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The “Diindene” ArInInAr (Ar = C_6H_3-2,6-$Dipp_2$, Dipp = C_6H_3-2,6-$Pr^i{}_2$). Dimeric versus Monomeric In(I) Aryls: *para*-Substituent Effects in Terphenyl Ligands

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Metal−metal bonded clusters of the heavier group 13 elements of formula $(MR)_n$ (M = Al, Ga, In, or Tl; R = organo group) are an unusual compound class that has expanded rapidly over the past decade.[1] They were originally isolated as cyclopentadienide derivatives which crystallize as tetramers (e.g., $\{Al(\eta^5\text{-}C_5Me_5)\}_4\})^2$, loosely bonded dimers (e.g., $[M\{\eta^5\text{-}C_5(CH_2Ph)_5\}]_2$, M = In[3a] or Tl[3b]), or hexamers $\{M(\eta^5\text{-}C_5Me_5)\}_6$ (M = Ga[4] or In[5]).[6] Monodentate ligands, for example, $C(SiMe_3)_3$ or $Si(SiMe_3)_3$, also yielded tetramers which dissociate to monomers in solution or the vapor phase.[7] However, use of a bulky terphenyl ligand afforded the monomers MC_6H_3-2,6-$Trip_2$ (M = In[8a] or Tl;[8b] Trip = C_6H_2-2,4,6-$Pr^i{}_3$), which have a one-coordinate metal in the solid state. The absence of stable, neutral dimeric or trimeric clusters with significant[9] M−M bonding is notable.[10] Dimers of formula RMMR (M = B−Tl, R = organic group) are of high current interest since they are formally double-bonded. Calculations have predicted a linear triplet structure for the diborene[11] and a planar trans-bent structure with no unpaired electrons for the heavier congeners.[12] Here, it is shown that use of a modified terphenyl ligand $-C_6H_3$-2,6-$Dipp_2$ (Dipp = C_6H_3-2,6-$Pr^i{}_2$) enables the isolation of a stable dimeric group 13 “dimetallene” species (**1**) ArInInAr (Ar = C_6H_3-2,6-$Dipp_2$).

Compound **1** was isolated[13] as dark red crystals by treatment of InCl with LiAr[14] in PhMe. It was characterized by ^1H and ^{13}C NMR, UV/vis spectroscopy, and X-ray crystallography.[15] The structure (Figure 1) shows that **1** exists as centrosymmetric dimers with a trans-bent C(1)−In(1)−In(1A)−C(1A) array, In−In and In−C distances of 2.9786(5) and 2.256(2) Å, as well as a In−In−C angle of 121.23(6)°. The angle between the In_2C_2 core and the central aryl ring is 39.3°. The In lies 0.36 Å from the plane of the C(1) ring, and there is an angle of 9.3° between In(1)−C(1) and the C(1)−C(4) vectors. The dimeric **1** may be compared to the monomeric InC_6H_3-2,6-$Trip_2$,[8a] which differs from **1** only in that it has *para*-Pr^i groups on the flanking aryl rings. Their absence permits dimerization through In−In bonding in **1**. In cyclohexane solution, however, **1** is extensively dissociated (cryoscopy), indicating that the In−In bond is weak. The In−In distance is shorter than the 3.329 Å calculated for trans-bent HInInH (cf. 2.545 Å predicted for the triplet form),[16a] but is closer to the 3.0596 Å obtained in more recent calculations.[16b] It lies above the currently known range (2.696(2)−2.938(1) Å) for In−In single bonds[17,18] and resembles the ca. 3.0 Å in electron-deficient $(InR)_4$ tetramers (R = $C(SiMe_3)_3$, $C(SiMe_2Et)_3$, or $C(SiMeEt_2)_3$).[19] The In−C distance in **1**, 2.256(2) Å, is indistinguishable from the 2.260(7) Å observed for the monomer InC_6H_3-2,6-$Trip_2$,[8a] which indicates that dimerization has little effect on the In−C bond length.

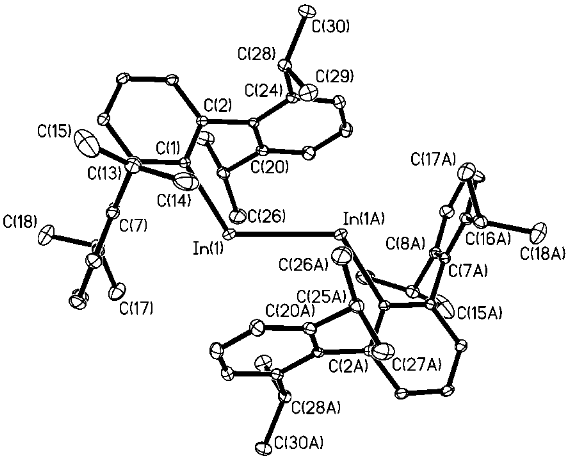

Figure 1. Selected bond lengths (Å) and angles (deg) for **1**. H atoms are not shown. In(1)−In(1A) = 2.9786(5), In(1)−C(1) = 2.256(2), C(1)−C(2) = 1.406(3), C(1)−C(6) = 1.405(3), In(1)−In(1A)−C(1A) = 121.23(6), C(2)−C(1)−C(6) = 118.6(2), In(1)−C(1)−C(2) = 119.95(15), In(1)−C(1)−C(6) = 120.47(16)°.

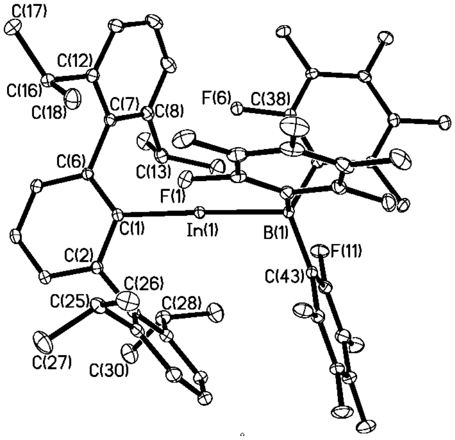

Figure 2. Selected bond lengths (Å) and angles (deg) for one of the molecules of **2**. H atoms are not shown. The numbers in braces refer to **3**. In(1)−C(1) = 2.139(2) {2.152(2)}, In−B(1) = 2.299(2) {2.322(2)}, In(1)···F(1) = 2.535(2) {2.587(2)}, C(1)−In(1)−B(1) = 176.21(9) {176.27(6)}, In(1)−C(1)−C(2) = 110.3(2) {117.0(1)}, In(1)−C(1)−C(6) = 128.5(2) {121.7(1)}, av In(1)−B(1)−C(ipso) = 105.7(3)° {106.1(1.5)}.

Weak In−In bonding is also supported by the rapid reaction of **1** with $B(C_6F_5)_3$ in PhMe at ca. 25 °C to afford 2,6-$Dipp_2H_3C_6$-$InB(C_6F_5)_3$ (**2**).[13] Reaction of InC_6H_3-2,6-$Trip_2$ with $B(C_6F_5)_3$ also occurred to give 2,6-$Trip_2H_3C_6InB(C_6F_5)_3$ (**3**).[13] The structure of **2** (Figure 2)[15] features two independent molecules with average In−B and In−C distances of 2.298(2) and 2.139(2) Å and a C−In−B angle of 176.4(2)°. For **3**, the In−B (2.322(2) Å) and In−C (2.152(2) Å) bonds are marginally longer than those in **2**, whereas the C−In−B angle (176.27(6)°) is unchanged. The longer In−B and In−C bonds in **3** are probably due to the steric effects of the *para*-Pr^i groups. The In−B bond lengths in **2** and **3** are in fair

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agreement with the sum (2.2 Å)[20] of the covalent radii of In and B and fall within the 2.25−2.52 Å range observed in In−B cages.[21] The In atoms are two-coordinate, although there are close contacts (In···F = 2.54−2.72 Å) between In and one or two of the six *ortho*-fluorines. The interacting C−F bonds (e.g., F(1)−C(32) = 1.372(3) Å and F(6)−C(38) = 1.375(2) Å) in **1** are ca. 0.03 Å longer than the average (ca. 1.34 Å) for the remaining C−F bonds in the molecule. The amount of geometrical change from planarity to tetrahedral in $B(C_6F_5)_3$ has been viewed as an indicator of the strength of donor acceptor interactions.[22] The sums of the C−B−C angles in **2** (338.89 and 339.76°) and **3** (337.79°) may be compared to 339.8(2), 342.2(2), or 333.5° reported for η^5-$C_5Me_5AlB(C_6F_5)_3$,[23] η^5-$C_5Me_5GaB(C_6F_5)_3$,[24,25] or HC{(Me)C(Dipp)N}$_2$GaB(C_6F_5)$_3$,[24] suggesting that **1** and InC_6H_3-2,6-Trip$_2$ are similar to these in donor strength. The C−B−C angular sum in **2** is slightly greater than that in **3** despite the shorter In−B bond. The greater pyramidal distortion in the $B(C_6F_5)_3$ moiety in **3** further supports the important steric effects of the *para*-Pr^i substituents. A feature of the structures of **2** and **3** is that their In−C bonds are (ca. 0.1 Å) shorter than those in **1** or InC_6H_3-2,6-Trip$_2$. The decrease in the ligand group 13 bond distance upon complexation is common in donors of this type.[1d] It is probably due to an increase in $In^{\delta+}-C^{\delta-}$ polarity and bond strength upon removal of electron density from In through donor action. The In−C shortening in **2** and **3** contrasts with its absence upon formation of the dimer **1**, a fact which underlines the weakness of the In−In association in this molecule.

In summary, the In−In bond in **1** is weak and corresponds to a bond order less than unity. The compounds **1**−**3** illustrate the important effects of flanking ring *para*-substituents of terphenyl ligands on the structures of weakly bonded species.

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Supporting Information Available: X-ray data (PDF and CIF) for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Under anaerobic and anhydrous conditions, a solution of LiAr[14] (2.5 g, 6.2 mmol) in PhMe (80 mL) was added dropwise to a rapidly stirred slurry of InCl (0.93 g, 6.2 mmol) in PhMe (20 mL) at −78 °C. The PhMe mixture was allowed to warm to ca. 25 °C overnight. The precipitates were allowed to settle over ca. 5 h to afford a dark red solution which was filtered. The volume was reduced to ca. 20 mL under reduced pressure. Dark red crystals of $(InAr)_2$, **1**, were obtained upon overnight storage in a ca. −20 °C freezer. Yield: 1.15 g, 36.2%. Mp 201−203 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 12H, o-CH(CH_3)$_2$), 1.15 (d, $^3J_{HH}$ = 6.9 Hz, 12H, o-CH(CH_3)$_2$), 3.03 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 7.14 (m, 6H, m-C_6H_3 m-Dipp), 7.22 (m, 3H, p-C_6H_3 p-Dipp). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 25 °C): δ 24.64 (CH(CH_3)$_2$), 25.36 (CH(CH_3)$_2$), 30.70 (CH(CH$_3$)$_2$), 119.77 (m-Dipp), 127.00 (p-C_6H_3), 141.12 (i-Dipp), 144.79 (o-C_6H_3), 147.32 (o-Dipp), 204.02 (i-C_6H_3), m-C_6H_3 p-Dipp obscured by C_6D_6. UV/vis (hexanes): λ_{max} nm (ϵ mol L^{-1} cm^{-1}): 335 (17 800), 441 (18 070). **2**: **1** (0.45 g, 0.44 mmol) and $B(C_6F_5)_3$ (0.45 g, 0.88 mmol) were combined in a Schlenk tube. Toluene (40 mL) was added, and the colorless solution was stirred (ca. 1 h). The solvent was evaporated, and the residue was redissolved in hexane (60 mL). The volume was reduced to ca. 20 mL, and the precipitate was redissolved by warming. Cooling to ca. 25 °C over a period of ca. 3 h afforded the product as colorless crystals. Yield: 0.48 g, 53.3%. Mp 195−197 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.90 (d, $^3J_{HH}$ = 6.9 Hz, 12H, o-CH(CH_3)$_2$), 1.06 (d, $^3J_{HH}$ = 6.9 Hz, 12H, o-CH(CH_3)$_2$), 2.77 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 6.97 (d, $^3J_{HH}$ = 8.0 Hz, 4H, m-Dipp), 7.10 (d, 2H, m-C_6H_3), 7.17 (m, $^3J_{HH}$ = 8.0 Hz, 3H, p-C_6H_3 and p-Dipp). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 25 °C): δ 23.64 (CH(CH_3)$_2$), 25.90 (CH(CH_3)$_2$), 31.27 (CH(CH$_3$)$_2$), 124.53 (m-Dipp), 129.43 (p-Dipp), 130.75 (p-C_6H_3), 130.81 (m-C_6H_3), 136.84 (br, $^3J_{CF}$ = 251 Hz, C_6F_5), 139.33 (br, $^3J_{CF}$ = 251 Hz, C_6F_5), 139.89 (i-Dipp), 141.83 (br, $^3J_{CF}$ = 251 Hz, C_6F_5), 146.72 (o-C_6H_3), 146.93 (br, $^3J_{CF}$ = 234 Hz, C_6F_5), 147.85 (o-Dipp), 149.27 (br, $^3J_{CF}$ = 234 Hz, C_6F_5), 170.19 (i-C_6H_3). ^{11}B NMR (128 MHz, C_6D_6, 25 °C): δ −14.09. ^{19}F{^{1}H} NMR (376 MHz, C_6D_6, 25 °C): δ −128.13 (d, $^3J_{FF}$ = 25.0 Hz, o-C_6F_5), −154.50 (t, $^3J_{FF}$ = 25.0 Hz, p-C_6F_5), −159.55 (d, $^3J_{FF}$ = 25.0 Hz, m-C_6F_5). **3** was obtained as colorless crystals from InC_6H_3-2,6-Trip$_2$[8a] (0.60 g, 1.00 mmol) and $B(C_6F_5)_3$ (0.51 g, 1.00 mmol). Yield: 0.45 g, 41%. Mp 130−132 °C. ^{1}H (400 MHz, C_7D_8, 25 °C): δ 0.94 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.04 (d, $^3J_{HH}$ = 6.8 Hz, 24H, CH(CH_3)$_2$), 2.75 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, p-CH(CH$_3$)$_2$), 2.84 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, o-CH(CH$_3$)$_2$), 7.02−7.20 (m, aromatic). ^{13}C{^{1}H} NMR (100 MHz, C_7D_8, 25 °C): δ 22.95 (CH(CH_3)$_2$), 23.52 (CH(CH_3)$_2$), 25.50 (CH(CH_3)$_2$), 30.92 (o-CH(CH$_3$)$_2$), 34.19 (p-CH(CH$_3$)$_2$), 122.26 (m-Trip), 136.27 (br, $^3J_{CF}$ = 245 Hz, C_6F_5), 137.22 (i-Trip), 138.73 (br, $^3J_{CF}$ = 245 Hz, C_6F_5), 141.22 (br, $^3J_{CF}$ = 245 Hz, C_6F_5), 146.28 (br, $^3J_{CF}$ = 237 Hz, C_6F_5), 146.69 (p-Trip), 147.07 (o-C_6H_3), 148.65 (br, $^3J_{CF}$ = 237 Hz, C_6F_5), 150.52 (o-Trip), 169.53 (i-C_6H_3), p-C_6H_3 and m-C_6H_3 obscured by solvent. ^{11}B NMR (128 MHz, C_7D_8, 25 °C): δ −13.67. ^{19}F{^{1}H} NMR (376 MHz, C_7D_8, 25 °C): δ −126.75 (d, $^3J_{FF}$ = 19.9 Hz, o-C_6F_5), −154.90 (t, $^3J_{FF}$ = 19.9 Hz, p-C_6F_5), −159.42 (m, $^3J_{FF}$ = 19.9 Hz, m-C_6F_5).

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(15) Crystal data for compounds **1**, **2**, and **3** at 90 K with Mo Kα (λ = 0.71073 Å) radiation: (**1**) a = 20.648(4) Å, b = 15.622(2) Å, c = 16.294(3) Å, orthorhombic, space group $Pccn$, Z = 4, R1 = 0.0463 for 6650 ($I > 2\sigma(I)$) data, wR2 = 0.1251 for all (8503) data; (**2**) a = 17.2344(9) Å, b = 23.2126(12) Å, c = 22.2382(12) Å, β = 102.738(4)°, monoclinic, space group $P2_1/c$, Z = 4, R1 = 0.0401 for 20 506 ($I > 2\sigma(I)$) data, wR2 = 0.0965 for all (28 170) data; (**3**) a = 12.7252(11) Å, b = 20.684(2) Å, c = 21.7198(18) Å, β = 106.729(3)°, monoclinic, space group $P2_1/c$, Z = 4, R1 = 0.0338 for 13 843 ($I > 2\sigma(I)$) data, wR2 = 0.0984 for all (17 154) data.

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