10914 *J. Am. Chem. Soc.* **1996,** *118,* 10914−10915

A Monovalent Gallium Complex Supported by Tris(3,5-di-*tert*-butylpyrazolyl)hydroborato Ligation: The Syntheses and Structures of $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Ga}$ and Its $\mathrm{GaI_3}$ Adduct, $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Ga}\rightarrow\mathrm{GaI_3}$[1]

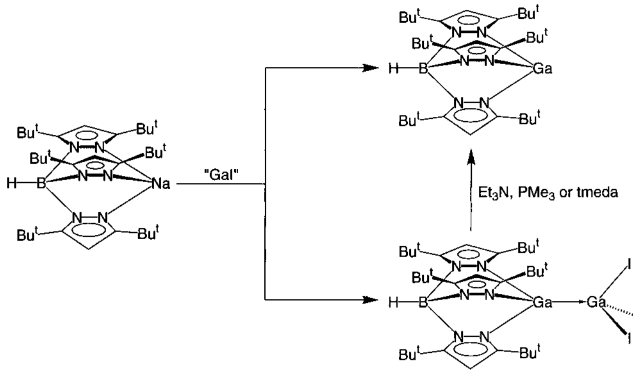
Matthew C. Kuchta, Jeffrey B. Bonanno, and Gerard Parkin*

Department of Chemistry
Columbia University
New York, New York 10027

Received August 2, 1996

The ability of the heavier group 13−16 elements to form complexes in which the elements exhibit the subvalent ($N - 2$) state is well-precedented (*i.e.*, the so-called "inert pair" effect).[2] The tendency to form such complexes diminishes quite rapidly upon ascending the periodic table. For example, whereas monovalent complexes of thallium and indium are reasonably well-known, such derivatives of the lighter group 13 elements (B, Al, Ga) are extremely rare.[2a] Specifically, with respect to gallium, aside from mixed-valent species (*e.g.*, $[\mathrm{Ga^I}][\mathrm{Ga^{III}X_4}]$[3,4]) and complexes with reduced formal oxidation states by virtue of the presence of Ga−Ga bonds[5,6] (*e.g.*, $[(\mathrm{Me_3Si})_3\mathrm{CGa}]_4$,[7] $[\{(\mathrm{Me_3Si})_2\mathrm{CH}\}_2\mathrm{Ga}]_2$,[8] $[(\mathrm{Me_3CCH_2})\mathrm{Ga}]_n$,[9] $[(\mathrm{dioxane})\mathrm{GaX_2}]_2$ (X = Cl, Br),[10] $\mathrm{Na_2}[(\mathrm{Mes_2C_6H_3})\mathrm{Ga}]_3$,[11] and $[\mathrm{Li}([12]\mathrm{crown}\text{-}4)_2]$-$\{[(\mathrm{Pr^i}_3\mathrm{C_6H_2})_2\mathrm{Ga}\}_2]$[12]), well-defined examples of subvalent complexes are uncommon.[2,13] Indeed, although precise details of their structures are unknown, monovalent gallium halide species, (*e.g.*, "GaCl"[14] and "GaI"[15]) have only recently been synthesized on a preparative scale. As a consequence, monovalent organogallium complexes, namely the cyclopentadienyl derivatives $[\mathrm{Cp^\dagger Ga}]$ [$\mathrm{Cp^\dagger} = \eta^5\text{-C_5H_5}$, $\eta^5\text{-C_5Me_5}$, $\eta^5\text{-C_5H_4Bu^t}$, $\eta^5\text{-C_5H_2(SiMe_3)_3}$, $\eta^5\text{-C_5(CH_2Ph)_5}$], have only existed since 1992.[16] In this paper, we describe the synthesis of the *tris*(3,5-di-*tert*-butylpyrazolyl)hydroborato derivative $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Ga}$, the first discrete (*i.e.*, not mixed-valent) monovalent gallium complex to be structurally characterized by X-ray diffraction.

Scheme 1



Recent studies have demonstrated that the tris(pyrazolyl)-hydroborato ligand system $[\mathrm{Tp^{RR'}}]$[17] is ideal for supporting mononuclear monovalent complexes of both indium[18] and thallium[19] (*e.g.*, $[\mathrm{Tp^{Ph}}]\mathrm{In}$,[20] $[\mathrm{Tp^{Bu^t}}]\mathrm{In}$,[21] and $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{In}$).[21b] In view of this demonstrated ability to sustain monomeric derivatives of indium(I) and thallium(I), we anticipated that *tris*-(pyrazolyl)hydroborato ligands could also provide a suitable environment for stabilizing monovalent complexes of the lighter group 13 elements, which do not commonly form such complexes. Significantly, the monovalent gallium complex $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Ga}$ is obtained by the reaction of "GaI"[15] with $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Na}$,[22] which also gives the adduct $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Ga}\rightarrow\mathrm{GaI_3}$.[23] The formation of the $\mathrm{GaI_3}$ adduct is not overly surprising, considering the paucity of monovalent gallium complexes, and is presumably a consequence of "GaI" disproportionation.[24−26] In solution, the $\mathrm{GaI_3}$ moiety of $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Ga}\rightarrow\mathrm{GaI_3}$ is readily abstracted by a Lewis base (*e.g.*, $\mathrm{Et_3N}$, $\mathrm{PMe_3}$ or TMEDA), thereby generating $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Ga}$ (Scheme 1).

---

[1] In memory of Brian Bent, a beloved friend and colleague, an outstanding chemist, and a wonderful person, who died suddenly at the age of 35 on July 23, 1996.

[2] (a) *Chemistry of Aluminum, Gallium, Indium, and Thallium*; Downs, A. J., Ed.; Chapman and Hall: New York, 1993. (b) Schwerdtfeger, P.; Heath, G. A.; Dolg, M.; Bennett, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 7518−7527. (c) Ng, S.-W.; Zuckerman, J. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 297−325.

[3] (a) Garton, G.; Powell, H. M. *J. Inorg. Nucl. Chem.* **1957**, *4*, 84−89. (b) Schmidbaur, H.; Nowak, R.; Bublak, W.; Burkert, P.; Huber, B.; Müller, G. *Z. Naturforsch. B: Chem. Sci.* **1987**, *42*, 553−556. (c) Gerlach, G.; Hönle, W.; Simon, A. *Z. Anorg. Allg. Chem.* **1982**, *486*, 7−21. (d) Hönle, W.; Simon, A.; Gerlach, G. *Z. Naturforsch. B: Chem. Sci.* **1987**, *42*, 546−552.

[4] For example, mixed-valent arene complexes are known. See: (a) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 893−904. (b) Schmidbaur, H.; Thewalt, U.; Zafiropoulos, T. *Organometallics* **1983**, *2*, 1550−1554. (c) Ulvenlund, S.; Wheatley, A.; Bengtsson, L. A. *J. Chem. Soc., Dalton Trans.* **1995**, 245−254. (d) Schmidbaur, H.; Nowak, R.; Huber, B.; Müller, G. *Polyhedron* **1990**, *9*, 283−287.

[5] Tuck, D. *Polyhedron* **1990**, *9*, 377−386.

[6] However, it should be noted that although by definition complexes with metal−metal bonds exhibit reduced oxidation states, it is not necessarily appropriate to consider such complexes to be subvalent. See: Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127−148.

[7] Uhl, W.; Hiller, W.; Layh, M.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1364−1366.

[8] Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289−300.

[9] Beachley, O. T., Jr.; Pazik, J. C.; Noble, M. J. *Organometallics* **1994**, *13*, 2885−2889.

[10] (a) Beamish, J. C.; Small, R. W. H.; Worrall, I. J. *Inorg. Chem.* **1979**, *18*, 220−223. (b) Small, R. W. H.; Worrall, I. J. *Acta Crystallogr.* **1982**, *B38*, 250−251.

[11] Li, X.-W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578−7579.

[12] He, X.; Bartlett, R. A.; Olmstead, M. M.; Ruhlandt-Senge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 717−719.

[13] (a) Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1386−1397. (b) Dohmeier, C.; Loos, D.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 129−149. (c) Schneider, J. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1830−1832. (d) Paetzold, P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 544−546. (e) Dreiss, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828−856.

[14] Tacke, M.; Kreienkamp, H.; Plaggenborg, L.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1991**, *604*, 35−38.

[15] Green, M. L. H.; Mountford, P.; Smout, G. J.; Speel, S. R. *Polyhedron* **1990**, *9*, 2763−2765.

[16] (a) Loos, D.; Schnöckel, H.; Gauss, J.; Schneider, U. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1362−1364. (b) Loos, D.; Schnöckel, H. *J. Organomet. Chem.* **1993**, *463*, 37−40.

[17] For the abbreviations of tris(pyrazolyl)hydroborato ligands, see: Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980.

[18] For a review of poly(pyrazolyl)borate complexes of gallium and indium, see: Reger, D. L. *Coord. Chem. Rev.* **1996**, *147*, 571−595.

[19] For a compilation of thallium(I) derivatives, $[\mathrm{Tp^{RR'}}]\mathrm{Tl}$, see: Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291−393.

[20] Frazer, A.; Piggott, B.; Hursthouse, M. B.; Mazid, M. *J. Am. Chem. Soc.* **1994**, *116*, 4127−4128.

[21] (a) Dias, H. V. R.; Huai, L.; Wiechang, J.; Bott, S. G. *Inorg. Chem.* **1995**, *34*, 1973−1974. (b) Kuchta, M. C.; Dias, H. V. R.; Bott, S. G.; Parkin, G. *Inorg. Chem.* **1996**, *35*, 943−948.

[22] Dowling, C. M.; Leslie, D.; Chisholm, M. H.; Parkin, G. *Main Group Chem.* **1995**, *1*, 29−52.

[23] $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Ga}$ is readily separated from $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{Ga}\rightarrow\mathrm{GaI_3}$ by extraction of the former into pentane.

[24] Products derived from disproportionation, (*e.g.*, $\mathrm{Ph_3PGaI_3}$ and $(\mathrm{THF})\mathrm{GaI_3}$), have been observed in other reactions of "GaI". Green, M. L. H. Personal communication.

[25] Disproportionation products have also been observed in the the reaction of InCl with Cp*Li to give $[\mathrm{Cp^*In}]_6$. See: Beachley, O. T., Jr.; Blom, R.; Churchill, M. R.; Faegri, K., Jr.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346−356.

[26] For an example of a related indium complex, see: Frazer, A.; Hodge, P.; Piggott, B. *J. Chem. Soc., Chem. Commun.* **1996**, 1727−1728.

S0002-7863(96)02698-4 CCC: $12.00

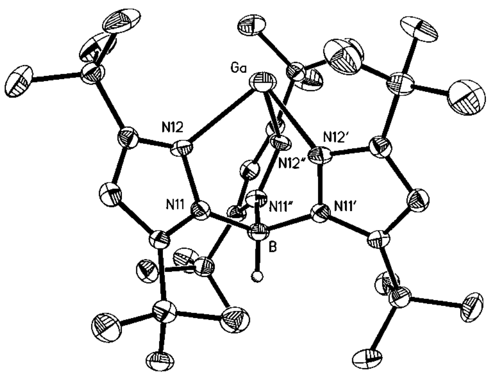


Figure 1. Molecular structure of [Tp$^{\mathrm{Bu^t}_2}$]Ga.

Table 1. Structural Comparisons of [Tp$^{\mathrm{Bu^t}_2}$]Ga with Related Complexes

	***d*(Ga-X)/Å**^{a}	***d*(In-X)/Å**^{a}	***d*(In-X) − *d*(Ga-X)/Å**^{a}
[Tp$^{\mathrm{Bu^t}_2}$]M	2.230(5)^b	2.468[9]^c	0.24
{[Tp$^{\mathrm{Me}_2}$]$_2$M}$^+$	2.064[6]^d	2.25[2]^e	0.19
(η^5-C$_5$Me$_5$)M(g)	2.405(4)^f	2.592(4)^g	0.19
MCl$_{(g)}$	2.202^h	2.401^h	0.20

[a] X = N, C, Cl. [b] This work. [c] Reference 21b. [d] Reference 33. [e] Frazer, A.; Piggott, B.; Harman, M.; Mazid, M.; Hursthouse, M. B. *Polyhedron* **1992**, *11*, 3013−3017. [f] Reference 28. [g] Reference 25. [h] Haaland, A.; Hammel, A.; Martinsen, K.-G.; Tremmel, J.; Volden, H. V. *J. Chem. Soc., Dalton Trans.* **1992**, 2209−2214.

Of most importance, [Tp$^{\mathrm{Bu^t}_2}$]Ga is the first discrete monovalent gallium complex to be structurally characterized by X-ray diffraction (Figure 1).[27] The closest Ga···Ga distance is *ca.* 10.4 Å, so that the structure consists of well-separated monomers. In this regard, it should be noted that although the pentamethylcyclopentadienyl analogue [(η^5-C$_5$Me$_5$)Ga] has been structurally characterized as a monomer in the gas phase by electron diffraction,[28] it is unlikely to be mononuclear in the solid state since its aluminum and indium counterparts (which are also monomeric in the gas phase[25,29]) exist as tetranuclear [(η^5-C$_5$Me$_5$)Al]$_4$[30] and hexanuclear [(η^5-C$_5$Me$_5$)In]$_6$[25] clusters in the crystalline form.[31,32]

As expected, the structure of [Tp$^{\mathrm{Bu^t}_2}$]Ga is closely related to its indium[21b] and thallium[22] counterparts, both of which exhibit a pronounced twisting of the [Tp$^{\mathrm{Bu^t}_2}$] ligand. Comparison of the structures of the monovalent gallium and indium complexes demonstrates that the average Ga−N bond length in [Tp$^{\mathrm{Bu^t}_2}$]Ga is *ca.* 0.24 Å shorter than the average In−N bond length in [Tp$^{\mathrm{Bu^t}_2}$]In (Table 1). This difference is comparable to the difference in M−C and M−Cl bond lengths of the (η^5-C$_5$Me$_5$)M and MCl derivatives in the gas phase (Table 1). The data listed in Table 1 also permit comparison of the coordination of tris(pyrazolyl)hydroborato ligands to well-defined monovalent and trivalent gallium centers. In particular, the average Ga−N bond length in monovalent [Tp$^{\mathrm{Bu^t}_2}$]Ga is substantially longer, by *ca.* 0.17 Å, than that of trivalent {[Tp$^{\mathrm{Me}_2}$]$_2$Ga}$^+$.[33]

The structure of the adduct [Tp$^{\mathrm{Bu^t}_2}$]Ga→GaI$_3$ has also been determined by X-ray diffraction.[26] Interestingly, the average Ga−N bond length of 2.05[2] Å in [Tp$^{\mathrm{Bu^t}_2}$]Ga→GaI$_3$ is more akin to those of Ga(III) complexes than those of the gallium(I) complex [Tp$^{\mathrm{Bu^t}_2}$]Ga. Such an effect is presumably a consequence of the formal positive charge on the gallium center (*i.e.*, [Tp$^{\mathrm{Bu^t}_2}$]$\overset{+}{\mathrm{Ga}}$−$\overset{-}{\mathrm{Ga}}$I$_3$.[34] Although the gallium atoms of [Tp$^{\mathrm{Bu^t}_2}$]Ga→GaI$_3$ are formally linked by a dative interaction, the Ga−Ga bond length of 2.506(3) Å is within the range known for normal covalent bonds in other dinuclear complexes: for example, [(η^2-Bu^{t}NCHCHNBu^t)Ga]$_2$, 2.333(1) Å;[35] [Ga]$_2$[Ga$_2$I$_6$], 2.388(5) Å;[3c] [{(Me$_3$SiC)$_2$(BH)$_4$}Ga]$_2$, 2.340(2) Å;[36] [{(CF$_3$)$_3$C$_6$H$_2$}$_2$Ga]$_2$, 2.479(1) Å;[37] [(Pr$^i_3$C$_6$H$_2$)$_2$Ga]$_2$, 2.515(3) Å;[12] [{(Me$_3$Si)$_2$CH}$_2$Ga]$_2$, 2.541(1) Å.[8,38,39]

In summary, the bulky tris(3,5-di-*tert*-butylpyrazolyl)hydroborato ligand has allowed isolation of the monovalent gallium complex [Tp$^{\mathrm{Bu^t}_2}$]Ga and its GaI$_3$ adduct [Tp$^{\mathrm{Bu^t}_2}$]Ga→GaI$_3$. [Tp$^{\mathrm{Bu^t}_2}$]Ga is the first mononuclear monovalent gallium complex to be structurally characterized by X-ray diffraction.

Acknowledgment. We thank the National Science Foundation (CHE 93-00398) for support of this research and Professor M. L. H. Green for advice concerning the synthesis of “GaI”. G.P. is the recipient of a Camille and Henry Dreyfus Teacher−Scholar Award (1991−1996) and a Presidential Faculty Fellowship Award (1992−1997).

Supporting Information Available: Experimental details and tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for [Tp$^{\mathrm{Bu^t}_2}$]Ga and [Tp$^{\mathrm{Bu^t}_2}$]Ga→GaI$_3$ (19 pages). See any current masthead page for ordering and Internet access instructions.

JA962698F

---

(27) [Tp$^{\mathrm{Bu^t}_2}$]Ga·(C$_6$H$_6$)$_{0.5}$ is cubic, $Pa\bar{3}$ (No. 205), $a = b = c = 19.869(4)$ Å, $V = 7844(2)$ Å^3, $Z = 8$. [Tp$^{\mathrm{Bu^t}_2}$]Ga→GaI$_3$ is orthorhombic, $Pna2_1$ (No. 33), $a = 20.294(7)$ Å, $b = 11.044(4)$ Å, $c = 19.819(6)$ Å, $V = 4442(3)$ Å^3, $Z = 4$.

(28) Haaland, H.; Martinsen, K.-G.; Volden, H. V.; Loos, D.; Schnöckel, H. *Acta Chem. Scand.* **1994**, *48*, 172−174.

(29) Haaland, A.; Martinsen, K.-G.; Shlykov, S. A.; Volden, H. V.; Dohmeier, C.; Schnöckel, H. *Organometallics* **1995**, *14*, 3116−3119.

(30) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564−565.

(31) The significance of metal−metal bonding in cyclopentadienyl derivatives of the heavier group 3 elements is currently a matter of some debate. See: (a) Janiak, C.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1688−1690. (b) Schwerdtfeger, P. *Inorg. Chem.* **1991**, *30*, 1660−1663. (c) Budzelaar, P. H. M.; Boersma, J. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 187−189.

(32) Furthermore, although [(Me$_3$Si)$_3$CGa] is tetranuclear in the solid state (ref 7), it exists as a monomer in dilute solutions and in the gas phase, as demonstrated by electron diffraction studies. See: Haaland, A.; Martinsen, K.-J.; Volden, H. V.; Kaim, W.; Waldhör, E.; Uhl, W.; Schütz, E. *Organometallics* **1996**, *15*, 1146−1150.

(33) Cowley, A. H.; Carrano, C. J.; Geerts, R. L.; Jones, R. A.; Nunn, C. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 277−278.

(34) The Ga−N interactions are a composite of normal-covalent and dative-covalent bonds and, as such, are sensitive to the formal charge on the gallium center (see: Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992−1007). Furthermore, in accordance with Green’s classification of covalent compounds (ref 6), the valence number for both gallium centers in [Tp$^{\mathrm{Bu^t}_2}$]GaGaI$_3$ is 3.

(35) Brown, D. S.; Decken, A.; Cowley, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 5421−5422.

(36) Saxena, A. K.; Zhang, H.; Maguire, J. A.; Hosmane, N. S.; Cowley, A. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 332−334.

(37) Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070−2071. Data is cited in ref 35.

(38) For further comparison, the Ga−Ga bond lengths in [GaCl$_2$(OEt$_2$)]$_3$Ga[GaCl(OEt$_2$)$_2$] range from 2.417(2) to 2.450(2) Å (Loos, D.; Schnöckel, H.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1059−1060) while the Ga−Ga bond lengths in the tetranuclear complex [(Me$_3$Si)$_3$CGa]$_4$ range from 2.678(4) to 2.702(4) Å (ref 7).

(39) Examples of complexes with Ga−Ga multiple bond character include: [Li([12]crown-4)$_2$]{[(Pr$^i_3$C$_6$H$_2$)$_2$Ga}$_2$], 2.343(2) Å (ref 12) and Na$_2$[(Mes$_2$C$_6$H$_3$)Ga]$_3$, 2.441(1) Å (ref 11).