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Multiple Bonding to Indium: The Synthesis and Structure of $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{InSe}$, a Terminal Selenido Complex Supported by Tris(3,5-di-*tert*-butylpyrazolyl)hydroborato Ligation

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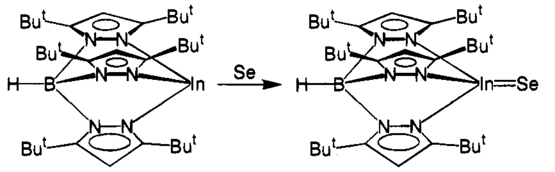
Multiple bonding between pairs of atoms is an area of chemistry that has attracted considerable attention for both the transition[1] and main group elements.[2] With respect to the main group elements, most progress has been observed for the group 14−16 elements.[2] Thus, well-defined examples of multiple bonds are now precedented for many of the group 14−16 elements, although the tendency to partake in multiple bonding is indeed diminished for the heavier congeners.[3] However, in marked contrast to the many advances achieved for the group 14−16 elements, there has been surprisingly little progress in the area of multiple bonding of the group 13 elements (B, Al, Ga, In, Tl). For example, in comparison to the second-row elements carbon, nitrogen, and oxygen, for which multiple bonding represents an important aspect of their chemistry, boron forms few stable complexes that exhibit well-characterized $[\mathrm{B{=}Y}]$ valence multiple bonds.[4] Thus, multiply bonded molecules of the type $\mathrm{XB{=}Y}$ are typically unstable with respect to oligomerization and the concomitant eradication of the $\mathrm{B{=}Y}$ multiple bond. Nevertheless, significant progress has recently been achieved by the use of bulky substituents to inhibit oligomerization, and complexes with $\mathrm{B{=}B}$,[5] $\mathrm{B{=}C}$,[6] $\mathrm{B{\equiv}C}$,[7] $\mathrm{B{=}N}$,[4c,8] $\mathrm{B{=}P}$,[4d,9,10] and $\mathrm{B{=}As}$[4d,11] multiple bonds are now known. However, well-characterized examples of complexes with valence multiple bonds are not well known for the heavier congeners of group 13.[12,13] In this paper, we extend our studies of multiple bonding of the main group elements[14] with the synthesis of a terminal selenido complex of indium, $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{InSe}$, the first structurally characterized mononuclear indium derivative with a valence multiple bond.

As part of our recent studies of the group 2 and 12 elements,[15] we have employed alkyl-substituted tris(pyrazolyl)hydroborato ligands $[\mathrm{Tp}^{\mathrm{RR'}}]$[16] to support monomeric four-coordinate terminal alkyl, hydride, and hydroxide derivatives of the type $[\mathrm{Tp}^{\mathrm{RR'}}]\mathrm{MX}$ (X = H, R, OH).[15] With respect to the group 13 elements, we rationalized that the sterically demanding environment offered by the tris(pyrazolyl)hydroborato ligands could also support monomeric four-coordinate multiply bonded terminal chalcogenido complexes of the type $[\mathrm{Tp}^{\mathrm{RR'}}]\mathrm{ME}$. Indeed, we report here that the terminal selenido complex $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{InSe}$ may be obtained by addition of selenium to the vacant axial coordination site of the three-coordinate indium(I) complex $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{In}$[17,18] (eq 1).[19] In contrast, a terminal selenido complex is not obtained by the reaction of the indium(I) alkyl $[\{(\mathrm{Me_3Si})_3\mathrm{C}\}\mathrm{In}]_4$ with elemental selenium; rather, a cubane-type derivative $[\{(\mathrm{Me_3Si})_3\mathrm{C}\}\mathrm{InSe}]_4$ is obtained preferentially.[20]



(1)

The molecular structure of $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{InSe}$ has been determined by X-ray diffraction (Figure 1),[21] thereby confirming the presence of the multiply bonded terminal selenido ligand. Of most significance, the In≈Se bond length of 2.376(1) Å in $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{InSe}$ is considerably shorter than In−Se bond lengths that have been reported for other complexes, *ca.* 2.65 Å (see

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[2] For some leading articles on multiple bonding of the main group elements, see: (a) Jutzi, P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 232−245. (b) Norman, N. C. *Polyhedron* **1993**, *12*, 2431−2446. (c) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Satge, J. *Coord. Chem. Rev.* **1994**, *130*, 427−480. (d) Okazaki, R.; Tokitoh, N.; Ishii, A.; Ishii, N.; Matsuhashi, Y.; Matsumoto, T.; Suzuki, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 49−66. (e) Regitz, M. *Chem. Rev.* **1990**, *90*, 191−213. (f) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 361−374.

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[4] The term valence multiple bond is used to provide a distinction with a multiple bond that is derived from *dative* π-donation to an electron deficient center.[4a] Such interactions are well-known in complexes of the types $\mathrm{R_2BER'}$ (E = O, S),[4b] $[\mathrm{RBNR}]_n$,[4c] $\mathrm{R_2BPR_2}$,[4d] $\mathrm{R_2BAsR_2}$,[4d] and $[\mathrm{RBPR}]_3$.[4d,e] (a) Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992−1007. (b) Ashby, M. T.; Sheshtawy, N. A. *Organometallics* **1994**, *13*, 236−243. (c) Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123−170. (d) Power, P. P.; Moezzi, A.; Pestana, D. C.; Petrie, M. A.; Shoner, S. C.; Waggoner, K. M. *Pure Appl. Chem.* **1991**, *63*, 859−866. (e) Power, P. P. *J. Organomet. Chem.* **1990**, *400*, 49−69.

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[13] For a gallium complex with a terminal tellurido ligand, $[\mathrm{Ph_4P}]\mathrm{Ga(Te)_2(en)_2}$, see: Warren, C. J.; Ho, D. M.; Haushalter, R. C.; Bocarsly, A. B. *J. Chem. Soc., Chem. Commun.* **1994**, 361−362.

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[16] The abbreviations adopted here are based on that described by Trofimenko, in which tris(pyrazolyl)hydroborato ligands are represented by the abbreviation Tp, with the 3- and 5-alkyl substituents listed respectively as superscripts. See: Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980.

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[18] Related tris(pyrazolyl)hydroborato indium(I) complexes In(I), $[\mathrm{Tp}^{\mathrm{Ph}}]\mathrm{In}$[18a] and $[\mathrm{Tp}^{\mathrm{Bu^t}}]\mathrm{In}$,[18b] have recently been reported. (a) Frazer, A.; Piggott, B.; Hursthouse, M. B.; Mazid, M. *J. Am. Chem. Soc.* **1994**, *116*, 4127−4128. (b) Dias, H. V. R.; Huai, L.; Wiechang, J.; Bott, S. G. *Inorg. Chem.* **1995**, *34*, 1973−1974.

[19] A mixture of $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{In}$ (0.23 g, 0.35 mmol) and excess Se (0.18 g, 2.3 mmol) was stirred in pentane (*ca.* 7 mL) at room temperature for *ca.* 18 h. The mixture was filtered, and the residue was washed with pentane (10 mL). The residue was extracted into benzene (15 mL) and filtered and the solvent removed under reduced pressure to give $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{InSe}$ as a pale yellow solid (0.13 g, 51%).

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[21] $[\mathrm{Tp}^{\mathrm{Bu^t}_2}]\mathrm{InSe}$ is triclinic, $P\bar{1}$ (No. 2), $a = 10.992(2)$ Å, $b = 13.237(2)$ Å, $c = 13.290(3)$ Å, $\alpha = 95.21(2)°$, $\beta = 93.92(2)°$, $\gamma = 101.56(2)°$, $Z = 2$. $R = 0.0352$, $R_w = 0.0390$, and GOF = 1.03 for 384 parameters and 3445 reflections with $F > 4\sigma(F)$.

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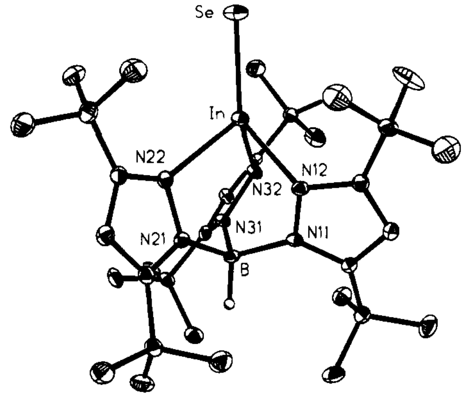

Figure 1. Molecular structure of [Tp$^{\mathrm{Bu^t_2}}$]InSe.

Table 1. Representative In−Se Bond Lengths

	d(In−Se)/Å	ref
[Tp$^{\mathrm{Bu^t_2}}$]InSe	2.376(1)	this work
$[\{(\mathrm{Me_3Si})_3\mathrm{C}\}\mathrm{InSe}]_4$	2.671[7]	*a*
$[\{\mathrm{CpFe(CO)_2}\}\mathrm{InSe}]_4$	2.67[2]	*b*
In[Se(2,4,6-$\mathrm{Bu^t_3C_6H_2}$)]$_3$	2.506[4]	*c*
$[\{(\mathrm{Me_3Si})_3\mathrm{CSe}\}_3\mathrm{In}]$	2.53[2]	*d*
$[\{(\mathrm{Me_3Si})_3\mathrm{SiSe}\}_3\mathrm{In}]_2(\mu\text{-dmpe})$	2.55[2]	*d*
$[\mathrm{In(SePh)_3}]_x$	2.776[10]	*e*
$[(\mathrm{Bu^tCH_2})_2\mathrm{In}(\mu\text{-SePh})]_2$	2.744[10]	*f*
$[(\mathrm{Bu^tCH_2})\mathrm{In}]_2(\mu\text{-PBu^t})(\mu\text{-SePh})$	2.759[10]	*g*
$[\mathrm{Mes_2In}(\mu\text{-SePh})]_2$	2.732[5]	*h*
$[\mathrm{Mes_2In}(\mu\text{-SeMes})]_2$	2.72[1]	*h*
$[\mathrm{MeIn}(\mu\text{-SePh})(\mathrm{SePh})]_\infty$	$2.68[5]_{\mathrm{bridge}}$ $2.542[1]_{\mathrm{term}}$	*h*
$(\eta^2\text{-}\mathrm{Et_2NCSe_2})_3\mathrm{In}$	2.72[4]	*i*
$\{\eta^2\text{-}\mathrm{Et_2NC(Se)NC(O)Ph}\}_3\mathrm{In}$	2.650[7]	*j*
$(\mathrm{Ph_3P})_2\mathrm{Cu}(\mu\text{-SeEt})_2\mathrm{In(SeEt)_2}$	$2.611(2)_{\mathrm{bridge}}$ $2.557(2)_{\mathrm{term}}$	*k*
$\mathrm{K_8[In_4Se_{10}]\cdot 16H_2O}$	$2.571(2)_{\mathrm{bridge}}$ $2.542(2)_{\mathrm{term}}$	*l*

[a] Uhl, W.; Graupner, R.; Layh, M.; Schütz, U. *J. Organomet. Chem.* **1995**, *493*, C1−C5. [b] Merzweiler, K.; Rudolph, F.; Brands, L. *Z. Naturforsch.* **1992**, *47B*, 470−476. [c] Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 3478−3481. [d] Wuller, S. P.; Seligson, A. L.; Mitchell, G. P.; Arnold, J. *Inorg. Chem.* **1995**, *34*, 4854−4861. [e] Annan, T. A.; Kumar, R.; Mabrouk, H. E.; Tuck, D. G.; Chada, R. K. *Polyhedron* **1989**, *8*, 865−871. [f] Beachley, O. T., Jr.; Lee, J. C., Jr.; Gysling, H. J.; Chao, S.-H. L.; Churchill, M. R.; Lake, C. H. *Organometallics* **1992**, *11*, 3144−3148. [g] Beachley, O. T., Jr.; Chao, S.-H. L.; Churchill, M. R.; Lake, C. H. *Organometallics* **1993**, *12*, 5025−5028. [h] Rahbarnoohi, H.; Kumar, R.; Heeg, M. J.; Oliver, J. P. *Organometallics* **1995**, *14*, 3869−3875. [i] Saluschke, S.; Pink, M.; Dietzsch, W.; Kirmse, R.; Law, N. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1862−1868. [j] Schuster, M.; Bensch, W. *Z. Anorg. Allg. Chem.* **1994**, *620*, 737−742. [k] Hirpo, W.; Dhingra, S.; Sutorik, A. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 1597−1599. [l] Krebs, B.; Voelker, D.; Stiller, K.-O. *Inorg. Chim. Acta* **1982**, *65*, L101−L102.

Table 1),[22,23] The shortness of the In≈Se bond in [Tp$^{\mathrm{Bu^t_2}}$]InSe clearly attests to the multiply bonded nature of the [In≈Se] moiety, which may be viewed in terms of the resonance structures shown below:[24]

$$\overset{+}{\mathrm{In}}-\overset{-}{\mathrm{Se}} \longleftrightarrow \mathrm{In}=\mathrm{Se} \longleftrightarrow \overset{-}{\mathrm{In}}\equiv\overset{+}{\mathrm{Se}}$$

It is also appropriate to compare the structure of [Tp$^{\mathrm{Bu^t_2}}$]InSe with the monovalent three-coordinate precursor, [Tp$^{\mathrm{Bu^t_2}}$]In,[17] as summarized in Table 2. Thus, it is interesting to note that even though the [Tp$^{\mathrm{Bu^t_2}}$] ligand in both [Tp$^{\mathrm{Bu^t_2}}$]In and [Tp$^{\mathrm{Bu^t_2}}$]InSe adopts a highly twisted propeller-like array,[25] a significant difference is in fact observed in the degree of interaction of the [Tp$^{\mathrm{Bu^t_2}}$] ligand with the indium centers. Specifically, the average In−N bond length in the In(III) complex [Tp$^{\mathrm{Bu^t_2}}$]InSe (2.242[4] Å) is substantially shorter, by *ca.* 0.2 Å, than that in the In(I) derivative [Tp$^{\mathrm{Bu^t_2}}$]In (2.48[2] Å).[26] Consequently, the indium center in [Tp$^{\mathrm{Bu^t_2}}$]InSe is displaced by *ca.* 0.3 Å less from the coordinating N_3 plane than is observed for [Tp$^{\mathrm{Bu^t_2}}$]In. A similar trend was also noted in the comparison of [η^4-$\mathrm{Me_8taa}$]SnE (E = S, Se) with [η^4-$\mathrm{Me_8taa}$]Sn.[14b]

Table 2. Comparison of the Structures of [Tp$^{\mathrm{Bu^t_2}}$]InSe and [Tp$^{\mathrm{Bu^t_2}}$]In

	[Tp$^{\mathrm{Bu^t_2}}$]InSe	[Tp$^{\mathrm{Bu^t_2}}$]In[a]
d(In−Se)/Å	2.376(1)	
$d(\mathrm{In-N_{av}})$/Å	2.242[4]	2.468[9]
$\mathrm{N-In-N_{av}}$/deg	87[4]	80[3]
$d(\mathrm{In\cdots N_3})$/Å[b]	1.37	1.66
twist angle, τ/deg[c]	17.7	22.4

[a] Reference 17. [b] $d(\mathrm{In\cdots N_3})$ is the displacement of In from the coordinating N_3 plane. [c] The twist angle of the [Tp$^{\mathrm{Bu^t_2}}$] ligand is defined as the average N−In···B−N torsion angle.

In summary, the terminal selenido indium complex [Tp$^{\mathrm{Bu^t_2}}$]InSe has been prepared by addition of selenium to the three-coordinate indium(I) complex [Tp$^{\mathrm{Bu^t_2}}$]In, thereby providing the first structurally characterized example of an indium complex with a valence multiple bond.

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Supporting Information Available: Tables of analytical, spectroscopic, and crystallographic data and preparative details for [Tp$^{\mathrm{Bu^t_2}}$]InSe (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(22) For reference, the mean In−Se bond length for complexes listed in the Cambridge Structural Database (Version 5.09, April 1995) is 2.65 Å (with a range of 2.50−2.85 Å), comparable to the value of 2.61 Å for the sum of the single-bond covalent radii of In (1.44 Å) and Se (1.17 Å). See: Pauling, L. *The Nature of The Chemical Bond*, 3rd. ed.; Cornell University Press: Ithaca, 1960; pp 224, 246.

(23) For additional In−Se bond lengths in infinite lattice and polyselenide complexes, see: (a) Hogg, J. H. C.; Sutherland, H. H.; Williams, D. J. *Acta Crystallogr.* **1973**, *B29*, 1590−1593. (b) Aleandri, L. E.; Ibers, J. A. *J. Solid State Chem.* **1989**, *79*, 107−111. (c) Eisenmann, B.; Hofmann, A. *Z. Anorg. Allg. Chem.* **1990**, *580*, 151−159. (d) Kanatzidis, M. G.; Dhingra, S. S. *Inorg. Chem.* **1993**, *32*, 1350−1362. (e) Kanatzidis, M. G.; Dhingra, S. *Inorg. Chem.* **1989**, *28*, 2024−2026. (f) Krebs, B.; Bobb, W.; Wellmer, H.-J.; Wiesmann, K. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1234−1246.

(24) Since π-interactions must occur in a pairwise manner in complexes with C_3 symmetry, it may be viewed that the double-bond representation [In=Se] would not be particularly appropriate for [Tp$^{\mathrm{Bu^t_2}}$]InSe, *per se* (*cf.* the bonding scheme for $\mathrm{R_3PO}$ and $\mathrm{R_3PCH_2}$). However, since [Tp$^{\mathrm{Bu^t_2}}$]InSe does not exhibit strict molecular C_3 symmetry (*e.g.*, the Se−In−N bond angles range from 121.0(1)° to 136.6(1)°), the [In=Se] representation is not invalid. See ref 14a and references therein.

(25) Such twisting is a distinctive feature of all structurally characterized [Tp$^{\mathrm{Bu^t_2}}$]M and [Tp$^{\mathrm{Bu^t_2}}$]MX complexes. See: Dowling, C. M.; Leslie, D.; Chisholm, M. H.; Parkin, G. *Main Group Chem.* **1995**, *1*, 29−52.

(26) [Tp$^{\mathrm{RR'}}$]$\mathrm{In^I}$ complexes typically exhibit longer In−N bond lengths than [Tp$^{\mathrm{RR'}}$]$\mathrm{In^{III}}$ derivatives. See, for example: Kuchta, M. C.; Parkin, G. *Main Group Chem.*, in press.