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COMMUNICATION

Structural characterization of *bis*(pyrazolyl)hydroborato thallium complexes: monomeric "two-coordinate" thallium derivatives supplemented by [Tl···H–B] interactions

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Abstract—The syntheses and structural characterization of a series of mononuclear *bis*(pyrazolyl)hydroborato thallium complexes $Tl[Bp^{Bu^t,R}]$ (R = Me, Pr^i, Bu^t) are described. In each case, the two-coordinate Tl(I) centers of $Tl[Bp^{Bu^t,R}]$ are supplemented by secondary [Tl···H–B] interactions. © 1997 Elsevier Science Ltd

Keywords: thallium, pyrazolylborate; coordination number.

Although monovalent thallium is known to form a large range of complexes with coordination numbers of up to 12 [1], low-coordinate Tl^I derivatives are rare [2]. For example, an attempt to synthesize a monocoordinate Tl^I complex yielded the tetranuclear derivative $[\{2,6\text{-}Pr^i_2C_6H_3(Me_3Si)N\}Tl]_4$ instead of the mononuclear counterpart [3]. In contrast to monocoordination, however, two-coordinate Tl^I is precedented for dinuclear systems. For example, the dinuclear thiolate derivative, $[Tl\{\mu\text{-}SSi(OBu^t)_3\}]_2$, reported in 1985 by von Schnering, is the first structurally characterized example of which we are aware [4–6]. Following von Schnering's report of $[Tl\{\mu\text{-}SSi(OBu^t)_3\}]_2$, closely related examples of dinuclear aryloxide and amide complexes, e.g. $[Tl\{\mu\text{-}OC_6H_2(CF_3)_3\}]_2$ [7] $[Tl\{\mu\text{-}OC_6H_4(C_6H_4)OH\}]_2$ [8], and $[Tl\{\mu\text{-}N(SiMe_3)_2\}]_2$ [9], each with a 4-membered $[Tl_2X_2]$ motif have subsequently been described [10,11,12]. By comparison to these dinuclear species, however, well-defined mononuclear two-coordinate Tl^I complexes are not well-known, since such environments typically result in an expanded coordination sphere *via* either supplementary Tl···Tl interactions or interactions with heteroatoms (which may be either intramolecular or intermolecular). In this paper, we describe the syntheses and structural characterization of a series of mononuclear *bis*(pyrazolyl)hydroborato thallium complexes $Tl[Bp^{Bu^t,R}]$ (R = Me, Pr^i, Bu^t) in which each of the thallium centers is protected by bulky t-butyl substituents in the 3-positions of the pyrazolyl groups [13].

The *bis*(3-t-butylpyrazolyl)hydroborato thallium complex $Tl[Bp^{Bu^t}]$ was first described by Trofimenko in 1987 and was prepared by metathesis of the potassium derivative $K[Bp^{Bu^t}]$ with $Tl(NO_3)$ [14,15]. The counterparts with alkyl substituents in the 5-positions, namely $Tl[Bp^{Bu^t,R}]$ (R = Me, Pr^i, Bu^t), may likewise be synthesized from the appropriate pyrazole by reaction with $LiBH_4$ followed by metathesis with TlOAc, as illustrated in Scheme 1.

The molecular structures of $Tl[Bp^{Bu^t,R}]$ (R = Me, Pr^i, Bu^t) have been determined by X-ray diffraction (Figs 1–3) and selected metrical data are presented in Table 1 [16]. In each case, the Tl—N bond lengths and N—Tl—N bond angles are comparable to the corresponding average values for the *tris*(pyrazolyl)hydroborato derivatives $Tl[Tp^{Bu^t}]$

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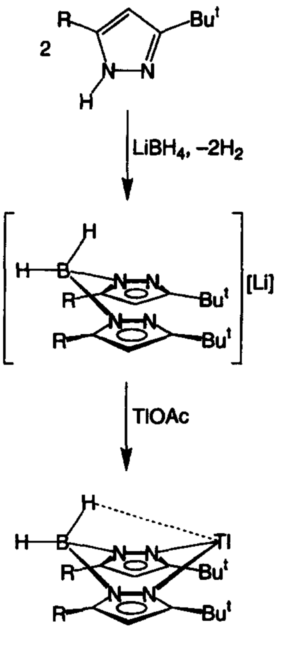

(R = Me, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$)

Scheme 1.

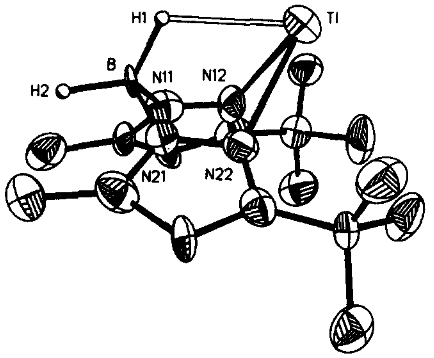

Fig. 1. Molecular Structure of $\mathrm{Tl[Bp^{Bu^t,Me}]}$.

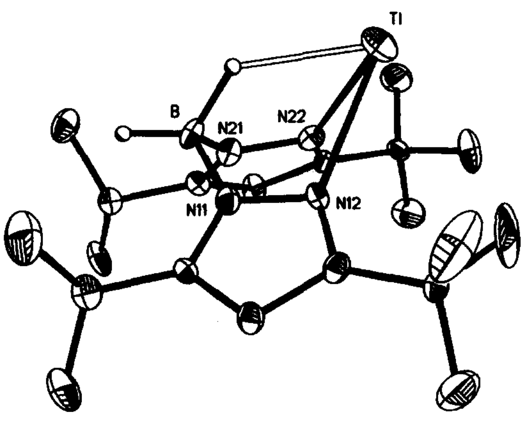

Fig. 2. Molecular Structure of $\mathrm{Tl[Bp^{Bu^t,Pr^i}]}$.

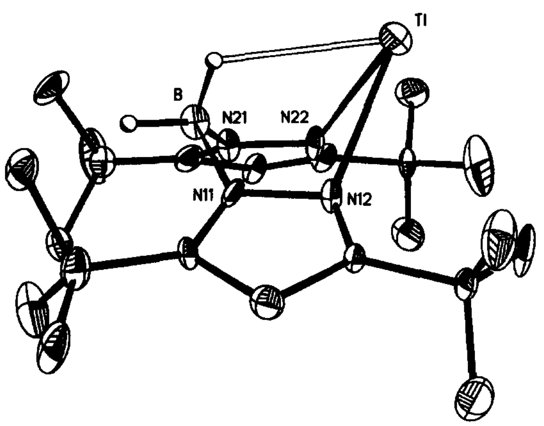

Fig. 3. Molecular Structure of $\mathrm{Tl[Bp^{Bu^t_2}]}$. The hydrogen atoms attached to boron were not located and their positions are only intended to be illustrative.

[2.59(1) Å and 78(3)°] [17], $\mathrm{Tl[Tp^{Bu^t,Me}]}$ [2.50(2) Å and 78(1)°] [18], and $\mathrm{Tl[Tp^{Bu^t_2}]}$ [2.57(3) Å and 78(3)°] [19]. The intermolecular Tl···N separations in $\mathrm{Tl[Bp^{Bu^t,R}]}$ [20], however, are (i) considerably longer than the Tl-N bond lengths and (ii) comparable to or greater than the sum of their van der Waals radii (3.51 Å) [21], so that the structures are appropriately described as consisting of well-separated monomeric units [22].

The monomeric nature of $\mathrm{Tl[Bp^{Bu^t,R}]}$ contrasts with the oligomeric character of many other thallium(I) derivatives of 3-electron donor LX-type ligands [23]. For example, the 2-pyridyl-cyanoxime complex $\mathrm{Tl\{\eta^2\text{-}N(O)C(CN)(C_5H_4N)\}}$ is related to $\mathrm{Tl[Bp^{Bu^t,R}]}$ in that it is also a derivative of a bidentate nitrogen donor ligand [24,25], but the coordination about $\mathrm{Tl^I}$ in this species is also supplemented by several short intermolecular contacts, one of which includes a Tl···O separation of 2.81 Å [26]. As a further example, rather than existing as a two-coordinate monomer, the structure of the β-diketonate derivative, $\mathrm{Tl\{\eta^2\text{-}OC(Ar)CHC(Ar)O\}}$ (Ar = p-$\mathrm{C_6H_4OMe}$), consists of a Tl···Tl bonded dimer (with a Tl···Tl separation of 3.747(1) Å) which is further aggregated into an infinite columnar array *via* intramolecular Tl···O interactions [27,28]. Finally, the dithiocarbamate complexes $\mathrm{[Tl\{\eta^2\text{-}(S)_2CNR_2\}]_2}$ (R = Me, $\mathrm{Pr^n}$, $\mathrm{Pr^i}$) are dinuclear by virtue of supplementary Tl–S interactions such that the $\mathrm{Tl^I}$ centers are 4-coordinate [29,30].

In contrast to the above examples which supplement the bonding to $\mathrm{Tl^I}$ *via* intermolecular interactions, the "two-coordinate" $\mathrm{Tl^I}$ centers of $\mathrm{Tl[Bp^{Bu^t,R}]}$ are each augmented by means of an intramolecular [Tl···H–B] interaction. Related 3-center-2-electron [M···H–B] interactions are well precedented for transition metal complexes [31,32]. In the cases of $\mathrm{Tl[Bp^{Bu^t,Me}]}$ and $\mathrm{Tl[Bp^{Bu^t,Pr^i}]}$, the bridging hydrogen atom was located in the X-ray diffraction study, thereby determining values of 2.44 Å and 2.26 Å, respectively, for the Tl···H separations in these

Table 1. Selected Metrical Data for $Tl[Bp^{Bu^t,R}]$

	d(Tl—N)/(Å)	N—Tl—N/(°)	d(Tl···H)/(Å)	d(Tl···B)/(Å)
$Tl[Bp^{Bu^t,Me}]$	2.592(25) 2.597(16)	73.6(6)	2.44(13)	3.12
$Tl[Bp^{Bu^t,Pr^i}]$	2.628(10) 2.665(10)	72.1(3)	2.26[a]	3.18
$Tl[Bp^{Bu^t_2}]$	2.632(12) 2.644(12)	67.5(4)	[b]	3.18

[a] H atom located in difference map but not refined.
[b] H atom not located.

complexes. Although the magnitude of such interactions are longer than that of diatomic Tl–H in the gas phase (1.87 Å) [33,34], it is substantially shorter than the sum of their van der Waals radii (3.16 Å) [21], and is therefore presumably indicative of a weak attractive interaction. We are not, however, aware of any structurally characterized thallium hydride complexes with which to draw comparisons. The only complexes of which we are aware that exhibit comparable Tl···H interactions are thallium(III) methyl derivatives [35], for which the short distances are presumably a consequence of the geometry imposed within a [Tl–CH_3] moiety [36,37]. Consistent with the presence of [Tl···H–B] interactions, the non-bonded Tl···B separations in $Tl[Bp^{Bu^t,R}]$ (3.12–3.18 Å; Table 1) are considerably less than the range observed for *tris*(pyrazolyl)hydroborato derivatives (3.46–3.90 Å [38]. For example, the non-bonded Tl···B separations in the 3-*t*-butyl derivatives $Tl[Tp^{Bu^t}]$ [17], $Tl[Tp^{Bu^t,Me}]$ [18], and $Tl[Tp^{Bu^t_2}]$ [19] are 3.56, 3.53 and 3.44 Å, respectively [39].

The IR spectra of $Tl[Bp^{Bu^t,R}]$ derivatives show absorptions at *ca*, 2500 cm^{-1} and *ca* 2200 cm^{-1} attributable to [B–H] stretching vibrations. For example, $Tl[Bp^{Bu^t,Pr^i}]$ exhibits absorptions at 2481 cm^{-1} and 2202 cm^{-1}, which have been confirmed by comparison with the deuterated analogue: ν[B–D] = 1852 cm^{-1} ($\nu_H/\nu_D = 1.34$) and 1625 cm^{-1} ($\nu_H/\nu_D = 1.36$) [40]. Transition metal *bis*(pyrazolyl)hydroborato complexes [31] are also characterized by two absorptions of the [BH_2] moiety, with the lower energy absorption (typically in the range *ca* 1800–2000 cm^{-1}) being associated with that of the [M···H–B] interaction. By inference, the absorptions at *ca* 2200 cm^{-1} may be assigned to the [Tl···H–B] interaction. However, since these absorptions are at higher energy than those of related transition metal complexes, it is evident that the [Tl···H–B] interaction in these complexes should not be regarded as being of comparable strength to those in electronically unsaturated transition metal complexes.

In summary, a series of *bis*(pyrazolyl)hydroborato Tl^I complexes with *t*-butyl groups in the 3-positions of the pyrazolyl groups, $Tl[Bp^{Bu^t,R}]$ (R = Me, Pr^i, Bu^t) have been synthesized. X-ray diffraction studies demonstrate that the complexes are monomeric and that the two-coordinate Tl^I centers are supplemented by [Tl···H–B] interactions.

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37. In addition, the ruthenium complex $[\{[\mathrm{Ph_2PCH_2CH_2})_3\mathrm{P}\}\mathrm{RuH(ClTl)}]_2$ exhibits a Tl$\cdots$H separation of 2.6(2) Å. See reference [11].
38. Data taken from Cambridge Structural Database (Version 5.12, October 1996)
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40. The IR spectra of $\mathrm{Tl[Bp^{Bu^t_2}]}$ and $\mathrm{Tl[Bp^{Bu^t,Me}]}$ are more complicated than that of $\mathrm{Tl[Bp^{Bu^t,Pr^i}]}$, with the lower energy band in the vicinity of 2200 cm^{-1} being composed of several absorptions ($\mathrm{Tl[Bp^{Bu^t_2}]}$: 2552, 2188, 2161 cm^{-1}; $\mathrm{Tl[Bp^{Bu^t,Me}]}$: 2458, 2274, 2226, 2186 cm^{-1}). Likewise, the IR spectrum of the parent derivative $\mathrm{Tl[Bp^{Bu^t}]}$ is surprisingly complicated, with Trofimenko having reported [B–H] stretches at 2410, 2355, 2290, 2275, 2218, and 2178 cm^{-1} (reference [14]). In this regard, Trofimenko has also noted that pyrazabole has a complex set of absorptions in both the solid state and solution. See: Trofimenko, S., *J. Am. Chem. Soc.*, 1967, **89,** 3165.