

Unusual Inorganic Ring Systems of Scandium and Yttrium Containing Group 13 Metals: Coordination of Monomeric Me₂InOMe to Yttrium†

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Novel transformations of lanthanide(III) disiloxanediolates with group 13 metal trialkyls are reported. Treatment of the scandium metallacrown complex $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{DME})\}_2]\text{ScCl}\cdot\text{THF}$ (**1**) with AlMe_3 resulted in an Li–Al exchange reaction and the formation of the heterotrimetallic inorganic ring system $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}_2\text{AlMe}_2]\text{ScCl}\cdot\text{THF}$ (**2**). The related yttrium metallacrown $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}_2]\text{YCl}\cdot\text{THF}$ (**3**) reacts with InMe_3 under the formation of the heterobimetallic Y/In disiloxanediolate complex $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{InMe}_2(\text{OMe})\}_2\text{InMe}_2]\text{Y}$ (**4**). In the latter, two monomeric Me₂InOMe ligands are stabilized through coordination to yttrium.

The chemistry of metallasiloxanes derived from silanediols, disiloxanediols, and related Si–OH species continues to be an area of vigorous research activities^{1–7} because such compounds are valuable precursors for metal oxides and silicates^{2,3} as well as models for silica-supported heteroge-

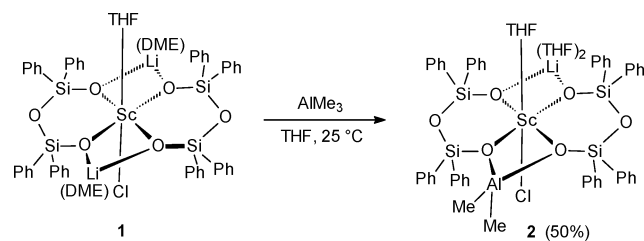
neous catalysts^{1,4} or are catalytically active themselves.⁵ A particularly useful ligand in this field is the tetraphenyl-disiloxanediolate dianion $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$, which gives rise to a variety of unusual and unexpected structures especially when combined with alkali metals⁶ and early transition metals.^{2b,6,7} The starting material tetraphenyldisiloxanediol, $\text{Ph}_2\text{Si}(\text{OH})\text{OSiPh}_2(\text{OH})$, is readily accessible from cheap precursors.⁸ Soluble aluminosiloxanes have become increasingly important in recent years,⁹ and some exciting chemistry has been developed by Veith and co-workers around the polycyclic aluminum tetraphenyldisiloxanediolate derivative $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_4$.¹⁰ A rare example of an indium disiloxanediolate, $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\text{InMe}\{\mu\text{-Li}(\text{THF})_2\}_2]$, was prepared from $\text{Ph}_2\text{Si}(\text{OH})\text{OSiPh}_2(\text{OH})$ and $\text{Li}[\text{InMe}_4]$.¹¹ Group 3 metal (Sc/Y) and lanthanide complexes containing the $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$ ligand have been investigated in our laboratory.¹² It was discovered that the small Sc^{3+} and Y^{3+} ions form heterobimetallic complexes in which the group 3 metal

† Dedicated to Professor Ken Wade on the occasion of his 75th birthday.
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Scheme 1



is located in the center of an inorganic ring system formed by two lithium disiloxanediolate units. Additional chloro functions and solvent molecules are arranged in the trans positions. Thus, these complexes can be regarded as metal-lacrown derivatives of scandium and yttrium. We report here the initial results of reactions of these species with group 13 metal trialkyls, leading to the formation of unusual inorganic ring systems containing two (Y/In) or three (Sc/Al/Li) different metal atoms.

Treatment of the scandium complex **1**^{12c} (Scheme 1) with an excess of trimethylaluminum in toluene afforded a colorless solution, from which colorless, block-shaped single crystals could be isolated in 50% yield.¹³ This reaction was initially performed with the aim of replacing the chloro ligand in the trans position by a methyl group. However, an X-ray crystal structure determination¹⁴ revealed the presence of a unique heterotrimetallic (Sc/Al/Li) disiloxanediolate complex **2**, as illustrated in Scheme 1.

The most surprising result of this reaction was the replacement of one $\text{Li}(\text{DME})^+$ unit in **1** by an AlMe_2^+ moiety under retention of the chloro function in the trans position. Despite the use of an excess of AlMe_3 , only one lithium was replaced. The fate of the latter, however, is not clear. If a stoichiometric amount of methyllithium is formed in the course of this reaction, it could add to AlMe_3 to form

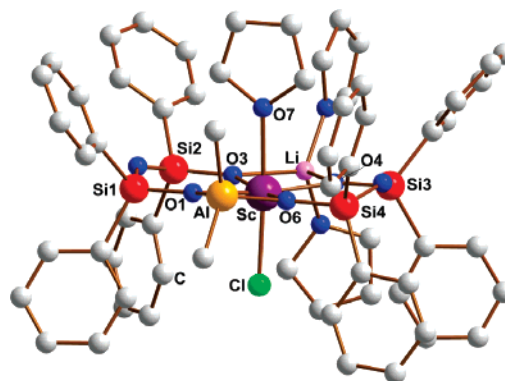


Figure 1. Molecular structure of $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}\text{AlMe}_2]\text{ScCl} \cdot \text{THF}$ (**2**). Selected bond lengths (Å) and angles (deg): Sc–O1 2.186(3), Sc–O3 2.018(3), Sc–O4 2.019(3), Sc–O6 2.182(3), Sc–O7 2.271(3), Sc–Cl 2.434(1), Al–O1 1.837(3), Al–O6 1.836(3), Li–O4 2.023(9), Li–O3 2.036(9), O1–Sc–O6 73.3(1), O3–Sc–O4 90.3(1), O1–Al–O6 90.4(1), O3–Li–O4 89.6(3), C1–Al–C2 117.6(2), O(THF)–Li–O(THF) 105.7(4), O1–Sc–O3 98.6(1), O4–Sc–O6 96.6(1), O7–Sc–Cl 175.1(1), O3–Sc–O6 168.8(1), O4–Sc–O1 166.8(1).

LiAlMe_4 ,¹⁵ a reaction that would account for the fairly low isolated yield of **2**. Another plausible reaction pathway would involve the formation of a $\text{MeLi} \cdot \text{DME}$ adduct, which has been reported to exhibit reduced reactivity and solubility.¹⁶ Like the starting material **1**, the trimetallic product **2** also adopts the metallacrown form with the central Sc^{3+} ion accommodated well within the plane of the slightly puckered inorganic ring system (Figure 1). As in the starting material **1**, one THF ligand and the chloride ion occupy the trans positions. Figure 1 also clearly shows how the central metallacrown core is efficiently shielded by eight phenyl substituents and three coordinated THF molecules, which accounts for the high solubility of the complex in toluene.

A similar reaction carried out with the yttrium metallacrown precursor **3** and an excess of trimethylindium took an entirely different course. In this case, colorless prism-shaped crystals were isolated in 81% yield by slow concentration of the filtered reaction mixture.¹⁷ An ^1H NMR spectrum of the product indicated the incorporation of three

- (13) Preparation of **2**: A total of 0.36 g (0.30 mmol) of $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{DME})_2\}\text{ScCl} \cdot \text{THF}$ (**1**) was dissolved in 10 mL of THF. To the clear, colorless solution was added 0.06 g (0.83 mmol) of neat AlMe_3 via syringe under vigorous stirring at ambient temperature, and stirring was continued for 30 min. Slow concentration of the solution in the drybox afforded colorless, block-shaped crystals suitable for X-ray diffraction. Yield: 0.20 g (50%). Mp: 154 °C (dec). Anal. Calcd for $\text{C}_{70}\text{H}_{86}\text{AlClLiO}_{11}\text{ScSi}_4$ ($M_r = 1330.08$): C, 63.21; H, 6.52. Found: C, 62.70; H, 6.46. ^1H NMR (400.1 MHz, $\text{THF}-d_8$, 20 °C): δ 8.04–6.77 (m, 40H, Ph), 3.53 (4H, THF), 1.67 (4H, THF), –1.01 (6H, AlMe_2). ^{13}C NMR (100.6 MHz, $\text{THF}-d_8$, 20 °C): δ 140.03 (*ipso*-C, Ph), 135.80, 134.80, 129.59, 127.97 (Ph), 127.23 (br m), 68.12 (THF), 26.27 (THF). ^{29}Si NMR (79.5 MHz, $\text{THF}-d_8$, 20 °C): δ –42.8. IR (KBr): 3437, 3069, 3049, 3001, 2978, 2930, 2888, 1592, 1568, 1488, 1460, 1429, 1370, 1307, 1244, 1183, 1124, 1116, 1050, 1026, 997, 930, 873, 744, 717, 701, 678, 620, 571, 523, 490, 450 cm^{-1} .
- (14) Data collection for **2**: $\text{C}_{70}\text{H}_{86}\text{AlClLiO}_{11}\text{ScSi}_4$, $M_r = 1330.08$, crystal dimensions $0.40 \times 0.20 \times 0.20 \text{ mm}^3$, monoclinic ($C2/c$), $a = 28.680(6)$ Å, $b = 22.212(4)$ Å, $c = 25.817(5)$ Å, $\beta = 117.09(3)^\circ$, $V = 14643(5)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 1.207 \text{ g mm}^{-3}$, $\mu = 0.269 \text{ mm}^{-1}$, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $T = 180(2)$ K, reflections measured = 62 950, unique reflections = 19 787 ($R_{\text{int}} = 0.1505$), absorption correction = spherical, final R indices $R1 = 0.0597$ and $wR2 = 0.1460$, largest difference peak and hole = $+1.583$ and -0.352 e Å^{-3} . Data collection for **4**: $\text{C}_{56}\text{H}_{64}\text{In}_3\text{O}_8\text{Si}_4\text{Y}$, $M_r = 1410.80$, crystal dimensions $0.40 \times 0.30 \times 0.20 \text{ mm}^3$, monoclinic ($C2/c$), $a = 19.832(4)$ Å, $b = 12.054(2)$ Å, $c = 26.508(5)$ Å, $\beta = 103.29(3)^\circ$, $V = 6167(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.520 \text{ g mm}^{-3}$, $\mu = 2.165 \text{ mm}^{-1}$, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $T = 173(2)$ K, reflections measured = 37 383, unique reflections = 8332 ($R_{\text{int}} = 0.0969$), absorption correction = none, final R indices $R1 = 0.0465$ and $wR2 = 0.1107$, largest difference peak and hole = $+1.435$ and -1.440 e Å^{-3} .

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- (17) Preparation of **4**: Toluene (30 mL) was added to a dry mixture of 0.54 g (0.41 mmol) of $[\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}_2\text{YCl} \cdot \text{THF}$ (**3**) and 0.13 g (0.81 mmol) of InMe_3 . The resulting yellowish suspension was stirred for 60 h at ambient temperature and for an additional 4 h at reflux temperature. Filtration through a thin layer of Celite resulted in a clear yellow solution. Slow concentration of the filtrate inside the drybox afforded colorless prisms suitable for X-ray diffraction. Yield: 0.47 g (81%). Mp: 106 °C (dec). Anal. Calcd for $\text{C}_{56}\text{H}_{64}\text{In}_3\text{O}_8\text{Si}_4\text{Y}$ ($M_r = 1410.80$): C, 47.68; H, 4.57. Found: C, 46.88; H, 4.51. ^1H NMR (400.1 MHz, C_6D_6 , 20 °C): δ 8.50–6.50 (m, Ph, 40H), 2.10 (s, *OMe*, 6H), –0.01 (d, *InMe*, 12 H), –0.43 (d, *InMe*, 6H). ^{13}C NMR (100.6 MHz, C_6D_6 , 20 °C): δ 137.65–136.76 (m, Ph, *ipso*-C), 136.16, 135.12, 134.90, 130.76–130.16 (m), 129.29–127.54 (m, Ph), 21.38 (*OMe*), –1.73, –4.96 (*InMe*). ^{29}Si NMR (79.5 MHz, C_6D_6 , 20 °C): δ –34.67, –35.34. IR (KBr): 3437, 3069, 3050, 3001, 2923, 2811, 1591, 1568, 1486, 1450, 1429, 1385, 1306, 1252, 1182, 1123, 1058, 1035, 1018, 996, 921, 743, 716, 700, 533, 493, 478, 428 cm^{-1} .

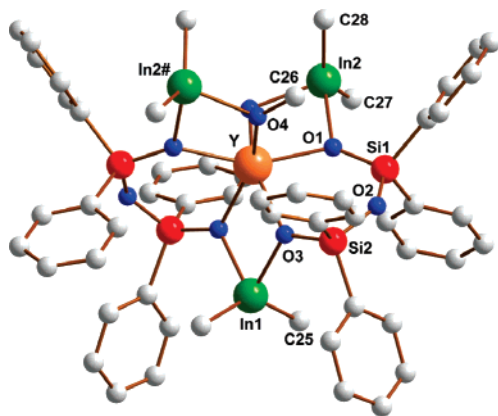
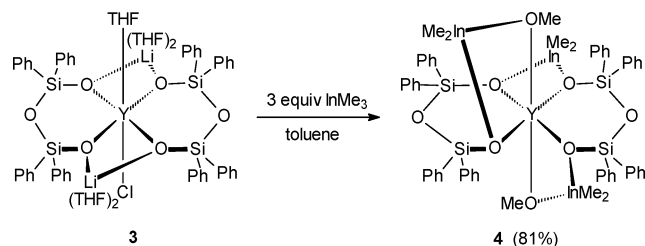


Figure 2. Molecular structure of $[(\text{Ph}_2\text{SiO})_2\text{O}]_2[\text{InMe}_2(\text{OMe})]_2\text{InMe}_2\text{Y}$ (**4**). Selected bond lengths (Å) and angles (deg): Y–O1 2.290(3), Y–O3 2.277(3), Y–O4 2.223(3), In1–O3 2.208(3), In2–O4 2.161(3), In2–O1# 2.211(3), O4–Y1–O4# 101.39(16), O3–Y1–O1# 115.88(9), O4–Y1–O3 97.81(11), O4–Y1–O1# 74.56(11), O4#–Y1–O3 151.07(10), O3–Y1–O1, 84.01(10), O4–Y1–O1 90.15(11), O1#–Y1–O1 155.98(14), O3–Y1–O3# 74.10(13), C25#–In1–C25 138.8(4), O3–In1–O3# 76.85(14), C28–In2–C27 137.8(2), O4–In2–O1# 77.40(11), In1–O3–Y1 104.52(11), In2–O4–Y1 104.51(14), In2#–O1–Y1 100.74(12) (# denotes symmetry-related atoms).

Scheme 2



InMe₂ units in two different ways (the intensity ratio of the InCH₃ resonances was 2:1) and replacement of all coordinated THF. Again, unequivocal structural characterization proved to be possible only with the aid of an X-ray diffraction study,¹⁴ which revealed the formation of a novel inorganic ring system **4** containing both yttrium and indium (Scheme 2).

In the molecular structure of **4** (Figure 2), the central yttrium is coordinated by six oxygen atoms in a slightly distorted octahedral fashion. The crystal structure analysis confirmed the incorporation of three InMe₂⁺ moieties. One of them had replaced a Li(THF)₂⁺ unit within the metalla-

crown ring system, while the other two were converted into Me₂InOMe ligands, probably through methylation of a siloxide oxygen during the course of the reaction. However, the latter assumption is purely speculative at this stage, and clearly more work is needed in order to gain more insight into the reaction pathways leading to the novel complexes **3** and **4**.

The significantly lower solubility of **4** in toluene as compared to **2** can be traced back to the much less effective shielding of the “inorganic” metallacrown core by phenyl substituents. The most remarkable structural feature of **4**, however, is the complex stabilization of two monomeric Me₂InOMe ligands. Free liquid dimethylindium methoxide was first reported by Coates and co-workers¹⁸ in 1956 and later shown by Weidlein and co-workers¹⁹ to have a trimeric In₃O₃ ring structure. In **4**, two monomeric Me₂InOMe units are stabilized through interaction with disiloxanediolate oxygens and coordination of the methoxy groups to yttrium.

In summary, transformations of heterobimetallic group 3 metal disiloxanediolates with trialkyls of aluminum and indium have been shown to yield novel bi- or trimetallic inorganic ring systems. The Sc/Al/Li complex **2** was formed via an unexpected Li–Al exchange reaction. Complex stabilization of monomeric Me₂InOMe was observed in the novel Y/In disiloxanediolate derivative **4**. The two initial reactions reported here were selected in order to get a first impression of the scope of this chemistry. Given the large variety of potential precursors, it can be readily anticipated that further research in this area will produce many more surprising and exciting results in the future.

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Supporting Information Available: ORTEP drawings and X-ray structural data as well as complete CIF files for **3** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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