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Communications

α,ω-Alkanediyldiindium

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Summary: The reaction of indium(I) bromide with α,ω-alkanediylbis(bromomercury) complexes (alkane = butane, pentane, and hexane) resulted in formation of the corresponding α,ω-alkanediylbis(dibromoindium) compounds, which were isolated as THF adducts. The THF molecules of the complexes are easily displaced by bromide anions, thus affording the corresponding α,ω-alkanediylbis(tribromoindate) dianions.

While there exists a wide variety of α,ω-alkanediyldiamines or -diphosphines such as the commercially available tmeda (tetramethylethylenediamine) or diphos (1,2-bis(diphenylphosphino)ethane), the reverse-charge analogs in which the alkane chain is terminated by Lewis acidic group 13 elements are far less developed. In addition to the known methylene dialuminum[1] and diindium complexes,[2] the only other reports concern α,ω-diborylalkanes.[3] In principle, this type of compounds could serve as anion receptors[3a,b,4] or as building blocks for the synthesis of Lewis acidic macrocycles.[5] With this as an incentive, we have set out to prepare α,ω-alkanediyldiindium complexes.

We chose to attempt the synthesis of the target compounds by reaction of α,ω-alkanediylbis(bromomercury) with InBr. These transmetalation reactions present the advantage of yielding mercury metal as a sole byproduct.[6] Following a synthesis analogous to that of 1,5-pentanediylbis(bromomercury) (**2**),[7] 1,4-butanediylbis(bromomercury) (**1**) and 1,6-hexanediylbis(bromomercury) (**3**) were synthesized in moderate yield (Scheme 1). Both compounds **1** and **3** are high melting and virtually insoluble in any solvent including hot DMSO. In contrast, compound **2** melts at 150 °C and readily dissolves in DMSO, which allowed its ^{1}H, ^{13}C, and ^{199}Hg NMR spectroscopic characterization.[8] Compounds **1**−**3** were analyzed by CI mass spectrometry. While the base peak of the mass spectrum of compound **3** corresponds to the molecular ion, only low-intensity molecular peaks were detected in the mass spectra of **1** and **2** and the base peaks in their mass spectra correspond to fragments generated by extrusion of two and one methylene units, respectively.

Compounds **1**−**3** react smoothly in THF with 2 equiv of InBr to afford 1,4-butanediyl- (**4**), 1,5-pentanediyl- (**5**), and 1,6-hexanediylbis[bis(tetrahydrofuran)dibromo-

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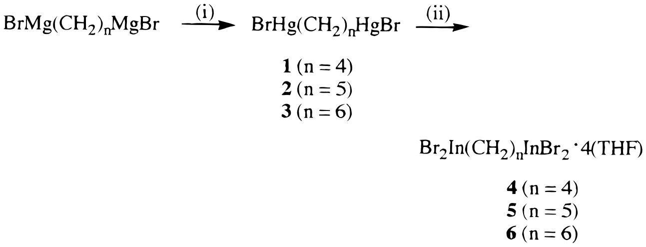
Scheme 1[a]



[a] Key: (i) 2 $HgBr_2$, THF, 0 °C; (ii) 2 InBr, THF, 25 °C.

indium] (**6**), respectively (Scheme 1).[9] After filtration of the metallic precipitate and concentration of the solutions, compounds **4**−**6** can be isolated as air-sensitive, crystalline solids in 25−60% yield by slow cooling of the solutions. Compounds **4**−**6** are insoluble in Et_2O, toluene, and hexane. Single crystals could be easily obtained for compounds **4** and **6** which have an even number of methylene groups in the alkanediyl chain, whereas compound **5** was always obtained as a microcrystalline solid. The ^1H and ^{13}C NMR spectra of **4**−**6** were recorded in THF-d_8.[8] The assignment of all methylene ^1H and ^{13}C NMR signals could be easily derived from their respective multiplicity, intensity, and chemical shift. Due to the strong quadrupolar moment of indium ($I = {}^9/_2$), the α-methylene carbon signals are broad and extended accumulation was required for their detection. While a correct elemental analysis could be obtained for **4**, the analytical data for both **5** and **6** indicated loss of part of the THF component, which is in agreement with the observation that **5** and **6** slowly become brittle at room temperature.

Treatment of **4** and **6** with 2 equiv of tetraphenylphosphonium bromide led to the displacement of the coordinated THF molecules and formation of the tetraphenylphosphonium salts of the dianions 1,4-butanediyl- (**7**) and 1,6-hexanediylbis(tribromoindate) (**8**), respectively (Scheme 2).[9] Both salts are moderately air sensitive. In comparison to **7** which dissolves only in MeCN and CH_2Cl_2, compound **8,** with its longer hydrocarbon chain, exhibits, as expected, an increased solubility in organic solvents of medium polarity such as THF. The ^1H and ^{13}C NMR spectroscopic data of compounds **7** and **8** are very similar to those of **4** and **6**.[8]

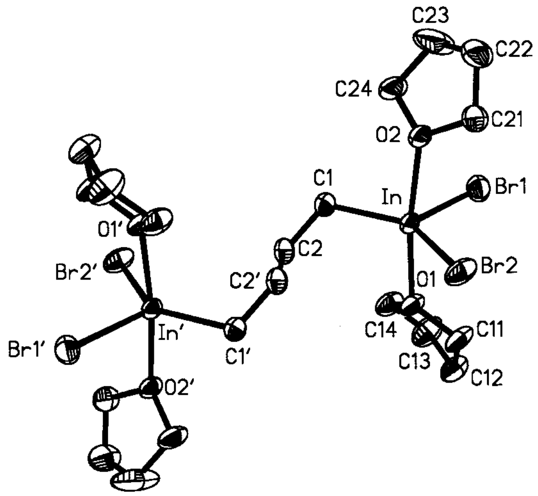
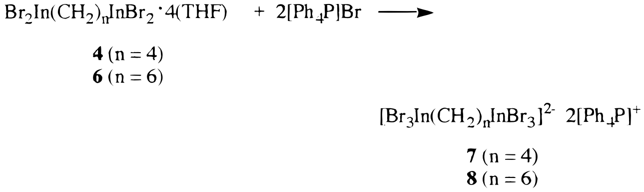


Figure 1. Crystal structure of **4**. ORTEP drawing with 50% probability ellipsoids; H atoms omitted for clarity. Selected bond lengths (Å), bond angles (deg), and torsional angles (deg): In−C(1) 2.145(4), In−Br(1) 2.544(1), In−Br(2) 2.517(1), In−O(1) 2.357(3), In−O(2) 2.406(3), C(1)−C(2) 1.531(6), C(2)−C(2′) 1.51(1); C(1)−In−Br(1) 119.3(2), C(1)−In−Br(2) 131.1(2), Br(1)−In−Br(2) 109.24(2), C(1)−In−O(1) 98.4(2), C(1)−In−O(2) 89.0(2), O(2)−In−O(1) 172.6(1), In−C(1)−C(2) 117.9(3), C(1)−C(2)−C(2′) 112.9(5); In−C(1)−C(2)−C(2′) 63.6, C(1)−C(2)−C(2′)−C(1′) 180.0.

Scheme 2



Single crystals suitable for X-ray analyses were obtained for compounds **4**, **7**, and **8**.[10] The crystal lattices of **7** and **8** are composed of independent tetraphenylphosphonium cations and bis(tribromoindate) dianions with no unusually close interionic contacts.

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(8) NMR data are as follows. ^1H NMR (400 MHz): **2** (DMSO-d_6) δ 1.35 (p, ^3J = 6.7 Hz, 2 H, γ-CH_2), 1.73 (tt, ^3J = 6.7 Hz, ^3J = 7.3 Hz, 4 H, β-CH_2), 1.82 (t, ^3J = 7.3 Hz, 4 H, α-CH_2); **4** (THF-d_8) δ 1.17 (br, 4 H, α-CH_2), 1.76 (br, 4 H, β-CH_2), 1.77 (m, 16 H, OCH_2CH_2), 3.61 (m, 16 H, OCH_2); **5** (THF-d_8) δ 1.15 (t, ^3J = 7.3 Hz, 4 H, α-CH_2), 1.55 (br, 2 H, γ-CH_2), 1.76 (br, 4 H, β-CH_2), 1.77 (m, 16 H, OCH_2CH_2), 3.61 (m, 16 H, OCH_2); **6** (THF-d_8) δ 1.16 (t, ^3J = 7.8 Hz, 4 H, α-CH_2), 1.45 (br, 4 H, γ-CH_2), 1.76 (br, 4 H, β-CH_2), 1.77 (m, 16 H, OCH_2CH_2), 3.61 (m, 16 H, OCH_2); **7** (MeCN-d_3) δ 1.09 (br, 4 H, α-CH_2), 1.68 (br, 4 H, β-CH_2), 7.66−7.94 (m, 40 H, P(C_6H_5)); **8** (MeCN-d_3) δ 1.08 (t, ^3J = 8.1 Hz, 4 H, α-CH_2), 1.36 (br, 4 H, γ-CH_2), 1.60 (br, 4 H, β-CH_2), 7.66−7.94 (m, 40 H, P(C_6H_5)). $^{13}C\{^1H\}$ NMR (100.5 MHz): **2** (DMSO-d_6) δ 27.9 (γ-C), 34.3 (β-C), 39.0 (α-C); **4** (THF-d_8) δ 20.8 (br, α-*C*), 26.4 (OCH_2CH_2), 32.6 (β-*C*), 68.2 (OCH_2); **5** (THF-d_8) δ 20.9 (br, α-*C*), 26.4 (OCH_2CH_2), 27.4 (γ-*C*), 39.6 (β-*C*), 68.2 (OCH_2); **6** (THF-d_8) 21.0 (br, α-*C*), 26.4 (OCH_2CH_2), 27.7 (γ-*C*), 34.7 (β-*C*), 68.2 (OCH_2); **7** (MeCN-d_3) δ 21.7 (br, α-*C*), 31.3 (β-*C*); [Ph_4P^+] δ 118.4 (*C*-*ipso*), 130.3 (d, $^2J_{CP}$ = 13.0 Hz, C-*meta)*, 134.6 (d, $^3J_{CP}$ = 10.7 Hz, C-*ortho*), 135.4 (C-*para*); **8** (MeCN-d_3) δ 21.7 (br, α-*C*), 27.0 (γ-*C*), 33.3 (α-*C*); [Ph_4P^+] δ 118.4 (*C*-*ipso*), 130.3 (d, $^2J_{CP}$ = 13.0 Hz, C-*meta)*, 134.7 (d, $^3J_{CP}$ = 10.0 Hz, C-*ortho*), 135.4 (C-*para*). $^{199}Hg\{^1H\}$ NMR (71.56 MHz, DMSO-d_6): **2** δ −1089.

(9) Synthesis of **4**: InBr (0.215 g, 1.1 mmol) and **1** (0.310 g, 0.5 mmol) were stirred together at room temperature in THF (5 mL) for 3 h, after which time the reaction mixture was filtered to remove the metallic grey precipitate. Concentration of the filtrate followed by cooling to −25 °C afforded a 60% yield (0.27 g) of crystalline **4**, mp 147 °C. Anal. Calcd for $C_{20}H_{40}Br_4In_2O_4$: C, 26.87; H, 4.48. Found: C, 26.80; H, 4.49. Compounds **5** and **6** were prepared in 25 and 46% yield (respectively) following a similar procedure. Synthesis of **7**: Compound **4** (0.05 mmol, 44.7 mg) and tetraphenylphosphonium bromide (0.1 mmol, 42 mg) were dissolved in THF (1 mL). Compound **7** precipitated immediatly as a white powder in 90% yield (65 mg), mp 136 °C. Anal. Calcd for $C_{52}H_{48}Br_6In_2P_2$: C, 43.24; H, 3.33. Found: C, 42.92; H, 3.47. Compound **8** was prepared in a 85% yield following a similar procedure, mp 155 °C. Anal. Calcd for $C_{54}H_{52}Br_6In_2P_2$: C, 44.05; H, 3.54. Found C, 43.87; H, 3.58.

(10) Crystal structure determination data for **4**, **7**, and **8**. **4**: M = 893.80; monoclinic space group $P2_1/c$; a = 9.325(1) Å, b = 13.721(1) Å, c = 12.125(1) Å, β = 109.16(1)°, V = 1465.4(2) Å^3; Z = 2; D_c = 2.026 g/cm^3; *F(000)* = 860. **7**: M = 1443.94; monoclinic space group $P2_1/c$, a = 12.466(2) Å, b = 7.576(1) Å, c = 28.846(4) Å, β = 98.89(1)°, V = 2691.6(7) Å^3; Z = 2; D_c = 1.782 g/cm^3; *F(000)* = 1396. **8**: M = 1472.00; monoclinic space group $P2_1/c$; a = 7.689(1) Å, b = 14.585(1) Å, c = 25.014(3) Å, β = 96.59(1)°, V = 2786.6(5) Å^3; Z = 2; D_c = 1.754 g/cm^3; *F(000)* = 1428. Enraf-Nonius CAD4 diffractometer; Mo Kα radiation (λ = 0.710 73 Å); T = −74 °C. The structures were solved by direct methods (SHELXS-86) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically. All H atoms of compounds **7** and **8** were calculated in idealized geometry and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5U_{eq}$ of the attached C atom), whereas the methylene hydrogen atoms of **4** were found and refined with isotropic contributions. The structure of **4** converged for 152 refined parameters to R1 (wR2) = 0.0351 (0.0885) for 3250 reflections with $F > 4\sigma(F)$. The structure of **7** converged for 280 refined parameters to R1 (wR2) = 0.0417 (0.0728) for 5205 reflections with $F > 4\sigma(F)$. The structure of **8** converged for 289 refined parameters to R1 (wR2) = 0.0315 (0.0588) for 5283 reflections with $F > 4\sigma(F)$.

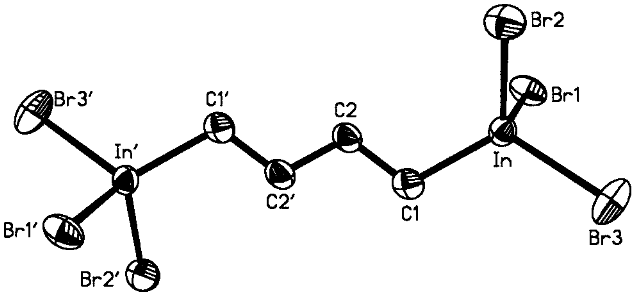

Figure 2. Crystal structure of the dianion of **7**. ORTEP drawing with 50% probability ellipsoids; H atoms omitted for clarity. Selected bond lengths (Å), bond angles (deg) and torsional angles (deg): In–C(1) 2.146(5), In–Br(1) 2.543(1), In–Br(2) 2.548(1), In–Br(3) 2.539(1), C(1)–C(2) 1.520(7), C(2)–C(2′) 1.52(1); Br(1)–In–Br(2) 105.44(2), Br(1)–In–Br(3) 102.15(3), Br(2)–In–Br(3) 106.91(3), C(1)–In–Br(1) 117.0(1), C(1)–In–Br(2) 109.8(1), C(1)–In–Br(3) 114.7(1), In–C(1)–C(2) 113.1(3), C(1)–C(2)–C(2′) 113.0(5); In–C(1)–C(2)–C(2′) 173.7, C(1)–C(2)–C(2′)–C(1′) 180.0.

Molecules of neutral **4** (Figure 1), as well as the dianionic components of **7** (Figure 2) and **8** (Figure 3), are centrosymmetric with an inversion center located at the midpoint of the C2–C2′ (**4** and **7**) and C3–C3′ (**8**) vectors, respectively. Examination of the torsional angles along the alkanediyldiindium chains indicates that **4**, the dianion of **7**, and the dianion of **8** adopt a G(+)AG(−), AAA, and G(+)AAAG(−) conformation, respectively (G = *gauche*, A = *anti*). The indium centers of **4** are pentacoordinated in a trigonal bipyramidal manner with the α-methylene group and the two bromine atoms at the equatorial positions while two THF molecules occupy the axial sites. Altogether, the coordination sphere of the indium center in **4** is very similar to that encountered in the structure of PhCH$_2$InBr$_2$(THF)$_2$[11] and all bond lengths and angles are comparable. The indium centers of **7** and **8** are tetracoordinated in a tetragonal fashion which does not exhibit any strong distortion.

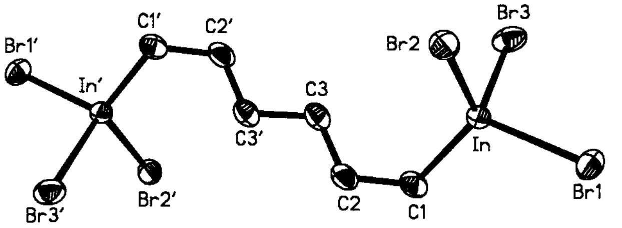

Figure 3. Crystal structure of the dianion of **8**. ORTEP drawing with 50% probability ellipsoids; H atoms omitted for clarity. Selected bond lengths (Å), bond angles (deg), and torsional angles (deg): In–C(1) 2.151(4), In–Br(1) 2.555(1), In–Br(2) 2.560(1), In–Br(3) 2.540(1), C(1)–C(2) 1.519(5), C(2)–C(3) 1.515(6); C(3)–C(3′) 1.537(7); Br(1)–In–Br(2) 100.35(2), Br(1)–In–Br(3) 104.00(2), Br(2)–In–Br(3) 104.13(2), C(1)–In–Br(1) 115.1(1), C(1)–In–Br(2) 118.8(1), C(1)–In–Br(3) 112.6(1), In–C(1)–C(2) 116.6(3), C(1)–C(2)–C(3) 114.4(3), C(2)–C(3)–C(3′) 114.0(4); In–C(1)–C(2)–C(2′) 62.4, C(1)–C(2)–C(3)–C(3′) 171.7, C(2)–C(3)–C(3′)–C(2′) 180.0.

The present results indicate that bifunctional Lewis acids with flexible backbones can be easily synthesized. Although the indium centers of compounds **4**–**6** are coordinated by THF molecules, the isolation of compounds **7** and **8** indicates that the THF molecules are labile and can be displaced by stronger nucleophiles. Present investigations are focused on the reactions of compounds **4** and **6** with polyfunctional bases for the synthesis of coordination polymers and dendrimers.

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Supporting Information Available: Text giving the experimental procedure and NMR and elemental analysis data for **1**–**8** and tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and thermal parameters for **4**, **7**, and **8** (23 pages). Ordering information is given on any current masthead page.

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