Ph_3SiO– ligands. There was no evidence for coordinated amide or amine. Furthermore, the infrared spectrum showed no bands in the ν(O–H) region, indicating that complex **1** does not contain coordinated silanol. Since attempts to obtain samples of $[Y(OSiPh_3)_3]_n$ 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 $[Y(OSiPh_3)_3]_n$ in tetrahydrofuran, followed by concentration in vacuo and addition of diethyl ether caused well-formed, colorless prisms of *fac*-$[Y(OSiPh_3)_3(THF)_3]\cdot THF$ (**2**) to precipitate.[5] Crystalline *fac*-$[Y(OSiPh_3)(py)_3]$ (**3**) was prepared analogously by using pyridine (py) in place of tetrahydrofuran.[5] These conversions were nearly quantitative, so the formulation of **1** as a homoleptic yttrium silyloxide is confirmed.

The X-ray structure determination of $[Y(OSiPh_3)_3(THF)_3]\cdot THF$ 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 $Y-O(CH_2CH_2)_2$] indicates extensive yttrium–silyloxy oxygen multiple bonding. Reinforcing this view is the facial orientation of the bulky Ph_3SiO– ligands, which minimizes competition among the silyloxy oxygen π-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 ^1H and ^{13}C NMR spectra, the facial orientation of the silyloxy ligands is retained in solution at ambient temperature. However, the tetrahydrofuran ligands in $[Y(OSiPh_3)_3(THF)_3]\cdot THF$ are labile, as demonstrated by observation of a single set of THF-based ^1H NMR resonances upon spiking a chloroform-d_1 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 $CDCl_3$.

The ease with which $[Y(OSiPh_3)_3]_n$ 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.

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

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Synthesis and Structure of the Ruthenium Carbonyl "Boride" Cluster $HRu_6(CO)_{17}B$

Although a number of transition-metal clusters containing an encapsulated main-group element are now known,[1] only two examples of molecular clusters that contain an internal boron atom have been reported previously. These are the neutral heterometallic boride[2] $Fe_4(CO)_{12}B(AuPh_3)_3$, which has a molecular structure that is not a closed polyhedron, and the anionic heterometallic boride[3] $[Fe_4Rh_2(CO)_{16}B]^-$, which contains a boron atom inside an octahedron of metal atoms.

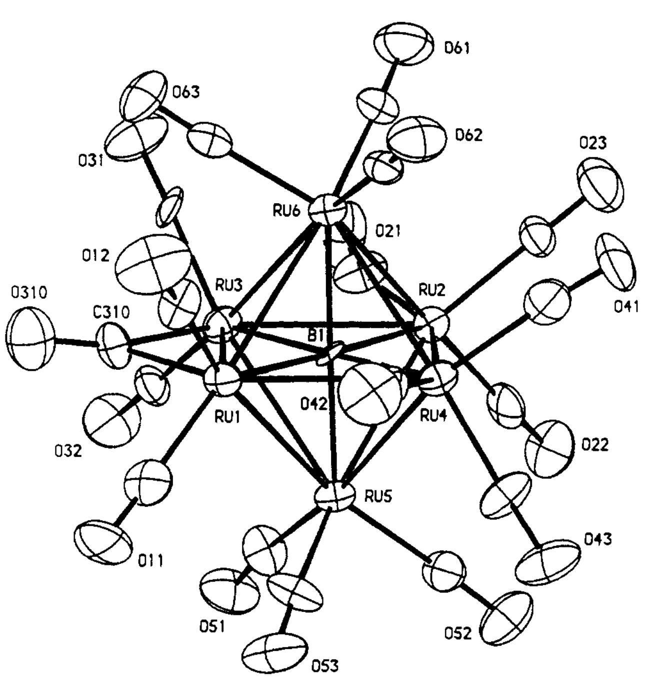

Figure 1. Arrangement of non-hydrogen atoms in $HRu_6(CO)_{17}B$ (ORTEP plot with 50% probability ellipsoids). Selected bond distances (Å): Ru1–Ru3 = 2.832 (2), Ru1–Ru4 = 2.994 (2), Ru1–Ru5 = 2.925 (2), Ru1–Ru6 = 2.889 (2), Ru2–Ru3 = 2.912 (3), Ru2–Ru4 = 2.914 (2), Ru2–Ru5 = 2.892 (2), Ru2–Ru6 = 2.910 (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).

We wish to report the preparation of the ruthenium carbonyl boride cluster $HRu_6(CO)_{17}B$, the first example of a molecular homometallic cluster containing an encapsulated boron atom. This complex was obtained through the reaction

$$THF\cdot BH_3 + Ru_3(CO)_{12} \xrightarrow[\text{toluene}]{75\ ^\circ C} HRu_6(CO)_{17}B \qquad (1)$$

The yield of crude product is about 10%.

In a typical reaction a 1.1-g quantity (1.7 mmol) of $Ru_3(CO)_{12}$ was placed in a 50-mL Schlenk flask with 15 mL of toluene. At room temperature, 7.0 mL of 1 M $BH_3\cdot THF$ 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_2Cl_2, and the solution was passed through a silica gel column. The product was isolated from the CH_2Cl_2 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 $HRu_6(CO)_{17}B$ is depicted in Figure 1.[4] Ruthenium

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(4) Crystal data for $H(CO)_{17}Ru_6B$ (−50 °C): space group $P2_1/n$, $a = 9.119$ (5) Å, $b = 32.019$ (7) Å, $c = 9.514$ (3) Å, $\beta = 111.5$ (4)°, $V = 2585$ Å^3, ρ(calcd) = 2.812 g cm^{-3} for $M_r = 1094.4$, $Z = 4.00$, $\mu = 34.34$ cm^{-1} for Mo Kα. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer. All data were corrected for Lorentz and polarization effects. An empirical absorption correction was made. Crystallographic computations were carried out on a PDP 11/44 computer using the SDP (Structure Determination Package). The structure was solved by the direct method MULTAN 11/82 and difference Fourier syntheses. $R_F = 0.035$ and $R_{wF} = 0.037$ (371 parameters refined) for 1886 reflections ($I \geq 3.0\sigma(I)$) of 3036 unique reflections collected in the range $4° \leq 2\theta \leq 50°$.

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atoms reside at the corners of an octahedron, and the boron atom is in the approximate center of the octahedron, being effectively equidistant from each ruthenium atom. The boron atom and the carbon of the bridging carbonyl (C310) are 0.021 (14) and 0.103 (13) Å, respectively, out of the least-squares plane defined by Ru1–Ru2–Ru3–Ru4. This arrangement of the non-hydrogen atoms (Figure 1) is similar to that described for $Ru_6(CO)_{17}C$.[5] The space groups are not interconvertible, however. Although the position of the hydrogen atom was not located from the X-ray data, the presence of hydrogen in the single crystal from which the X-ray data were obtained was demonstrated by dissolving the crystal in $CDCl_3$ and obtaining the ^1H NMR spectrum of the resulting solution. A single proton signal was observed, which had the same chemical shift as that of the bulk sample.

The ^{11}B NMR spectrum of $HRu_6(CO)_{17}B$ consists of a single signal at 193.8 ppm ($CDCl_3$; $\delta(BF_3{\cdot}OEt_2) = 0.00$ ppm). This large downfield shift is consistent with observed[6] ^{11}B chemical shifts for the borides $Fe_4(CO)_{12}(AuPR_3)_3B$ and $[Fe_4Rh_2(CO)_{16}B]^-$. It is also consistent with the fact that large downfield ^{13}C chemical shifts are observed for the encapsulated carbon in transition-metal carbide clusters.[7] The ^1H NMR spectrum consists of a single signal at −17.8 ppm ($CDCl_3$; $\delta(TMS) = 0.00$ ppm), which falls in the range observed for hydrogen in Ru–H–Ru bonds, in neutral ruthenium hydrido carbonyl clusters.[8] The infrared spectrum (CH_2Cl_2, 25 °C; ν 2079 (s), 2065 (vs), 2049 (s), 2028 (s) cm^{-1}) of the boride is similar to, but differs in detail from, that of the isoelectronic analogue $Ru_6(CO)_{17}C$. The mass spectrum (calcd for $^{104}Ru_6{}^{12}C_{17}{}^{16}O_{17}{}^{11}B^1H$, *m/e* 1096; found, *m/e* 1095) reveals a highest mass and a sequential loss of 17 carbonyls.

The reaction of $HRu_6(CO)_{17}B$ with excess (PPN)Cl (PPN = bis(triphenylphosphine)nitrogen(1+)) in CH_3OH for 30 min at room temperature causes loss of the proton signal. This is consistent with the deprotonation of $HRu_6(CO)_{17}B$ and is the expected reaction in view of the well-known tendency for (PPN)Cl to deprotonate transition-metal hydrido carbonyl clusters.[9] The ^{11}B NMR signal of the proposed anion $[Ru_6(CO)_{17}B]^-$, at 196 ppm, is only 2 ppm from that of the neutral complex, which suggests that the proton was not removed from the boron. It has been shown that the ^{11}B NMR chemical shift is nearly independent of charge on the cluster when a proton that is not bonded to boron is removed from a metal-rich metallaborane cluster.[10] Where a proton is removed from a boron atom, as in the deprotonation of $Fe_4(CO)_{12}BH_3$ to form $[Fe_4(CO)_{12}BH_2]^-$, the ^{11}B signal shows a significant shift.[10] Reprotonation of the proposed anion $[Ru_6(CO)_{17}B]^-$ with phosphoric acid gives the neutral boride as evidenced from its ^{11}B and ^1H spectra.

In addition to $HRu_6(CO)_{17}B$, the previously reported compound[11] $BH_2Ru_4(CO)_{12}H$ was detected (^{11}B NMR ($CDCl_3$) 110 ppm (t, 1:2:1, $J_{BH} = 65$ Hz); ^1H NMR −8.5 ppm (2 H, q, 1:1:1:1, $J = 65$ Hz), −21.1 ppm (1 H)). The analogous "butterfly" complex[12] $BH_2Fe_4(CO)_{12}H$ produces similar NMR spectra. The complex $BH_2Ru_4(CO)_{12}H$ was also obtained from the following reaction:

$$\mathrm{THF{\cdot}BH_3 + H_4Ru_4(CO)_{12} \xrightarrow{CH_2Cl_2} BH_2Ru_4(CO)_{12}H + 2H_2} \tag{2}$$

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Supplementary Material Available: Listings of bond distances, bond angles, positional parameters, and anisotropic thermal parameters (10 pages); a table of calculated and observed structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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