.12 (n.r., 2H, H-4,6), 7.24, 7.25 (2 × n.r., 2 × 4H, pzH-3,5), 7.37−7.46 (mult, 18H, PhH-m,p), 7.50−7.60 (mult, 12H, PhH-o), 7.77 (s, 1H, H-2). ^{13}C{^{1}H} NMR (100.6 MHz, d_8-THF): δ 30.9 (CH$_3$), 102.9 (pzC-4), 125.8 (C-5), 129.7 (d, $^3J_{\mathrm{PC}}$ = 9.9 Hz, PhC-m), 131.1 (d, $^4J_{\mathrm{PC}}$ = 1.7 Hz, PhC-p), 134.1 (d, $^1J_{\mathrm{PC}}$ = 37.1 Hz, PhC-i), 134.5 (C-4,6), 134.6 (d, $^2J_{\mathrm{PC}}$ = 15.8 Hz, PhC-o), 138.2, 140.4 (pzC-3,5), 144.2 (C-2), n.o. (CB). Anal. Calcd for C$_{62}$H$_{64}$B$_2$Cu$_2$N$_8$P$_2$ (1131.87) × 0.5CHCl$_3$ (119.38): C, 63.00; H, 5.46; N, 9.40. Found: C, 62.83; H, 5.48; N, 9.46.

Synthesis of [Ag(PPh$_3$)]$_2$[1,3-C$_6$H$_4$(tBuBpz$_2$)$_2$] (1Ag). In a Schlenk flask wrapped with aluminum foil, neat AgOTf (110 mg, 0.43 mmol) was added at room temperature to a solution of PPh$_3$ (113 mg, 0.43 mmol) in toluene (20 mL). After the mixture had been stirred for 1 h, it was cooled to −78 °C and a solution of **1Tl** (187 mg, 0.21 mmol) in toluene (20 mL) was added via a dropping funnel. The reaction mixture was allowed to warm to room temperature and stirred overnight. After filtration, the colorless filtrate was evaporated in vacuo and the solid residue recrystallized from toluene/hexane (1:1) at −20 °C. Yield: 64 mg (25%). ^{11}B{^{1}H} NMR (128.4 MHz, d_8-THF): δ 3.7 ($h_{1/2}$ = 600 Hz). ^{31}P{^{1}H} NMR (162.0 MHz, d_8-THF): δ 16.4 (s, $h_{1/2}$ = 300 Hz). ^{1}H NMR (250.1 MHz,

d_8-THF): δ 0.89 (s, 18H, CH_3), 5.84 (vtr, 4H, $^3J_{HH} = 1.7$ Hz, pzH-4), 6.78 (d, 2H, $^3J_{HH} = 7.4$ Hz, H-4,6), 6.98 (tr, 1H, $^3J_{HH} = 7.4$ Hz, H-5), 7.25 (d, 4H, $^3J_{HH} = 1.8$ Hz, pzH-3 or 5), 7.28 (s, 1H, H-2), 7.38−7.50 (mult, 30H, PhH-o,m,p), 7.52 (d, 4H, $^3J_{HH} = 1.6$ Hz, pzH-5 or 3). $^{13}C\{^1H\}$ NMR (62.9 MHz, d_8-THF): δ 30.3 (CH_3), 101.3 (pzC-4), 124.0 (C-5), 128.4 (d, $^3J_{PC} = 10.1$ Hz, PhC-m), 130.0 (d, $^4J_{PC} = 1.9$ Hz, PhC-p), 131.9 (d, $^1J_{PC} = 33.3$ Hz, PhC-i), 132.2 (C-4,6), 133.5 (d, $^2J_{PC} = 17.6$ Hz, PhC-o), 135.5, 138.3 (pzC-3,5), 143.6 (C-2), n.o. (CB). Anal. Calcd for $C_{62}H_{64}Ag_2B_2N_8P_2$ (1220.51): C, 61.01; H, 5.29; N, 9.18. Found: C, 60.79; H, 5.22; N, 8.92.

Crystal Structure Determinations of 1Tl and 1Ag. The measurements were performed at a temperature of 173(2) K using a STOE IPDS-II two-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were made.[34,35] The structures were determined by direct methods using the program SHELXS[36] and refined by full-matrix least-squares calculations on F^2 using the program SHELXL97.[37] Hydrogen atoms were placed at calculated positions and were refined with fixed isotropic displacement parameters (riding model). One phenyl ring of **1Ag** is disordered over two (almost equally) occupied positions. Isotropic restraints were applied to the displacement ellipsoids of four ring atoms. CCDC reference numbers: 238535 (**1Tl**), 238536 (**1Ag**).

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Supporting Information Available: Crystallographic data of **1Tl** and **1Ag** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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