Terminal Chalcogenido Complexes of Gallium Supported by Tris(3,5-di-*tert*-butylpyrazolyl)hydroborato Ligation: [Tp^{But2}]GaE (E = Se, Te)

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The topic of multiple bonding to the heavier p-block elements has stimulated considerable interest over recent years. In particular, significant advances have been achieved with the elements of groups 14−16,[1] such that well-defined examples of valence[2] multiple bonds to many of these elements are now known. In marked contrast, however, even though reports of multiple bonding to the group 13 elements have appeared, the majority of these examples are concerned with *dative* multiple bonds.[3] Indeed, until very recently, complexes with valence multiple bonds were restricted to the lightest congener, boron.[4,5] Here we extend our studies of multiple bonding to the heavier main group elements with the syntheses of terminal chalcogenido complexes of gallium [Tp^{But2}]GaE (E = Se, Te) supported by tris(3,5-di-*tert*-butylpyrazolyl)hydroborato ligation.

We have previously described the syntheses of several examples of terminal chalcogenido complexes of germanium, tin, and indium, namely [η^4-Me$_8$taa]GeE (E = S, Se, Te),[6] [η^4-Me$_8$taa]SnE (E = S, Se),[7] and [Tp^{But2}]InSe,[8] by oxidative addition of the elemental chalcogen to the appropriate subvalent precursor. In view of the ability to isolate [Tp^{But2}]InSe, the first structurally characterized indium complex with a valence multiple bond, we rationalized that a similar methodology could be applied to stabilize multiply bonded gallium complexes. Although monomeric gallium(I) complexes are exceedingly rare, the required gallium(I) precursor, [Tp^{But2}]Ga,[9] has been recently synthesized and does indeed react with selenium and tellurium at room temperature to furnish the terminal chalcogenido complexes [Tp^{But2}]GaE (E = Se, Te) (eq 1). The importance
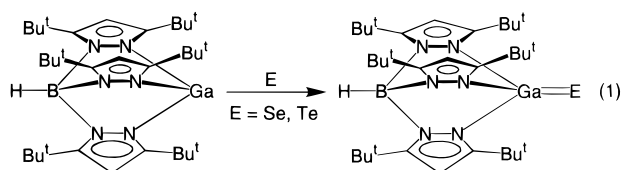
of the bulky tris(pyrazolyl)hydroborato ligand in stabilizing the terminal chalcogenido moiety is highlighted by the fact that the pentamethylcyclopentadienyl analogues, [(η^1-C$_5$Me$_5$)Ga(μ-Se)]$_4$[10] and [(η^1-C$_5$Me$_5$)Ga(μ-Te)]$_4$,[11] exist as tetranuclear clusters.[12]

[Tp^{But2}]GaSe and [Tp^{But2}]GaTe have been structurally characterized by X-ray diffraction (Figure 1)[13] and are characterized by Ga≈Se and Ga≈Te bond lengths[14a] of 2.214(1) and 2.422-(1) Å, respectively.[14b] Notably, there are relatively few other structurally-characterized complexes with either Ga−Se or Ga−Te bonds,[15−17] and it is significant that the aforementioned Ga≈Se and Ga≈Te bond lengths are shorter than those previously reported. For example, the shortest Ga−Se bond length listed in the Cambridge Structural Database is that of Ga[Se(2,4,6-Bu^{t}C$_6$H$_2$)]$_3$, with an average bond length of 2.324-

(1) For some leading articles on multiple bonding of the main group elements, see: (a) *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: San Diego, CA, 1996; Vol. 39. (b) Jutzi, P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 232−245. (c) Norman, N. C. *Polyhedron* **1993**, *12*, 2431−2446. (d) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J. *Coord. Chem. Rev.* **1994**, *130*, 427−480. (e) Okazaki, R.; Tokitoh, N.; Ishii, A.; Ishii, N.; Matsuhasi, Y.; Matsumoto, T.; Suzuki, H. *Phosphorus, Sulfur, Silicon* **1992**, *67*, 49−66. (f) Regitz, M. *Chem. Rev.* **1990**, *90*, 191−213. (f) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 361−374. (g) Cowley, A. H. *Polyhedron*, **1984**, *3*, 389−432. (h) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Anselme, G.; Delpon-Lacaze, G.; Chaubon, M.-A.; Rodi, K. A.; Satgé, J. *Main Group Met. Chem.* **1994**, *17*, 33−53. (i) Tokitoh, N.; Okazaki, R. *Main Group Chemistry News*; Vol. 3, No. 3, pp 4−11.

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(5) Power and Robinson have recently described [Li([12]crown-4)$_2$]-{[(Pr^i$_3$C$_6$H$_2$)$_2$Ga]$_2$}[a] and M$_2$[(Mes$_2$C$_6$H$_3$)Ga]$_3$ (M = Na, K),[5b−d] respectively, which are interesting examples of gallium complexes with Ga−Ga multiple bond character. (a) 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. (b) Li, X.-W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578−7579. (c) Li, X.-W.; Xie, Y.; Schreiner, P. R.; Gripper, K. D.; Crittendon, R. C.; Campana, C. F.; Schaefer, H. F.; Robinson, G. H. *Organometallics* **1996**, *15*, 3798−3803. (d) Xie, Y.; Schreiner, P.; Schaefer, H. F., III; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1996**, *118*, 10635−10639.

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(12) Furthermore, the selenido complex [Bu^{t}Ga(μ-Se)]$_4$ exists as a tetranuclear selenido-bridged complex. See: Power, M. B.; Ziller, J. W.; Tyler, A. N.; Barron, A. R. *Organometallics* **1992**, *11*, 1055−1063.

(13) [Tp^{But2}]GaSe is triclinic, P1̄ (No. 2), with *a* = 10.907(1) Å, *b* = 13.220-(1) Å, *c* = 13.231(1) Å, α = 95.49(1)°, β = 93.33(1)°, γ = 101.38-(1)°, Z = 2. [Tp^{But2}]GaTe is triclinic, P1̄ (No. 2), *a* = 11.084(1) Å, *b* = 13.248(1) Å, *c* = 13.255(2) Å, α = 95.11(1)°, β = 93.73(1)°, γ = 101.64(1)°, and Z = 2.

(14) (a) The symbol ≈ is intended to indicate a multiply bonded interaction for which the most appropriate resonance structure ([M$^+$−E$^-$], [M=E], [M≡E$^+$]) has not been determined unambiguously; see text. (b) Furthermore, the Ga−N bond lengths in [Tp^{But2}]GaSe [2.048(3)−2.061-(3) Å] and [Tp^{But2}]GaTe [2.053(3) Å−2.071(3) Å] are substantially shorter than in monovalent [Tp^{But2}]Ga [2.230(5) Å][9] but are comparable to the average Ga−N bond length of 2.064[6] Å in trivalent {[Tp^{Me2}]-Ga}$^+$ (Cowley, A. H.; Carrano, C. J.; Geerts, R. L.; Jones, R. A.; Nunn, C. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 277−278).

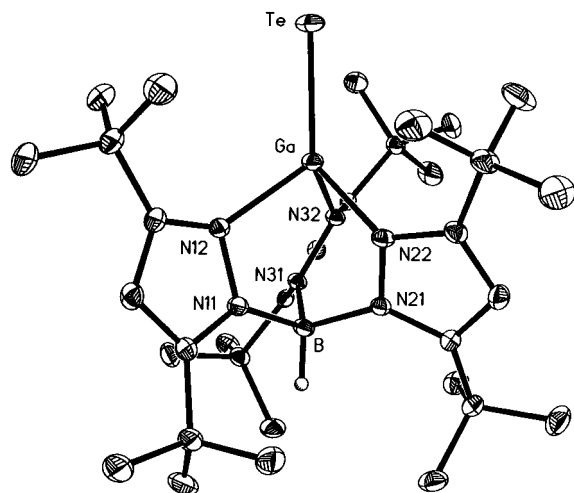(15) Oliver, J. P. *J. Organomet. Chem.* **1995**, *500*, 269−281.

Figure 1. Molecular structure of [Tp^{But_2}]GaTe.

(2) Å.[16a] The Ga≈E bond lengths for [Tp^{But_2}]GaE are, therefore, consistent with multiply bonded character. Although the precise details of the bonding in [Tp^{But_2}]GaE are unknown, the Ga≈E interactions may be described as a composite of the resonance structures [Ga$^+$−E$^-$], [Ga=E], and [Ga$^-$≡E$^+$]. Of these resonance structures, it is likely that the polar form [Ga$^+$−E$^-$] provides an important contribution to the overall description,[18] in which case the multiple bond is best viewed as being composed of both covalent and ionic interactions, *i.e.* a semipolar double bond.[19]

The isolation of the gallium tellurido complex [Tp^{But_2}]GaTe is of particular significance since the corresponding indium complex [Tp^{But_2}]InTe is not obtained from the reaction of [Tp^{But_2}]-In with elemental tellurium under comparable conditions. Moreover, the monovalent thallium analogue [Tp^{But_2}]Tl is likewise unreactive toward both elemental selenium and tellurium. While the inability to isolate the multiply bonded indium and thallium derivatives, [Tp^{But_2}]InTe and [Tp^{But_2}]TlE (E = Se, Te), cannot alone be taken as a thermodynamic indication of their instability, the observations are nevertheless

consistent with the notions that (i) the tendency to partake in multiple bonding[1,20] and (ii) the stability of the M(III) *versus* M(I) valence states[21] diminish for the heavier congeners of the main group elements, *i.e.* Ga > In > Tl. In accordance with these notions, selenido transfer from indium to gallium is observed upon reaction of [Tp^{But_2}]InSe with [Tp^{But_2}]Ga (eq 2).[22]

$$[Tp^{But_2}]InSe + [Tp^{But_2}]Ga \rightarrow [Tp^{But_2}]In + [Tp^{But_2}]GaSe \quad (2)$$

Furthermore, the selenido ligand of [Tp^{But_2}]InSe is also readily abstracted by PEt$_3$ giving [Tp^{But_2}]In (eq 3). In contrast, however,

$$[Tp^{But_2}]InSe + Et_3P \rightarrow [Tp^{But_2}]In + Et_3PSe \quad (3)$$
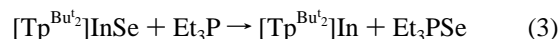
it is the reverse reaction, namely selenido transfer from Et$_3$PSe to [Tp^{But_2}]Ga, that occurs readily for the gallium system (eq 4).

$$[Tp^{But_2}]Ga + Et_3PSe \rightleftharpoons [Tp^{But_2}]GaSe + Et_3P \quad (4)$$
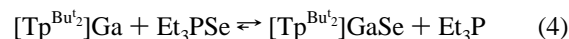
The latter reaction, however, is reversible, with addition of excess PEt$_3$ to [Tp^{But_2}]GaSe generating low equilibrium concentrations of the monovalent species [Tp^{But_2}]Ga (eq 4).[23] The temperature dependence of the equilibrium constant establishes values of $\Delta H° = 6.8(7)$ kcal mol^{-1} and $\Delta S° = 9(2)$ eu for selenido ligand abstraction from [Tp^{But_2}]GaSe. Consequently, the Ga≈Se interaction in [Tp^{But_2}]GaSe is *ca.* 7 kcal mol^{-1} stronger than the P≈Se bond in Et$_3$PSe.

In addition to selenido transfer between [Tp^{But_2}]Ga and Et$_3$-PSe, tellurido transfer is also observed from Et$_3$PTe to [Tp^{But_2}]-Ga, giving [Tp^{But_2}]GaTe (eq 5). Accordingly, it is evident that

$$[Tp^{But_2}]Ga + Et_3PTe \rightarrow [Tp^{But_2}]GaTe + Et_3P \quad (5)$$
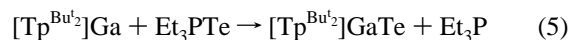
the strengths of the X≈E (E = Se, Te) interactions decrease in the sequence [Tp^{But_2}]GaE > Et$_3$PE > [Tp^{But_2}]InE.

In summary, the terminal gallium selenido and tellurido complexes [Tp^{But_2}]GaSe and [Tp^{But_2}]GaTe have been synthesized *via* the reaction of monovalent [Tp^{But_2}]Ga with the elemental chalcogens. The existence of a set of chalcogen transfer reactions demonstrates that the Ga≈E interactions are significantly stronger than the corresponding In≈E interactions.

Supporting Information Available: Tables of analytical, spectroscopic, and crystallographic data, text describing preparative details, and ORTEP diagrams for [Tp^{But_2}]GaE (E = Se, Te) (18 pages). Ordering information is given on any current masthead page.
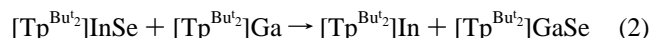
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(16) Ga−Se bond lengths span the range 2.32−2.51 Å. See ref 10 and: (a) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 3683−3686. (b) Uhl, W.; Gerding, R.; Hahn, I.; Pohl, S.; Saak, W.; Reuter, H. *Polyhedron* **1996**, *15*, 3987−3992. (c) Eisenmann, B.; Hofmann, A. *Z. Kristallogr.* **1991**, *197*, 149−150. (d) Eisenmann, B.; Hofmann, A. *Z. Kristallogr.* **1991**, *197*, 153−154. (e) Deiseroth, H.-J.; Fu-Son, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 962−963. (f) Power, M. B.; Ziller, J. W.; Tyler, A. N.; Barron, A. R. *Organometallics* **1992**, *11*, 1055−1063. (g) Kumar, R.; Dick, D. G.; Ghazi, S. U.; Taghiof, M.; Heeg, M. J.; Oliver, J. P. *Organometallics* **1995**, *14*, 1601−1607. (h) Harlan, C. J.; Gillan, E. G.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 5479−5488.

(17) Ga−Te bond lengths span the range 2.49−2.76 Å. See ref 10 and: (a) Wuller, S. P.; Seligson, A. L.; Mitchell, G. P.; Arnold, J. *Inorg. Chem.* **1995**, *34*, 4854−4861. (b) Park, C.-W.; Salm, R. J.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1879−1880. (c) Warren, C. J.; Ho, D. M.; Haushalter, R. C.; Bocarsly, A. B. *J. Chem. Soc., Chem. Commun.* **1994**, 361−362. (d) Uhl, W.; Layh, M.; Becker, G.; Klinkhammer, K. W.; Hildenbrand, T. *Chem. Ber.* **1992**, *125*, 1547−1551. (e) Uhl, W.; Schütz, U.; Hiller, W.; Heckel, M. *Organometallics* **1995**, *14*, 1073−1075. (f) Eisenmann, B.; Hofmann, A. *Z. Kristallogr.* **1991**, *197*, 145−146. (g) Banks, M. A.; Beachley, O. T., Jr.; Gysling, H. J.; Luss, H. R. *Organometallics* **1990**, *9*, 1979−1982.

(18) For example, as does the [P$^+$−O$^-$] resonance structure of R$_3$PO derivatives. See: (a) Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 1922−1930. (b) Schmidt, M. W.; Gordon, M. S. *Can. J. Chem.* **1985**, *63*, 1609−1615. (c) Streitwieser, A., Jr.; Rajca, A.; McDowell, R. S.; Glaser, R. *J. Am. Chem. Soc.* **1987**, *109*, 4184−4188. (d) Molina, P.; Alajarín, M.; Leonardo, C. L.; Claramunt, R. M.; Foces-Foces, M. C.; Cano, F. H.; Catalán, J.; de Paz, J. L. G.; Elguero, J. *J. Am. Chem. Soc.* **1989**, *111*, 355−363.

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(22) Similarly, the tin complexes [η^4-Me$_8$taa]SnE (E = S, Se) transfer their chalcogenido ligands to the germanium complex [η^4-Me$_8$taa]Ge.[7]

(23) For example, at 40 °C the equilibrium constant corresponding to eq 4 is 1.9(2) × 10^{-3}.