

**Monomeric InC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (Trip = -C<sub>6</sub>H<sub>2</sub>-2,4,6-*i*-Pr<sub>3</sub>) and Its Manganese Complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>MnInC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>: One-Coordinate Indium in the Solid State**

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Although the major oxidation state of the group 13 elements (i.e., B–Tl) is III, the univalent state becomes more stable with increasing atomic number so that Tl(I) is dominant in that element's chemistry.<sup>1</sup> In(I) is more unstable and readily disproportionates to give In(O) and In(III) products. Nonetheless, there is widespread interest<sup>2</sup> in its compounds as well as those of its less stable Ga(I) and Al(I) congeners.<sup>3</sup> A range of organometallic<sup>4–6</sup> and related<sup>7,8</sup> derivatives of In(I) have been synthesized. In the solid state, the organometallic compounds are associated and have a polymeric zig-zig arrangement in {In(C<sub>5</sub>H<sub>5</sub>)<sub>6</sub>},<sup>5c</sup> a hexameric structure in {In(C<sub>5</sub>Me<sub>5</sub>)<sub>6</sub>},<sup>5a,b</sup> and a weakly In–In bonded structure in dimeric [In{C<sub>5</sub>(CH<sub>2</sub>Ph)<sub>5</sub>}<sub>2</sub>].<sup>6</sup> In the vapor phase, however, In( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)<sup>5c</sup> and In( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sup>5b</sup> are monomers. The related trispyrazolylborate complexes In(pz)<sub>3</sub>BH (pz = 3-phenylpyrazolyl,<sup>7</sup> 3,5-di-*tert*-butylpyrazolyl,<sup>8a</sup> or 3-*tert*-butylpyrazolyl<sup>8b</sup>), in which In is coordinated by three N donors, are monomeric in the crystal phase. At present, however, there are no structures of a one-coordinate In(I) species in either the vapor or solid states. In fact, molecular In(I) derivatives of monodentate ligands of any kind are quite rare and limited to the complexes [In{C(SiMe<sub>3</sub>)<sub>3</sub>}<sub>4</sub>]<sup>9</sup> and [In{OC<sub>6</sub>H<sub>2</sub>-2,4,6-(CF<sub>3</sub>)<sub>3</sub>}<sub>2</sub>].<sup>10</sup> The former species was shown to have a tetrahedrane<sup>9</sup> In<sub>4</sub> arrangement (In–In = 3.002(1) Å<sup>9b</sup>) with an In–C distance of 2.250(5) Å.<sup>9b</sup> The structure of [In{OC<sub>6</sub>H<sub>2</sub>-2,4,6-(CF<sub>3</sub>)<sub>3</sub>}<sub>2</sub>]<sup>10</sup> involves the two metals bridged by two aryloxides which results in unique two-coordination for In. It is now shown that, by use of the crowding *o*-terphenyl ligand -C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (Trip = -C<sub>6</sub>H<sub>2</sub>-2,4,6-*i*-Pr<sub>3</sub>),<sup>11</sup> the monomeric compound InC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (**1**), which has a unique one-coordinate solid-phase structure, can be synthesized and characterized.

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Compound **1** was obtained<sup>12</sup> by treatment of InCl with (Et<sub>2</sub>O)-LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub><sup>12a</sup> in THF at ca. -78 °C. The bright-orange, very air-sensitive crystals of **1** display considerable thermal stability and decompose only above 216 °C. Its structure<sup>13</sup> (Figure 1) consists of well-separated InC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> monomers (shortest In···In distance = 6.890(2) Å) which have an In–C bond length of 2.260(7) Å. The In is displaced slightly (by ca. 0.23 Å) from the averaged plane of the C(1) ring. There are no close interactions between In and other atoms as indicated by the distances In···centroid C(7) or C(13) rings = ca. 3.90 Å, In···H(*i*-Pr, CH<sub>3</sub>) = 3.30 and 3.40 Å. The In–C bond is longer than the In–C  $\sigma$ -bonded distances (range ca. 2.11 → 2.17 Å) in In(III) derivatives of bulky ligands such as Mes\*(C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>), -C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>, or -C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>,<sup>14</sup> but is almost identical to the In–C distance(2.250(5) Å) in [In{C(SiMe<sub>3</sub>)<sub>3</sub>}<sub>4</sub>].<sup>9b</sup> A similar lengthening has been noted in its Ga(I) analogue [Ga{C(SiMe<sub>3</sub>)<sub>3</sub>}<sub>4</sub>]<sup>15</sup> whose Ga–C bonds average ca. 0.1 Å longer than those in sterically crowded Ga(III)–C compounds.<sup>14,16</sup> Furthermore, it is notable that the Ga–C distance in the vapor-phase structure of monomeric Ga{C(SiMe<sub>3</sub>)<sub>3</sub>}<sup>17</sup> remains essentially unchanged from that seen in [Ga{C(SiMe<sub>3</sub>)<sub>3</sub>}<sub>4</sub>].<sup>15</sup> Similarly, the In–N distances

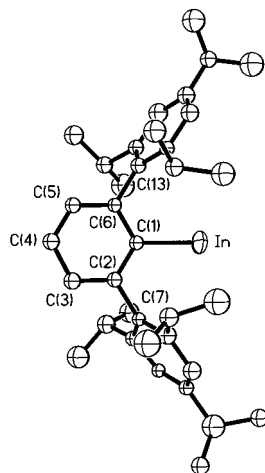
(12) Under anaerobic and anhydrous conditions (Et<sub>2</sub>O)LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub><sup>12a</sup> (1.00 g, 1.78 mmol) in THF (15 mL) at ca. -78 °C was added dropwise to a suspension of InCl (0.267 g, 1.78 mmol) at ca. -78 °C with rapid stirring. The solution was stirred at ca. -78 °C for 1.5 h and then warmed to ca. -10 °C. After an additional 1 h of stirring, the volatile materials were removed under reduced pressure at -10 °C. The solid residue was extracted with ca. 35 mL of cold hexane (ca. -10 °C). The solution was allowed to come to ambient temperature, where the dark precipitates (presumably In metal and LiCl) were allowed to settle. The orange-brown supernatant solution was then filtered through Celite. The filtrate was concentrated to incipient crystallization (ca. 20 mL) and stored at ca. -20 °C for 24 h to afford the product **1** as bright orange crystals: yield 0.37 g, 0.61 mmol, 34%; mp 216–220 °C (dec). LDI MS: *m/e* = 596.8. UV ( $\lambda_{max}$ ,  $\epsilon$ ): 280 nm, sh; 440 nm, 320; 368 nm, 760. Anal. Calcd for C<sub>36</sub>H<sub>40</sub>In: C, 72.47; H, 8.28; In, 19.25. Found: C, 72.38; H, 8.36; In, 19.11. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.17 (d, 12H, *J* = 6.9 Hz, *p*-CH(CH<sub>3</sub>)<sub>2</sub>); 1.25 (d, 12H, *J* = 7.2 Hz, *o*-CH(CH<sub>3</sub>)<sub>2</sub>); 1.27 (d, 12H, *J* = 7.2 Hz, *o*-CH(CH<sub>3</sub>)<sub>2</sub>); 2.85 (sept, 2H, *J* = 6.9 Hz, *p*-CH(CH<sub>3</sub>)<sub>2</sub>); 3.15 (sept, 4H, *J* = 7.2 Hz, *o*-CH(CH<sub>3</sub>)<sub>2</sub>); 7.19 (br s, 2H, *m*-C<sub>6</sub>H<sub>3</sub>); 7.25 (s, 4H, *m*-Trip); 7.26 (t, 1H, *p*-C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  24.76 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>); 24.99 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>); 30.49 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>); 30.82 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>); 34.74 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>); 121.00 (*m*-Trip); 126.93 (*p*-C<sub>6</sub>H<sub>3</sub>); 128.83 (*m*-C<sub>6</sub>H<sub>3</sub>); 137.73 (*o*-C<sub>6</sub>H<sub>3</sub>); 144.21 (*p*-Trip); 147.60 (*o*-Trip); 148.40 (*i*-Trip); 206.92 (*i*-C<sub>6</sub>H<sub>3</sub>). Mn( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub> (0.07 g, 0.34 mmol, Strem) in THF (5 mL) at ca. 25 °C was irradiated for 1 h with a UV lamp in a quartz Schlenk tube. The resultant bright red solution of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub>THF<sup>12b</sup> was treated with **1** (0.20 g, 0.34 mmol) via a solids addition tube. After 12 h of stirring, the volatile materials were removed under reduced pressure. The residue was extracted with hexane (ca. 10 mL), and the orange solution was filtered through Celite. Concentration to ca. 4 mL and storage at -20 °C for 48 h gave 2 as orange crystals: yield 0.12 g, 46%; mp 200 °C (dec). Anal. Calcd for C<sub>43</sub>H<sub>54</sub>InMnO<sub>2</sub>: C, 66.84; H, 7.04. Found: C, 67.10; H, 7.09. IR (Nujol, cm<sup>-1</sup>): 1940 s, 1864 s (CO). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.15 (d, 12H, *J* = 7.0 Hz, *p*-CH(CH<sub>3</sub>)<sub>2</sub>); 1.26 (d, 12H, *J* = 7.1 Hz, *o*-CH(CH<sub>3</sub>)<sub>2</sub>); 1.28 (d, 12H, 7.1 Hz, *o*-CH(CH<sub>3</sub>)<sub>2</sub>); 2.81 (sept, 2H, *J* = 7.0 Hz, *p*-CH(CH<sub>3</sub>)<sub>2</sub>); 3.12 (sept, 4H, *J* = 7.1 Hz, 4.72 (s, 5H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>); 7.12 (d, 2H, *J*<sub>HH</sub> = 7.7 Hz, *m*-C<sub>6</sub>H<sub>3</sub>); 7.24 (s, 4H, *m*-Trip); 7.28 (t, 1H, *J*<sub>HH</sub> = 7.3 Hz, *p*-C<sub>6</sub>H<sub>3</sub>). (a) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, 15, 958. (b) Strohmeyer, W.; Hillman, H. *Chem. Ber.* **1965**, 98, 1598.

(13) Crystallographic data for **1** (130 K) and **2** (170 K) with Mo K $\alpha$  ( $\lambda$  = 0.710 73 Å) radiation: **1**, *a* = 7.926(3) Å, *b* = 16.282(7) Å, *c* = 25.661(8) Å, *Z* = 4, space group *Pna*2<sub>1</sub>, *R*<sub>1</sub> = 0.066 for 2118 *I* > 2( $\sigma$ )*I* data; **2**, *a* = 9.513(2) Å, *b* = 9.831(2) Å, *c* = 21.083(4) Å,  $\alpha$  = 86.65(3)°,  $\beta$  = 81.40(3)°,  $\gamma$  = 89.32(3)°, *Z* = 2, space group *P1*, *R* = 0.047 for 7034 *I* > 2( $\sigma$ )*I* data.

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**Figure 1.** Computer-generated drawing of **1** with H atoms not shown. Selected bond distances (Å) and angles (deg): In–C(1) = 2.260(7), C(1)–C(2) = 1.39(2), C(2)–C(3) = 1.42(2), C(3)–C(4) = 1.44(2), C(4)–C(5) = 1.35(2), C(5)–C(6) = 1.39(2), C(1)–C(6) = 1.42(2), In–C(1)–C(2) = 121.9(14), In–C(1)–C(6) = 120.2(14), C(2)–C(1)–C(6) = 117.5(6), C(1)–C(2)–C(7) = 115(2), C(1)–C(6)–C(13) = 118(2).

in monomeric In(I) trispyrazolylborates may be as much as ca. 0.2 Å longer than those in related In(III) trispyrazolylborate species.<sup>8</sup> Thus, it seems that the longer In–C bond in **1** is consistent with known structural data for monomeric or weakly associated Ga(I) or In(I) species.

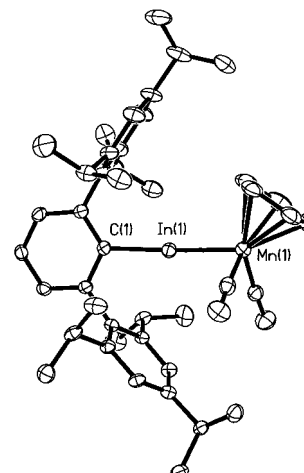
A further notable aspect of the structure of **1** is the one-coordination of the In center. One-coordination for a metal in the condensed phase has been claimed previously only for the compounds  $\text{MC}_6\text{H}_3\text{-2,4,6-Ph}_3$  (M = Cu or Ag).<sup>18</sup> However, a subsequent investigation indicated that the structural and spectroscopic data for these compounds were inconsistent with their formulation as Cu or Ag species.<sup>19</sup> The unique one-coordinate nature of In in **1** is undoubtedly due to the protection afforded it by the *o*-Trip substituents and the presence of a nonbonded lone-pair of electrons.

Initial investigations of the chemical properties of **1** show that the In center can function as a Lewis base. Thus, reaction of **1** with  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}(\text{THF})$ <sup>12b</sup> affords the complex  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{MnInC}_6\text{H}_3\text{-2,6-Trip}_2$ , **2**, as orange crystals.<sup>12a</sup> Its structure (Figure 2)<sup>13</sup> shows that **1** is bound in a terminal, monodentate fashion to the 16-electron  $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$  fragment with an Mn–In distance of 2.4102(9) Å and an almost linear geometry C(1)–In(1)–Mn(1) = 175.39(9)° at In. The In–Mn distance is ca. 0.2 Å shorter than those in related bridged complexes such as  $[\text{Mn}(\text{CO})_4\{\text{InC}(\text{SiMe}_3)_3\}]_2$ .<sup>20</sup> This can be attributed to the lower coordination number at In and the terminal

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**Figure 2.** Computer-generated drawing of **2** with H atoms not shown. Selected bond distances (Å) and angles (deg): In–C(1) = 2.155(3), In–Mn(1) = 2.4102(9), Mn–C(37) = 1.785(4), Mn–C(38) = 1.774(4), Mn–C( $\eta^5\text{-C}_5\text{H}_5$ ) = 2.115(3)–2.311(4), O(2)–C(37) = 1.168(5), O(1)–C(38) = 1.167(5), Mn–centroid( $\eta^5\text{-C}_5\text{H}_5$ ) = 1.757, C(1)–In(1)–Mn(1) = 175.39(9), C(37)–Mn(1)–C(38) = 91.7(2), In(1)–C(1)–C(2) = 123.8(2), In(1)–C(1)–C(6) = 114.7(2), C(2)–C(1)–C(6) = 121.4(3).

nature of the ligand. The In–C(1) bond in **2** (2.155(3) Å) is ca. 0.1 Å shorter than the corresponding distance in **1**. This is consistent with previous data for the  $[\text{Mn}(\text{CO})_4\text{In}\{\text{C}(\text{SiMe}_3)_3\}]_2$  complex<sup>20</sup> which has a shorter distance than that seen in  $[\text{In}\{\text{C}(\text{SiMe}_3)_3\}]_4$ .<sup>9b</sup> Carbonyl stretching frequencies in **2** ( $\nu(\text{CO}) \text{ cm}^{-1} = 1940 \text{ s}, 1864 \text{ s}$ ) are comparable to those of  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}(\text{THF})$  (1925 s, 1850 s) and  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{MnPh}_3$  (1932 s, 1869 s), indicating that **1** is, for the most part, a  $\sigma$ -donor with weak  $\pi$ -acceptor characteristics.<sup>12b</sup> This view of its bonding properties is in harmony with the metal–ligand bonding descriptions of  $(\text{CO})_4\text{FeAl}(\eta^5\text{-C}_5\text{Me}_5)$ <sup>21</sup> and  $(\text{CO})_4\text{FeIn}\{3,5\text{-Me}_2(\text{pz})\text{BH}\}$ <sup>22</sup> but does not support the reported FeGa triple bonding of the Ga(I) ligand in  $(\text{CO})_4\text{FeGaC}_6\text{H}_3\text{-2,6-Trip}_2$ .<sup>23</sup>

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**Supporting Information Available:** Tables of data collection parameters, atom coordinates, bond distances, angles, anisotropic thermal parameters and hydrogen coordinates (34 pages). An X-ray crystallographic file, in CIF format, is available through the Web only. See any current masthead page for ordering and Web access instructions.

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