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Synthesis and Molecular Structure of Bis(pyrazolyl)hydroborato Thallium $\{[\mathrm{Bp}]\mathrm{Tl}\}_2$: A $[\mathrm{Bp}^{\mathrm{RR}'}]\mathrm{Tl}$ Complex with an Unbridged Close $\mathrm{Tl^{I}\cdots Tl^{I}}$ Contact

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Introduction

It is widely appreciated that strong covalent bonds form between atoms that have open-shell configurations. Closed-shell species of zero or like charge are not expected to exhibit significant attractive interactions, but are rather expected to repel each other. The stability of the H_2 molecule and the instability of the He_2 molecule aptly illustrate these tenets. Recently, however, a variety of different systems have been discovered which indicates that certain closed-shell metal centers may interact attractively with each other. Specific examples include $d^{10}-d^{10}$ interactions, which are common in $\mathrm{Au^{I}}$ chemistry (the "aurophilic attraction"),[1] and s^2-s^2 interactions, as exemplified by certain $\mathrm{XM^{I}}$ (M = In, Tl),[2−4] $\mathrm{X_2Sn^{II}}$,[5] and $\mathrm{X_3M^{III}}$ (M = Sb, Bi)[6] fragments.[7,8] While relatively little is known concerning the precise nature of the bonding, the strength of the interaction is generally considered to be of a magnitude similar to that of a typical hydrogen bond,[9] such that it is sufficiently significant to influence structures in the solid state.[7,8] In this paper, we describe the molecular structure of the bis(pyrazolyl)hydroborato thallium complex $\{[\mathrm{Bp}]\mathrm{Tl}\}_2$.[10] By comparison with the structures of other $[\mathrm{Bp}^{\mathrm{RR}'}]\mathrm{Tl}$ derivatives, the structure of $\{[\mathrm{Bp}]\mathrm{Tl}\}_2$ demonstrates how the existence of $\mathrm{Tl^{I}\cdots Tl^{I}}$ interactions is highly dependent on the nature of the pyrazolyl substituents.

Results and Discussion

In 1987 Schumann reported that the pentabenzylcyclopentadienyl thallium complex $\{[\eta^5\text{-}\mathrm{C_5(CH_2Ph)_5}]\mathrm{Tl}\}_2$ adopted an unsupported dimeric structure in which two thallium centers were separated by 3.63 Å, only ca.0.2 Å longer than the shortest Tl−Tl separation in elemental thallium (3.41 Å).[11] Albeit considerably longer than expected for a conventional Tl−Tl covalent bond (2.73−2.97 Å),[12] the separation was less than twice the van der Waals radius of thallium (3.92 Å)[13] and was proposed to represent an attractive interaction since such a "head-to-head" structure would not be expected on the basis of the dipolar nature of the $\{[\eta^5\text{-}\mathrm{C_5(CH_2Ph)_5}]\mathrm{Tl}\}$ fragment. Following Schumann's report, a variety of other complexes which exhibit unsupported (i.e., unbridged) close $\mathrm{Tl^{I}\cdots Tl^{I}}$ contacts have been reported, as summarized in Table 1.[14,15] The theoretical significance of such interactions, however, remains a controversial issue. Thus, extended Hückel MO calculations by Janiak and Hoffmann support the notion of a $\mathrm{Tl^{I}\cdots Tl^{I}}$ bonding interaction in $[\mathrm{XTl^{I}}]_2$ complexes (X = H, OMe, Cp), invoking s−p hybridization to lower the energy of the antibonding s−s s* orbital.[16] Budzelaar and Boersma have also considered the nature of the $\mathrm{M^{I}\cdots M^{I}}$ interaction in $[\mathrm{CpIn}]_2$ and $[\mathrm{CpTl}]_2$ using theoretical methods and have suggested that the weak $\mathrm{M^{I}\cdots M^{I}}$ interactions may be likened to the donor−acceptor view of the

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(1) Bardaji, M.; Laguna, A. *J. Chem. Educ.* **1999**, *76*, 201−203. (b) Pyykkö, P.; Runeberg, N.; Mendizabal, F. *Chem.*−*Eur. J.* **1997**, *3*, 1451−1457. (c) Pyykkö, P.; Tamm, T. *Organometallics* **1998**, *17*, 4842−4852. (d) Schmidbaur, H. *Chem. Soc. Rev.* **1996**, *24*, 391−400.

(2) For example, $[\{\mathrm{(PhCH_2)_5C_5}\}\mathrm{In}]_2$,[a] $[\mathrm{(R_3Si)_3CIn}]_4$,[b−d] and $[\mathrm{Cp^*In}]_6$:[e,f] (a) Schumann, H.; Janiak, C.; Gorlitz, F.; Loebel, J.; Dietrich, A. *J. Organomet. Chem.* **1989**, *363*, 243−251. (b) Uhl, W.; Graupner, R.; Layh, M.; Schütz, U. *J. Organomet. Chem.* **1995**, *493*, C1−C5. (c) Uhl, W.; Jantschak, A.; Saak, W.; Kaupp, M.; Wartchow, R. *Organometallics* **1998**, *17*, 5009−5017. (d) Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Atwood, J. L. *J. Coord. Chem.* **1993**, *30*, 25−28. (e) Beachley, O. T.; Churchill, M. R.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *J. Am. Chem. Soc.* **1986**, *108*, 4666−4668. (f) Beachley, O. T.; Blom, R.; Churchill, M. R.; Faegri, K.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346−356.

(3) For example, $[\{\mathrm{(PhCH_2)_5C_5}\}\mathrm{Tl}]_2$[a,b] and $[\mathrm{(Me_3Si)_3CTl}]_4$.[c] (a) Schumann, H.; Janiak, C.; Pickardt, J.; Börner, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 789−790. (b) Schumann, H. *Pure Appl. Chem.* **1991**, *63*, 813−820. (c) Uhl, W.; Keimling, S. U.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 64−65.

(4) Murugavel, R.; Chandrasekhar, V. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1211−1215.

(5) For example, $\{[\mathrm{(CF_3)_3C_6H_2}]_2\mathrm{Sn}\}_2$ exists as a weakly bonded dimer with a separation of 3.64 Å, in contrast to the shorter 2.77 Å in the doubly bonded analogue $\mathrm{R_2Sn{=}SnR_2}$ [R = $\mathrm{CH(SiMe_3)_2}$]. See: Lay, U.; Prizkow, H.; Grützmacher, H. *J. Chem. Soc., Chem. Commun.* **1992**, 260−262.

(6) (a) Ashe, A. J., III; Butler, W.; Diephouse, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 207−209. (b) Ashe, A. J., III.; Diephouse, T. R.; Kampf, J. W.; Al-Taweel, S. M. *Organometallics* **1991**, *10*, 2068−2071. (c) Ashe, A. J., III; Kampf, J. W.; Puranik, D. B.; Al-Taweel, S. M. *Organometallics* **1992**, *11*, 2743−2745.

(7) For a recent review of closed-shell interactions, see: Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597−636.

(8) The term "metallophilic attraction" has been more generally used to describe these interactions. See: Pyykkö, P.; Li, J.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133−138.

(9) For example, in the case of gold, $\mathrm{Au^{I}\cdots Au^{I}}$ interactions in the range of ca. 6−11 kcal $\mathrm{mol^{-1}}$ have been measured. See Table 5 of ref 7. Also see (a) Harwell, D. E.; Mortimer, M. D.; Knobler, C. B.; Anet, F. A. L.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1996**, *118*, 2679−2685. (b) Narayanaswamy, R.; Young, M. A.; Parkhurst, E.; Ouellette, M.; Kerr, M. E.; Ho, D. M.; Elder, R. C.; Bruce, A. E.; Bruce, M. R. M. *Inorg. Chem.* **1993**, *32*, 2506−2517. (c) Schmidbaur, H.; Graf, W.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417−419.

(10) Bis- and tris(pyrazolyl)hydroborato ligands are represented by the abbreviations $[\mathrm{Bp}^{\mathrm{RR}'}]$ and $[\mathrm{Tp}^{\mathrm{RR}'}]$, with the 3- and 5-alkyl substituents listed, respectively, as superscripts.

(11) Pauling, L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 410.

(12) For example, the Tl−Tl bond lengths in $[\mathrm{(Me_3Si)_3Si}]_2\mathrm{Tl{-}Tl}[\mathrm{Si(SiMe_3)_3}\}_2]$,[a] $\mathrm{(Bu^t{}_3Si)_2Tl{-}Tl(SiBu^t{}_3)_2}$,[b] and $[\mathrm{MeC(CH_2NSiMe_3)_3Tl_2}]_2$[c] are 2.9142(5), 2.966(2), and 2.734(2) Å, respectively: (a) Henkel, S.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 681−683. (b) Wiberg, N.; Amelunxen, K.; Nöth, H.; Schmidt, M.; Schwenk, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 65−67. (c) Hellmann, K. W.; Gade, L. H.; Steiner, A.; Stalke, D.; Möller, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 160−163.

(13) The van der Waals radius of Tl is 1.96 Å. See: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(14) Janiak, C. *Coord. Chem. Rev.* **1997**, *163*, 107−216.

(15) Complexes with shorter $\mathrm{Tl^{I}\cdots Tl^{I}}$ interactions are also known, but these are typically characterized by the presence of ligands which *bridge* the two $\mathrm{Tl^{I}}$ centers. As such, the extent to which the bridge influences the $\mathrm{Tl^{I}\cdots Tl^{I}}$ separation is unknown. For examples, see: (a) Beck, J.; Strähle, J. *Z. Naturforsch.* **1986**, *41b*, 1381−1386. (b) Zahn, G.; Franke, A.; Dietzsch, W. *Acta Crystallogr.* **1995**, *C51*, 854−857.

(16) (a) Janiak, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 5924−5946. (b) Janiak, C.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1688−1689.

10.1021/ic990647o CCC: $18.00

Table 1. Complexes with Unsupported $Tl^{I}\cdots Tl^{I}$ Interactions < 4 Å[a]

complex	$d(Tl^{I}\cdots Tl^{I})$ (Å)	ref
$[\{(PhCH_2)_5C_5\}Tl]_2$	3.63	*b*
$\{(\eta^5{:}\eta^5\text{-}Bu^t{}_4C_{10}H_4)Tl_2\}_n$	3.76	*c*
$[(Me_3Si)_3CTl]_4$	3.33	*d*
$\{[(Me_3Si)_2NTl]_2\}_x$	3.94	*e*
$\{MeSi[N(Tl)Bu^t]_3\}_2$	3.15	*f*
$MeSi[SiMe_2N(Tl)Bu^t{}_3]_x$	3.67	*g*
$\{CH_2[CH_2N(Tl)SiMe_3]_2\}_n$	3.70	*h*
$[MeC\{CH_2N(Tl)SiMe_3\}_3]_2$	3.68	*i*
$[PhC\{CH_2N(Tl)SiMe_3\}_3]_2$	3.75	*j*
$[MeC\{MeN(Tl)SiMe_3\}]$ $[MeC\{CH_2NSiMe_3\}_3(H)(Tl)Li(THF)$	3.31	*k*
$[MeC\{CH_2NSiMe_3\}_3]_2(H)Tl_5$	3.41	*l*
$\{[Me_2C_2B_2H_9]Tl\}Tl$	3.67	*m*
$\{[Tp^{p-Tol}]Tl\}_2$	3.86	*n*
$\{[Tp^{c-Pr}]Tl\}_4$	3.65	*o*
[Bp]Tl	3.70	this work

[a] Only the shortest “intramolecular” interactions are listed. [b] Schumann, H.; Janiak, C.; Pickardt, J.; Börner, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 789−790. [c] Jutzi, P.; Schnittger, J.; Hursthouse, M. B. *Chem. Ber.* **1991**, *124*, 1693−1697. [d] Uhl, W.; Keimling, S. U.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 64−65. [e] Klinkhammer, K. W.; Henkel, S. *J. Organomet. Chem.* **1994**, *480*, 167−171. [f] Veith, M.; Spaniol, A.; Pöhlmann, J.; Gross, F.; Huch, V. *Chem. Ber.* **1993**, *126*, 2625−2635. [g] Hellmann, K. W.; Gade, L. H.; Scowen, I. J.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1996**, 2515−2516. [h] Hellmann, K. W.; Gade, L. H.; Fleischer, R.; Stalke, D. *Chem. Commun.* **1997**, 527−528. [i] Hellmann, K. W.; Gade, L. H.; Fleischer, R.; Kottke, T. *Chem.—Eur. J.* **1997**, *3*, 1801−1806. [j] Galka, C. H.; Gade, L. H. *Inorg. Chem.* **1999**, *38*, 1038−1039. [k] Hellmann, K. W.; Gade, L. H.; Fleischer, R.; Kottke, T. *Chem.—Eur. J.* **1997**, *3*, 1801−1806. [l] Hellmann, K. W.; Gade, L. H.; Steiner, A.; Stalke, D.; Möller, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 160−163. [m] Jutzi, P.; Wegner, D.; Hursthouse, M. B. *Chem. Ber.* **1991**, *124*, 295−299. [n] Ferguson, G.; Jennings, M. C.; Lalor, F. J.; Shanahan, C. *Acta. Crystallogr.* **1991**, *C47*, 2079−2082. [o] Rheingold, A. L.; Liable-Sands, L. M.; Trofimenko, S. *J. Chem. Soc., Chem. Commun.* **1997**, 1691−1692.

Sn═Sn bond in stanylene dimers.[17] Schwerdtfeger, on the other hand, suggested that the extended Hückel method overestimates the magnitude of the interaction between two $[HTl^{I}]$ units by at least a factor of 3 and has ascribed the weak $Tl^{I}\cdots Tl^{I}$ interaction to a correlation effect.[18,19]

Indeed, the latest results suggest that metallophilic bonding of this type is best described as correlation effects that are strongly enhanced by relativistic effects.[7,8,20] Regardless of the precise nature of the interaction, it is evident that the factors which dictate the occurrence of $Tl^{I}\cdots Tl^{I}$ interactions are not thoroughly understood, although it is generally recognized that incorporation of bulky substituents is likely to inhibit aggregation.[21] For this reason, we have elected to examine the influence of substituents on the nature of bis(pyrazolyl)hydroborato thallium complexes, $[Bp^{RR'}]Tl$.

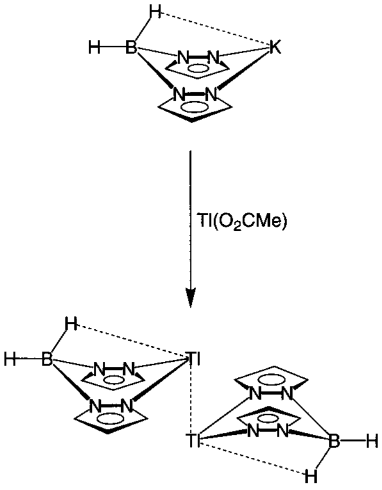
A variety of $[Bp^{RR'}]Tl$ complexes have recently been synthesized and structurally characterized by X-ray diffraction (Table 2).[22,23] These studies indicate that the bonding to the “two-coordinate” Tl^{I} centers is supplemented by means of a weak intramolecular $[Tl\cdots H{-}B]$ interaction and that the complexes are monomeric in the solid state. The bipyridyl-substituted complex $[Bp^{bipy}]Tl$ (bipy = 6−2,2-bipyridyl), however, provides an exception since the $Tl^{I}\cdots Tl^{I}$ separation is 3.93 Å,[23] although the close contact was proposed to be a consequence of π-stacking rather than due to a direct $Tl^{I}\cdots Tl^{I}$ interaction. Since each of the other monomeric $[Bp^{RR'}]Tl$ complexes listed in Table 2 possesses bulky R substituents at the 3-position of the pyrazolyl groups, which serve to protect the Tl^{I} centers from subsequent interactions, it was deemed appropriate to determine the structure of the parent compound [Bp]Tl to assess whether it would be possible for short $Tl^{I}\cdots Tl^{I}$ interactions in $[Bp^{RR'}]Tl$ complexes to exist in the absence of the proposed π-stack mechanism.

Table 2. Selected Metrical Data for $[Bp^{RR'}]Tl$ Complexes

	$d(Tl\cdots Tl)$ (Å)	$d(Tl{-}N_{av})$ (Å)	$d(Tl\cdots B)$ (Å)	ref
[Bp]Tl	3.70	2.81	3.34	this work
$[Bp^{Bu^t,Me}]Tl$	5.72	2.60	3.12	*a*
$[Bp^{Bu^t,Pr^i}]Tl$	5.46	2.65	3.18	*a*
$[Bp^{Bu^t{}_2}]Tl$	5.24	2.64	3.18	*a*
$[Bp^{Trip}]Tl$	7.11	2.70	3.31	*b*
$[Bp^{bipy}]Tl$	3.93	2.70	3.83	*b*
$Tl[H_2B(pz)(pz^{Bu^t{}_2})]$	4.57	2.67	3.22	*c*

[a] Dowling, C.; Ghosh, P.; Parkin, G. *Polyhedron* **1997**, *16*, 3469−3473. [b] Fillebeen, T.; Hascall, T.; Parkin, G. *Inorg. Chem.* **1997**, *36*, 3787−3790. [c] Fleming, J. S.; Psillakis, E.; Couchman, S. M.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1998**, 537−543. [d] Ghosh, P.; Hascall, T.; Dowling, C.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1998**, 3355−3357.

Scheme 1



The bis(pyrazolyl)hydroborato thallium(I) complex [Bp]Tl was obtained analogously to other $[Bp^{RR'}]Tl$ complexes by metathesis of [Bp]K[24] with $Tl(O_2CMe)$, as illustrated in Scheme 1. The molecular structure of $\{[Bp]Tl\}_2$ has been determined by X-ray diffraction, as illustrated in Figure 1, with selected bond lengths and angles listed in Table 3. The most significant feature is that the complex exists as a dimer with a $Tl^{I}\cdots Tl^{I}$

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(17) Budzelaar, P. H. M.; Boersma, J. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 187−189.

(18) Schwerdtfeger, P. *Inorg. Chem.* **1991**, *30*, 1660−1663.

(19) For additional calculations on $[HTl]_2$, see: Treboux, G.; Barthelat, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 4870−4878.

(20) Runeberg, N.; Schutz, M.; Werner, H. J. *J. Chem. Phys.* **1999**, *110*, 7210−7215.

(21) For example, the first and only example of a mono-coordinate thallium complex $[2,6\text{-}Trip_2C_6H_3]Tl$ (Trip = 2,4,6-$Pr^i{}_3C_6H_2$), stabilized by bulky substituents, exists as a discrete monomer with the closest $Tl^{I}\cdots Tl^{I}$ separation of 6.81 Å. See: Neimeyer, M.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1277−1279.

(22) (a) Fillebeen, T.; Hascall, T.; Parkin, G. *Inorg. Chem.* **1997**, *36*, 3787−3790. (b) Ghosh, P.; Hascall, T.; Dowling, C.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1998**, 3355−3357. (c) Dowling, C.; Ghosh, P.; Parkin, G. *Polyhedron* **1997**, *16*, 3469−3473.

(23) Fleming, J. S.; Psillakis, E.; Couchman, S. M.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1998**, 537−543.

(24) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170−3177.

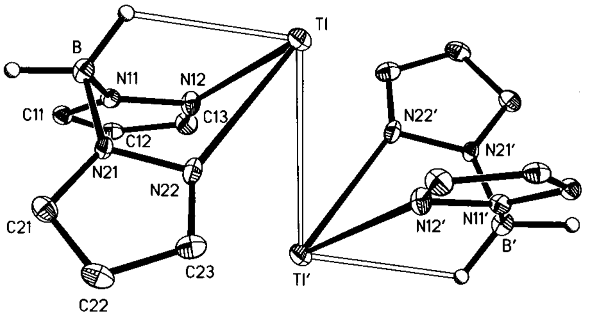

Figure 1. Molecular structure of $\{[Bp]Tl\}_2$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $\{[Bp]Tl\}_2$

Tl−N(12)	2.799(7)	Tl−N(22)	2.814(8)
Tl···H(1)	2.7(2)	Tl···Tl′	3.7001(6)
N(12)−Tl−N(22)	72.0(2)	N(12)−Tl−Tl′	55.5(2)
N(22)−Tl−Tl′	60.0(2)	H(1)−Tl−Tl′	101(4)

separation of 3.7001(6) Å, which is substantially shorter than that observed for other $[Bp^{RR'}]Tl$ derivatives (Table 2). A clear indication that this interaction should be considered significant is provided by the fact that it is less than twice the van der Waals radius of thallium (3.92 Å)[13] and only ca. 0.3 Å longer than the Tl−Tl separation in elemental thallium (3.41 Å).[11] In further support of the significance of this interaction, it is noteworthy that a parent ion corresponding to dinuclear $\{[Bp]Tl\}_2$ is observed in the DCI mass spectrum at $m/z = 704$, albeit a minor component compared to that for mononuclear [Bp]Tl.

Comparable unbridged $Tl^I\cdots Tl^I$ interactions have been observed for other oligonuclear thallium(I) complexes; for example, the $Tl^I\cdots Tl^I$ separation in $\{[\eta^5\text{-}C_5(CH_2Ph)_5]\}Tl\}_2$ is 3.632 Å.[3a] It is, however, evident that $Tl^I\cdots Tl^I$ separations in thallium(I) complexes span a rather wide range (Table 1), and at the short end actually approach a value typical for a normal Tl−Tl covalent bond.[12]

By comparison with monomeric $[Bp^{Bu^t,R}]Tl$ (R = Me, Pr^i, Bu^t), $[Bp^{Trip}]Tl$ and $[H_2B(pz)(pz^{Bu^t_2})]Tl$, each of which possesses substituents on the 3-positions of the pyrazolyl groups, the ability of [Bp]Tl to participate in a $Tl^I\cdots Tl^I$ interaction is presumably a result of diminished steric interactions. However, while it is clear that the $Tl^I\cdots Tl^I$ interaction is influenced by the substituents on the pyrazolyl groups, the extent to which "crystal packing effects" [25,26] are responsible for allowing the close approach of the Tl^I centers in $\{[Bp]Tl\}_2$ is uncertain.

It is also noteworthy that, despite the steric demands being lowest for the [Bp] ligand, the average Tl−N bond length in $\{[Bp]Tl\}_2$ is actually the longest of all other $[Bp^{RR'}]Tl$ complexes (Table 2). Furthermore, with the exception of $[Bp^{bipy}]Tl$, the Tl···B separation is the greatest for $\{[Bp]Tl\}_2$, so that it adopts a shallower boat configuration than do $[Bp^{RR'}]Tl$ derivatives with simple substituents. For comparison, the structure of the [Bp]Tl fragment is superimposed on that of $[Bp^{Bu^t,Me}]Tl$ in Figure 2.

The $Tl^I\cdots Tl^I$ separation in $\{[Bp]Tl\}_2$ is 0.23 Å shorter than in the only other dinuclear $\{[Bp^{RR'}]Tl\}_2$ complex, namely, $\{[Bp^{bipy}]Tl\}_2$ (3.93 Å). Furthermore, as noted above, the close separation in the latter complex was attributed to π-stacking, rather than representing a direct $Tl^I\cdots Tl^I$ interaction. The structures of the two dimers $\{[Bp]Tl\}_2$ and $\{[Bp^{bipy}]Tl\}_2$ are therefore quite different: i.e., the geometry at Tl in $\{[Bp]Tl\}_2$ is distinctly pyramidal (Figure 1),[27] whereas that in $\{[Bp^{bipy}]Tl\}_2$[28] (Figure 3) is much closer to planar. The angular nature is in line with the aforementioned calculations on XTl···TlX in which bending promotes s−p hybridization and reduces repulsion of the Tl lone pairs, although the significance of this observation is uncertain given the aforementioned role that correlation plays in determining the strength of the interaction.

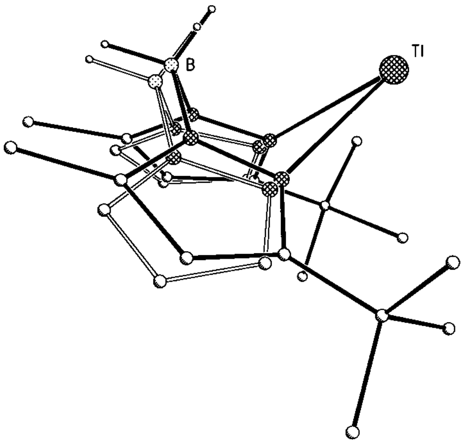

Figure 2. Superposition of [Bp]Tl (open bonds) and $[Bp^{Bu^t,Me}]Tl$ (solid bonds).

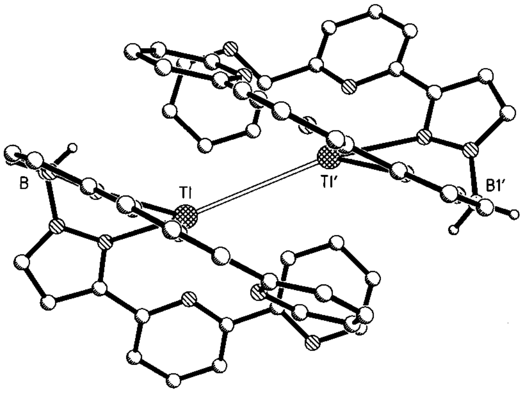

Figure 3. Molecular structure of $\{[Bp^{bipy}]Tl\}_2$ (data taken from ref 23).

It is also pertinent to compare the $Tl^I\cdots Tl^I$ interaction in $\{[Bp]Tl\}_2$ with those in tris(pyrazolyl)borato thallium counterparts, $[Tp^{RR'}]Tl$. As with $[Bp^{RR'}]Tl$ complexes, $[Tp^{RR'}]Tl$[13,29,30] complexes typically exist with discrete mononuclear structures that are devoid of $Tl^I\cdots Tl^I$ interactions.[31] Nevertheless, two $[Tp^{RR'}]Tl$ complexes have been reported to have short $Tl^I\cdots Tl^I$ contacts, namely, dinuclear $\{[Tp^{p\text{-}Tol}]Tl\}_2$ [3.8636(4) Å][32] and tetranuclear $\{[Tp^{c\text{-}Pr}]Tl\}_4$ [3.6468(4) Å].[33] Most surprisingly, however, the unsubstituted parent [Tp]Tl does *not* possess any

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(25) Martín, A.; Orpen, A. G. *J. Am. Chem. Soc.* **1996**, *118*, 1464−1470.

(26) Loos, D.; Baum, E.; Ecker, A.; Schnöckel, H.; Downs, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 860−862.

(27) The angular nature of the [Bp]Tl···Tl[Bp] interaction is indicated by the N_{cent}−Tl−Tl′ angle of 48.8°, where N_{cent} is the centroid of N(12) and N(22).

(28) The bonding at Tl in $[Bp^{bipy}]Tl$ is also supplemented by interactions with the pyridyl nitrogen atoms.

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Table 4. Crystal, Intensity Collection, and Refinement Data for $\{[Bp]Tl\}_2$

lattice	monoclinic	Z	2
empirical formula	$C_{12}H_{16}B_2N_8Tl_2$	temp (K)	223
fw	351.3	radiation (λ, Å)	0.710 73
space group	$P2_1/c$ (no. 14)	ρ(calcd) (g cm^{-3})	2.619
a (Å)	7.5887(2)	μ(Mo Kα) (mm^{-1})	18.07
b (Å)	7.1443(2)	θ(max) (deg)	28.06
c (Å)	16.484(1)	no. of data	1722
α (deg)	90	no. of params	116
β (deg)	94.391(2)	R1[a]	0.0390
γ (deg)	90	wR2[a]	0.1080
V (Å)^3	891.06(3)	GOF	1.113

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $I > 2\sigma(I)$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ for $I > 2\sigma(I)$.

significant $Tl^{I}\cdots Tl^{I}$ interactions.[34] Thus, while consideration of the structures of the bis(pyrazolyl)hydroborato complexes $[Bp^{RR'}]Tl$ suggests that $Tl^{I}\cdots Tl^{I}$ interactions are promoted for derivatives with less sterically demanding substituents,[35] consideration of the structures of tris(pyrazolyl)hydroborato complexes $[Tp^{RR'}]Tl$ indicates that the situation is not so simple. Moreover, the fact that $\{[\eta^5\text{-}C_5(CH_2Ph)_5]Tl\}$ crystallizes in two forms, one as a dimer with a $Tl^{I}\cdots Tl^{I}$ separation of 3.63 Å,[3] and one as a chain of monomers devoid of such an interaction,[36] indicates that the $Tl^{I}\cdots Tl^{I}$ bonds, regardless of their nature, must be regarded as weak.[37]

Experimental Section

All manipulations were performed using a combination of a glovebox and high-vacuum or Schlenk techniques.[38] Solvents were purified and degassed by standard procedures. Commercially available reagents were not further purified. ^1H and ^{13}C chemical shifts are reported in parts per million relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity or the ^{13}C resonances, respectively. All coupling constants are reported in hertz. C, H, and N elemental analyses were measured using a Perkin-Elmer 2400 CHN elemental analyzer. [Bp]K was prepared according to the literature method.[24] DCI (CH_4) mass spectra were obtained using a Nermag 10-10 spectrometer.

Synthesis of $\{[Bp]Tl\}_2$. A mixture of [Bp]K (0.5 g, 2.7 mmol) and $Tl(O_2CMe)$ (1.1 g, 4.0 mmol) in THF (ca. 30 mL) was stirred at room temperature for 40 min, after which the solvent was removed in vacuo. The residue was extracted into benzene, and the mixture was filtered. The volatile components were removed from the filtrate, and the residue was washed with pentane (ca. 20 mL) to give $\{[Bp]Tl\}_2$ as a white solid (0.3 g, 32%). Anal. Calcd for $C_6H_8N_4BTl$: C, 20.5; H, 2.3; N, 16.0. Found: C, 20.8; H, 2.3; N, 16.1. IR data (cm^{-1}), KBr pellet: 2372 and 2258 [ν(B$-$H)]. ^1H NMR data (C_6D_6): 6.13 [t, $^3J_{H-H} = 2$, 2 H of $2C_3N_2H_3$)], 7.31 [t, $^3J_{H-H} = 2$, 2 H of $2C_3N_2H_3$)], 7.67 [t, $^3J_{H-H} = 2$, 2 H of $2C_3N_2H_3$], BH_2 (not located). ^{13}C NMR data: 104.8 [d, $^1J_{C-H} = 176$, 2 C of $2C_3N_2H_3$], 136.8 [d, $^1J_{C-H} = 185$, 2 C of $2C_3N_2H_3$], 139.6 [d, $^1J_{C-H} = 182$, 2 C of $2C_3N_2H_3$].

X-ray Structure Determination. Crystal data, data collection, and refinement parameters for $\{[Bp]Tl\}_2$ are summarized in Table 4. X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector using graphite-monochromated Mo Kα X-radiation ($\lambda = 0.710\,73$ Å). The structure was solved using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures using SHELXTL.[39] Hydrogen atoms on carbon were included in calculated positions. Systematic absences for $\{[Bp]Tl\}_2$ were consistent uniquely with $P2_1/c$ (no. 14).

Conclusion

In summary, the $Tl^{I}\cdots Tl^{I}$ separation in $\{[Bp]Tl\}_2$ [3.7001(6)] is the shortest of all $[Bp^{RR'}]Tl$ complexes structurally characterized to date. With a value that is shorter than twice the van der Waals radius (3.92 Å), and only ca. 0.3 Å longer than the Tl$-$Tl separation in elemental thallium (3.41 Å), it is evident that the interaction must be regarded as structurally significant. However, as with other complexes that exhibit such interactions, the extent to which crystal packing effects are responsible for allowing the interaction to be stabilized is presently uncertain.

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Supporting Information Available: Crystallographic information for $\{[Bp]Tl\}_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) The structure of [Tp]Tl in the solid state is comprised of a zigzag array of molecules with internuclear Tl distances of 4.80 and 5.12 Å. See: Janiak, C.; Temizdemir, S.; Scharmann, T. G. *Z. Anorg. Allg. Chem.* **1998**, *624*, 755−756.

(35) In this regard, the difference in $Tl^{I}\cdots Tl^{I}$ separations for $CH_2[CH_2N(Tl)SiMe_3]$ (3.775 and 3.697 Å) and $CH_2[CH_2N(Tl)SiMe_2Bu^t]$ (>4.70 Å) has also been attributed to steric effects. See: Hellmann, K. W.; Gade, L. H.; Fleischer, R.; Stalke, D. *Chem. Commun.* **1997**, 527−528.

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(37) As another example, the $Tl^{I}\cdots Tl^{I}$ separations in the anionic thallocarborane $[closo\text{-}3,1,2\text{-}TlC_2B_9H_{11}]^-$ are counterion dependent (4.24 Å for $[PPN]^+$ and 7.80 Å for $[Ph_3PMe]^+$). See: Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 3589−3591.

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