

the proposed structure of the third isomer of  $[\text{Co}_2(\text{CO})_8]$ , C (eq 1), and has equivalent carbonyl and  $\text{CH}_2$  groups. There is no necessity for formation of the other likely isomer of eq 3, b', which could form via isomer c.

The activation energies,  $\Delta G^\ddagger$ , for exchange of **4a** or **5a** with **4b** or **5b** and for making equivalent the nonequivalent carbonyl,  $\text{Me}_2\text{P}$ , or  $\text{CH}_2$  groups of **4a** or **5a**, were identical within  $\pm 1$  kJ mol<sup>-1</sup> for a given complex and the data are given in Table I.<sup>12</sup> These data show clearly that the reaction of eq 2 is rate determining and that carbonyl exchange then occurs rapidly by way of eq 3. Furthermore, there is a very good correlation of the  $\Delta H^\circ$  and  $\Delta G^\ddagger$  values for the bridged  $\rightleftharpoons$  nonbridged reactions as shown in Table I. This relationship is expected<sup>12</sup> but has not previously been demonstrated for the important cobalt carbonyl dimers.

**Acknowledgment.** We thank the NSERC (Canada) for financial support.

**Supplementary Material Available:** Figure 1 (variable-temperature FTIR spectra of  $[\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})_2]$  in  $\text{CH}_2\text{Cl}_2$  (the arrows indicate growth of peaks due to **5a** at lower temperature) and the resulting plot of  $\ln K$  vs  $1/T$ , where  $K$  is the equilibrium constant for eq 2) and Figure 2 (variable-temperature <sup>13</sup>C NMR (75-MHz) and <sup>31</sup>P NMR (121-MHz) spectra for  $[\text{Co}_2(\text{CO})_4(\mu\text{-dppm})_2]$ ) (2 pages). Ordering information is given on any current masthead page.

(12) The  $\Delta G^\ddagger$  values were estimated by using the Eyring equation and were unchanged over the temperature range 213–243 K for **4** and 233–275 K for **5**. This suggests that  $\Delta S^\ddagger$  is small and hence  $\Delta G^\ddagger \sim \Delta H^\ddagger$ . The entropy term favors **4b** or **5b** because of the greater mobility compared to **4a** or **5a**, but libration about the Co–Co bond is not expected to be possible until the  $\mu\text{-CO}$  bonds in the bridged isomer are completely broken, and so the entropy of activation term is not expected to be an important contributor to  $\Delta G^\ddagger$ . If it were otherwise, the observed correlation of  $\Delta H^\circ$  and  $\Delta G^\ddagger$  would not be expected. The entropy term is probably also responsible for the relative instability of isomer b' (eq 3). Molecular models indicate that b' is strain free but the conformation is rigid, whereas in b libration about the Co–Co bond is possible.

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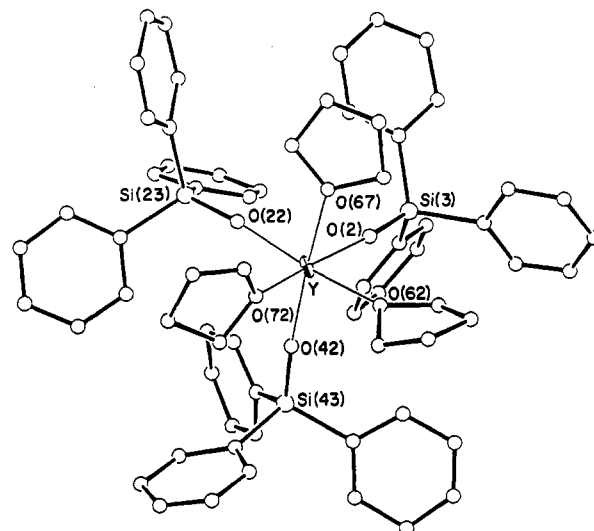
Received May 1, 1989

### Synthesis of Tris(triphenylsiloxy)yttrium and Derivatives: Crystal Structure of $[\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3]\cdot\text{THF}$

One approach to the incorporation of yttrium into mixed-metal, solid-state materials is envisioned as proceeding through *molecular* precursors that are ligand-bridged aggregates of the sort  $\text{Y}_m\text{M}_n\text{X}_n$  (M = any other metal; X = any bridging ligand).<sup>1</sup> Since an oxide lattice is frequently desired, the ligand complement to the molecular aggregate must be chosen, in part, for its ability to be subsequently removed by hydrolysis with concomitant introduction of oxo groups. In this regard yttrium alkoxides are relevant starting reagents for the assembly of preceramic aggregates, although they remain poorly characterized.<sup>2</sup> Initial efforts in

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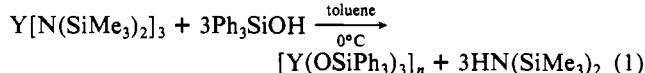
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**Figure 1.** ORTEP drawing of  $\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3$ , omitting hydrogens. Selected structural parameters: Y–O2 = 2.136 (17) Å, Y–O22 = 2.118 (18) Å, Y–O42 = 2.138 (18) Å, Y–O62 = 2.406 (21) Å, Y–O67 = 2.462 (21) Å, Y–O72 = 2.374 (20) Å, Si–O = 1.554 (19)–1.597 (20) Å. Angles: Y–O–Si = 168.5 (12)–174.4 (11)°, (Si)O–Y–O(Si) = 100.8 (7)–102.3 (7)°, (C<sub>4</sub>H<sub>9</sub>)O–Y–O(C<sub>4</sub>H<sub>9</sub>) = 79.6 (7)–82.2 (7)°. Unlabeled atoms are carbon atoms.

this laboratory at the preparation of tri-*tert*-butoxyyttrium complexes invariably led to the obtention of white, poorly soluble materials that could not be characterized further. Because heterolytic cleavage of the carbon–oxygen bond leading to yttrium oxides and organic products derived from the *tert*-butyl carbocation might be a facile decomposition pathway,<sup>3</sup> attention focused on yttrium silyloxides because of the strength of the Si–O linkage and the unfavorability of silyl cation formation. We now wish to report the synthesis of  $[\text{Y}(\text{OSiPh}_3)_3]_n$  (**1**) along with two monomeric Lewis base adducts, *fac*- $[\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3]\cdot\text{THF}$  (**2**) and *fac*- $[\text{Y}(\text{OSiPh}_3)_3(\text{py})_3]$  (**3**).

Tris(triphenylsiloxy)yttrium (**1**), formed from the reaction of  $[\text{Y}(\text{N}(\text{SiMe}_3)_2)_3]$ <sup>4</sup> with 3 equiv of  $\text{Ph}_3\text{SiOH}$  in toluene (eq 1), was



isolated as a colorless, feather-like solid.<sup>5</sup> The hydrogen-1 and carbon-13 NMR spectra of **1** showed only broad, complex resonances in the phenyl region, consistent with the formulation of this compound as an aggregate presumably involving bridging

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(5)  $[\text{Y}(\text{OSiPh}_3)_3]_n$  (**1**). IR (Nujol): no  $\nu(\text{O-H})$ ;  $\nu(\text{C-H})$  3030 cm<sup>-1</sup>; other bands 1100 (s), 695 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.5–6.5 (br mult). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): a complex set of resonances between  $\delta$  135.4 and 127.6. Anal. Calcd for C<sub>34</sub>H<sub>45</sub>O<sub>3</sub>Si<sub>3</sub>Y: C, 70.87; H, 4.97. Found: C, 69.99; H, 4.89.  $[\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3]\cdot\text{THF}$  (**2**). IR (Nujol): no  $\nu(\text{O-H})$ ;  $\nu(\text{C-H})$  3040, 3020 cm<sup>-1</sup>; aromatic overtones 1945, 1875, 1810, 1760 cm<sup>-1</sup>; other bands 1100 (vs), 695 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (THF-*d*<sub>6</sub>):  $\delta$  7.65 (d, 6.7 Hz, 18 H, ortho H), 7.09 (t, 7.5 Hz, 9 H, para H), 6.94 (~t, 7.1 Hz, 18 H, meta H), 3.58 (m, 16 H, THF), 1.74 (m, 16 H, THF). <sup>13</sup>C NMR (THF-*d*<sub>6</sub>):  $\delta$  142.4 (ipso), 136.4 (ortho), 128.7 (para), 127.8 (meta), 68.2 (THF), 26.4 (THF). Anal. Calcd for C<sub>70</sub>H<sub>77</sub>O<sub>3</sub>Si<sub>3</sub>Y: C, 69.85; H, 6.46. Found: C, 66.88; H, 6.15. Crystal data (–157 °C): monoclinic, space group *P2*<sub>1</sub>, *a* = 14.530 (7) Å, *b* = 16.407 (8) Å, *c* = 14.534 (8) Å,  $\beta$  = 114.32 (2)°, *V* = 3157.21 Å<sup>3</sup>, *Z* = 2. Refinement of 1926 reflections with  $|F^2| > 3\sigma(F^2)$  converged with final residuals *R* = 0.0841 and *R'* = 0.0790.  $[\text{Y}(\text{OSiPh}_3)_3(\text{py})_3]$  (**3**). IR (Nujol): no  $\nu(\text{O-H})$ ;  $\nu(\text{C-H})$  3040, 3020 cm<sup>-1</sup>;  $\nu(\text{C-N})$  1590 cm<sup>-1</sup>; other bands 1100 (vs), 695 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.35 (br s, 6 H, py  $\alpha$ ), 7.42 (br m, 3 H, py  $\beta$ ), 7.37 (d, 7.0 Hz, 18 H, ortho H), 7.10 (t, 7.4 Hz, 9 H, para H), 6.93 (~t, 7.4 Hz, 18 H, meta H), 6.74 (br s, 6 H, py  $\beta$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  149.9 (py  $\alpha$ ), 140.8 (ipso), 137.6 (py  $\beta$ ), 135.2 (ortho), 128.1 (meta), 127.1 (para), 123.8 (py  $\beta$ ). Anal. Calcd for C<sub>69</sub>H<sub>60</sub>N<sub>3</sub>O<sub>3</sub>Si<sub>3</sub>Y: C, 71.90; H, 5.26; N, 3.65. Found: C, 71.08; H, 5.60; N, 3.44.

Ph<sub>3</sub>SiO- ligands. There was no evidence for coordinated amide or amine. Furthermore, the infrared spectrum showed no bands in the  $\nu(\text{O-H})$  region, indicating that complex **1** does not contain coordinated silanol. Since attempts to obtain samples of [Y(OSiPh<sub>3</sub>)<sub>3</sub>]<sub>n</sub> in a form suitable for X-ray diffraction were unsuccessful, efforts focused on preparing Lewis base adducts in the hope of realizing improved crystallinity. Indeed, dissolution of [Y(OSiPh<sub>3</sub>)<sub>3</sub>]<sub>n</sub> in tetrahydrofuran, followed by concentration in vacuo and addition of diethyl ether caused well-formed, colorless prisms of *fac*-[Y(OSiPh<sub>3</sub>)<sub>3</sub>(THF)<sub>3</sub>] $\cdot$ THF (**2**) to precipitate.<sup>5</sup> Crystalline *fac*-[Y(OSiPh<sub>3</sub>)<sub>3</sub>(py)<sub>3</sub>] (**3**) was prepared analogously by using pyridine (py) in place of tetrahydrofuran.<sup>5</sup> These conversions were nearly quantitative, so the formulation of **1** as a homoleptic yttrium silyloxy is confirmed.

The X-ray structure determination of [Y(OSiPh<sub>3</sub>)<sub>3</sub>(THF)<sub>3</sub>] $\cdot$ THF revealed a monomeric complex with approximate octahedral geometry at the yttrium(III) core (Figure 1). The additional molecule of tetrahydrofuran does not coordinate (it fills a void in the crystal lattice), which demonstrates that, in this compound, yttrium(III) does not prefer a higher coordination number. Large Y-O-Si angles [171 (1)°, average], together with short Y-OSi distances [2.13 (2) Å average vs 2.41 (2) Å average for Y-O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>] indicates extensive yttrium-silyloxy oxygen multiple bonding. Reinforcing this view is the facial orientation of the bulky Ph<sub>3</sub>SiO- ligands, which minimizes competition among the silyloxy oxygen  $\pi$ -donor orbitals for the set of three yttrium-based  $d\pi$  acceptor functions. In response to the steric congestion imposed by this facial arrangement, the three phenyl groups attached to any one silicon interleave phenyl rings on adjacent ligands (see Figure 1). As judged by the simple pattern of resonances observed for the phenyl region (i.e., only one type of phenyl ring) in both <sup>1</sup>H and <sup>13</sup>C NMR spectra, the facial orientation of the silyloxy ligands is retained in solution at ambient temperature. However, the tetrahydrofuran ligands in [Y(OSiPh<sub>3</sub>)<sub>3</sub>(THF)<sub>3</sub>] $\cdot$ THF are labile, as demonstrated by observation of a single set of THF-based <sup>1</sup>H NMR resonances upon spiking a chloroform-*d*<sub>1</sub> solution of the yttrium complex with 1 equiv of free tetrahydrofuran. As more tetrahydrofuran was added, the THF-based resonances asymptotically approached the resonances for free tetrahydrofuran in CDCl<sub>3</sub>.

The ease with which [Y(OSiPh<sub>3</sub>)<sub>3</sub>]<sub>n</sub> fragments to monomeric units, effectively opening coordination sites at yttrium, makes this complex an attractive reagent for the synthesis of mixed-metal multimetallic alkoxide aggregates.

**Acknowledgment.** This work was supported by the Department of Energy. We thank Scott Horn for skilled technical assistance.

**Supplementary Material Available:** Tables of positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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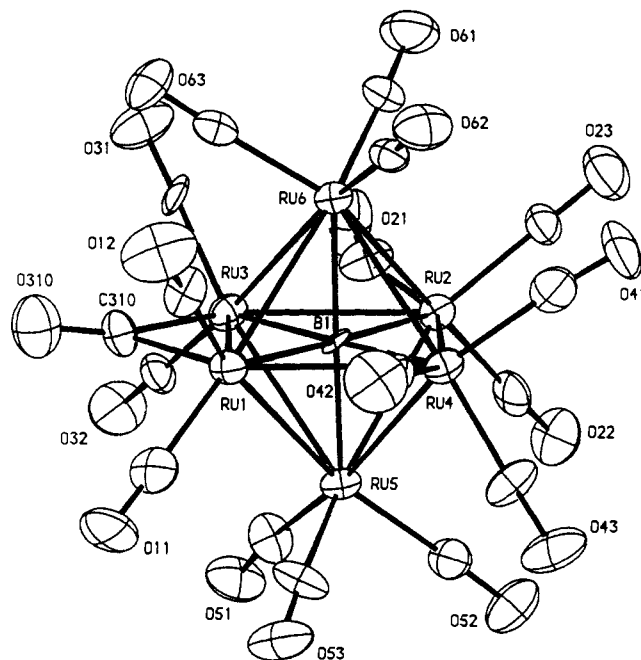
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Received June 7, 1989

### Synthesis and Structure of the Ruthenium Carbonyl "Boride" Cluster HRu<sub>6</sub>(CO)<sub>17</sub>B

Although a number of transition-metal clusters containing an encapsulated main-group element are now known,<sup>1</sup> only two ex-

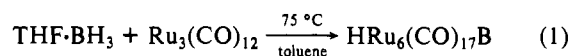
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**Figure 1.** Arrangement of non-hydrogen atoms in HRu<sub>6</sub>(CO)<sub>17</sub>B (ORTEP plot with 50% probability ellipsoids). Selected bond distances (Å): Ru1-Ru3 = 2.832 (2), Ru1-Ru4 = 2.994 (2), Ru1-Ru5 = 2.925 (2), Ru1-Ru6 = 2.889 (2), Ru2-Ru3 = 2.912 (3), Ru2-Ru4 = 2.914 (2), Ru2-Ru5 = 2.892 (2), Ru2-Ru6 = 2.910 (2), Ru3-Ru6 = 2.887 (2), Ru4-Ru5 = 2.867 (2), Ru4-Ru6 = 2.900 (2), Ru1-B1 = 2.06 (2), Ru2-B1 = 2.05 (2), Ru3-B1 = 2.07 (2), Ru4-B1 = 2.06 (2), Ru5-B1 = 2.04 (2), Ru6-B1 = 2.06 (2).

amples of molecular clusters that contain an internal boron atom have been reported previously. These are the neutral heterometallic boride<sup>2</sup> Fe<sub>4</sub>(CO)<sub>12</sub>B(AuPh<sub>3</sub>)<sub>3</sub>, which has a molecular structure that is not a closed polyhedron, and the anionic heterometallic boride<sup>3</sup> [Fe<sub>4</sub>Rh<sub>2</sub>(CO)<sub>16</sub>B]<sup>-</sup>, which contains a boron atom inside an octahedron of metal atoms.

We wish to report the preparation of the ruthenium carbonyl boride cluster HRu<sub>6</sub>(CO)<sub>17</sub>B, the first example of a molecular homometallic cluster containing an encapsulated boron atom. This complex was obtained through the reaction



The yield of crude product is about 10%.

In a typical reaction a 1.1-g quantity (1.7 mmol) of Ru<sub>3</sub>(CO)<sub>12</sub> was placed in a 50-mL Schlenk flask with 15 mL of toluene. At room temperature, 7.0 mL of 1 M BH<sub>3</sub>·THF in THF was injected into the flask, which was then placed in an oil bath at 75 °C. The solution was stirred for 5 h at this temperature. A red solid precipitated from solution. This solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and the solution was passed through a silica gel column. The product was isolated from the CH<sub>2</sub>Cl<sub>2</sub> solution by crystallization and was characterized by a single-crystal X-ray analysis and NMR, IR, and mass spectroscopy.

The arrangement of non-hydrogen atoms in the molecular structure of HRu<sub>6</sub>(CO)<sub>17</sub>B is depicted in Figure 1.<sup>4</sup> Ruthenium

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