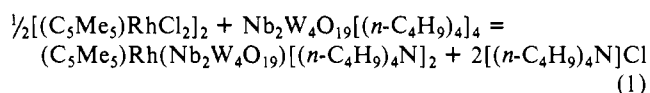


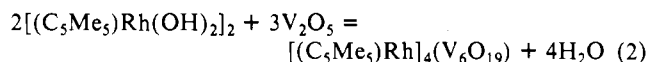
Communications

An Organometal Hydroxide Route to $[(C_5Me_5)Rh]_4(V_6O_{19})$

A large number of complex organometal oxides have been prepared during the past decade from organometal and oxoanion salts by simple metathesis reactions such as (1).^{1,2} Since the type



of compounds prepared in this fashion reflects in part the synthetic approach employed, we have sought to develop alternative routes that might yield new classes of materials. We report here such a route, namely, the reaction of organometal hydroxides with simple metal oxides. The specific system investigated, aqueous $[(C_5Me_5)Rh(OH)_2]_2$ plus V_2O_5 , yields $[(C_5Me_5)Rh]_4(V_6O_{19})$ according to (2).



Addition of 80 mg (0.44 mmol) of V_2O_5 to 2 mL of 0.28 M aqueous $[(C_5Me_5)Rh(OH)_2]_2$ (0.55 mmol) yields a yellow solution that gradually becomes brown. A dark brown precipitate is formed and may be isolated after 24 h, crystallized from moist CH_3OH/CH_3CN , and air-dried at ambient temperature for 48 h to give 116 mg of solvated $[(C_5Me_5)Rh]_4(V_6O_{19})^{4,5}$ in 49% yield based on vanadium.

X-ray structural analysis of crystalline $[(C_5Me_5)Rh]_4(V_6O_{19}) \cdot 3CH_3CN \cdot CH_3OH \cdot 3H_2O$ (**1**)⁶ revealed the presence of a neutral complex in which four $(\eta^5-C_5Me_5)Rh^{2+}$ cations are bound to a single $V_6O_{19}^{8-}$ anion (see Figure 1). Each d^6 rhodium(III) cation achieves an 18-electron configuration by being η^5 -bonded to a $Me_5C_5^-$ ligand and σ -bonded to three contiguous doubly bridging oxygens of a $V_6O_{19}^{8-}$ anion. Although the $[(\eta^5-C_5Me_5)Rh]_4(V_6O_{19})$ molecule approximates rather closely full tetrahedral T_d symmetry with $Rh-O_A-Rh$ angles ranging from 108.3 to 109.9°, it rigorously possesses only C_{2v} - $mm2$ symmetry in the solid state. Bond distances and angles at the rhodium centers

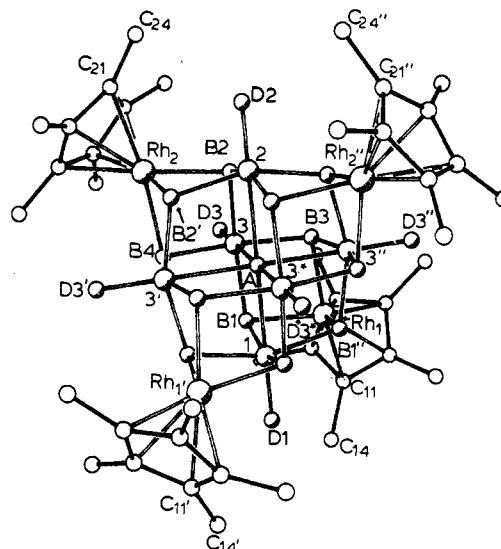


Figure 1. Perspective drawing of the $[(\eta^5-C_5Me_5)Rh]_4(V_6O_{19})$ molecule in **1** which possesses rigorous crystallographic C_{2v} symmetry in the solid state. Rhodium and vanadium atoms are represented by large- and medium-sized shaded spheres, respectively, while oxygen and carbon atoms are represented by small shaded and unshaded spheres, respectively. Rhodium and carbon atoms are labeled with subscripts to their atomic symbols, but vanadium and oxygen atoms are labeled only by their subscripts. $Rh_1, Rh_1', C_{11}, C_{14}, C_{11}', C_{14}', V_1, V_2, O_A, O_B, O_{B'}, O_{D1},$ and O_{D2} lie in one of the mutually perpendicular mirror planes, while $Rh_2, Rh_2', C_{21}, C_{24}, C_{21}', C_{24}', V_1, V_2, O_A, O_B, O_{B'}, O_{D1},$ and O_{D2} lie in the other. These mirror planes relate atoms labeled with a single prime or double prime to those labeled without primes. Selected average⁹ bond lengths and angles: $Rh-C, 2.132$ (9, 26, 11, 6) Å; $Rh-O, 2.108$ (5, 18, 5, 4) Å; $V-O_A, 2.246$ (7, 9, 6, 3) Å; $V-O_B, 1.916$ (4, 6, 4, 6) Å; $V-O_D, 1.604$ (9, 5, 3, 3) Å; ring C-C, 1.438 (12, 23, 16, 6) Å; ring-to-methyl C-C, 1.510 (14, 39, 22, 6) Å; $Rh-Cg, 1.748$ (-, 2, 2, 2) Å; $Cg-Rh-O, 134.2$ (-, 6, 4, 4)°; $O-Rh-O, 77.1$ (2, 6, 5, 4)°; $Rh-O-V, 95.8$ (2, 8, 5, 6)°; $V-O_B-V, 111.9$ (3, 4, 2, 4)°.

(see Figure 1 caption) are comparable to those observed in other polyoxoanion-supported $(\eta^5-C_5Me_5)Rh(III)$ complexes,

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- (4) Anal. Calcd for $C_{40}H_{60}Rh_4V_6O_{19} \cdot 3H_2O$: C, 29.73; H, 4.12; N, 0.00; Rh, 25.47; V, 18.91. Found: C, 29.20; H, 4.21; N, 0.19; Rh, 26.03; V, 18.68. 1H NMR (D_2O , TSP): δ 1.89 (CH_3, s). ^{13}C NMR (D_2O , TSP): δ 11.46 (s, C_5Me_5), 99.01 (d, $C_5Me_5, J_{Rh-C} = 9$ Hz). ^{51}V NMR ($D_2O, VOCl_3$): δ -511.6. IR (Nujol mull, 400-1000 cm^{-1}): 485 (s), 561 (m), 679 (s), 722 (sh), 936 (s) cm^{-1} .
- (5) The same complex has been mentioned in a meeting abstract: Hayashi, Y.; Ozawa, Y.; Isobe, K. *Abstracts of Papers, 38th Sakuen Kagaku Toronkai, Tokushima, October 1988*, No. 1A02; *Kagaku to Kogyo (Chem. Chem. Ind.)* **1988**, *41*, A645.

- (6) Single crystals of **1** are, at 20 ± 1 °C, orthorhombic, space group $Pnmm$ [an alternate setting of $Pnmm-D_{2h}^{13}$ (No. 59)], with $a = 11.678$ (2) Å, $b = 15.166$ (3) Å, $c = 18.566$ (3) Å, and $Z = 2$ formula units [$d_{calc} = 1.790$ $g\ cm^{-3}$; μ_a (Mo $K\alpha$) = 1.817 mm^{-1}]. A total of 4004 unique data having $2\theta_{Mo\ K\alpha} < 55^\circ$ were collected on a Nicolet P1 autodiffractometer using graphite-monochromated Mo $K\alpha$ radiation and full (0.9° wide) ω scans. The intensity data were corrected empirically for variable absorption effects and the structure was solved by using "direct methods" (SHELXTL) techniques. The resulting structural parameters have been refined⁷ by using counter-weighted cascade block-diagonal least-squares techniques to R_1 (unweighted, based on F) = 0.042 and R_2 (weighted, based on F) = 0.050 for 2262 independent absorption-corrected reflections having $2\theta_{Mo\ K\alpha} < 55^\circ$ and $I > 3\sigma(I)$.
- (7) See paragraph at end of paper regarding supplementary material.
- (8) Hayashi, Y.; Toriumi, K.; Isobe, K. *J. Am. Chem. Soc.* **1988**, *110*, 3666.

$[(C_5Me_5)Rh(Nb_2W_4O_{19})]^{2-2}$ and $[(C_5Me_5)Rh]_4(Mo_4O_{16})^8$. The $V_6O_{19}^{8-}$ core has the same structure as the $Nb_6O_{19}^{8-}$, $Ta_6O_{19}^{8-}$, $Mo_6O_{19}^{2-}$, and $W_6O_{19}^{2-}$ ions.^{1c} It thus represents the first observation of this hexametalate structure in polyvanadate chemistry, although mixed-metal species incorporating vanadium are known.^{1c}

Preliminary experiments indicate that several organo-transition-metal hydroxides are reactive toward both main-group and transition-metal oxides, demonstrating that the synthetic approach described here has considerable generality, particularly when hydrothermal techniques are employed.

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- (9) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements included in the averaged value.
- (10) Cg refers to the center of gravity for the five-membered ring of a $(CH_3)_5C_5^-$ ligand.

Supplementary Material Available: Crystal structure analysis report, Table I (fractional atomic coordinates for non-hydrogen atoms), Table II (anisotropic thermal parameters for non-hydrogen atoms), Table III (atomic coordinates for hydrogen atoms), Table IV [bond lengths and angles in $[(C_5Me_5)Rh]_4(V_6O_{19})$], Table V (bond lengths and angles in solvent molecules), Figure 2 [perspective thermal vibration ellipsoid drawings of $[(C_5Me_5)Rh]_4(V_6O_{19})$], Figure 3 [perspective drawing of $[(C_5Me_5)Rh]_4(V_6O_{19})$ including locatable hydrogen atoms], and Figure 4 (perspective drawings of solvent molecules in 1) (18 pages); structure factor tables for the crystal structure analysis of 1 (10 pages). Ordering information is given on any current masthead page.

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Articles

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Synthesis and Characterization of a Series of Antimony-Containing Iron Carbonyl Complexes: $[Et_4N]_3[SbFe_4(CO)_{16}]$, $[Et_4N]_2[HSbFe_4(CO)_{13}]$, $[Et_4N][H_2SbFe_4(CO)_{13}]$, and $[Et_4N]_2[CISbFe_3(CO)_{12}]$

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Reactions of $SbCl_3$ or $SbCl_5$ with $Na_2[Fe(CO)_4] \cdot 3/2$ dioxane or with $Fe(CO)_5/KOH/MeOH$ yield the anion $[SbFe_4(CO)_{16}]^{3-}$, which can be easily isolated as its $[Et_4N]^+$ salt, $[Et_4N]_3[I]$, which crystallizes in the monoclinic centrosymmetric space group $P2_1/n$ with $a = 13.415$ (2) Å, $b = 19.601$ (2) Å, $c = 19.156$ (2) Å, $\beta = 90.973$ (9)°, $Z = 4$, and $V = 5036.3$ (9) Å³. The Sb atom in this anion is tetrahedrally surrounded by four $Fe(CO)_4$ units with an average Sb-Fe bond distance of 2.666 (3) Å. When treated with 1 equiv of trifluoromethanesulfonic acid (CF_3SO_3H), $[Et_4N]_3[I]$ is converted into $[Et_4N]_2[HSbFe_4(CO)_{13}]$ ($[Et_4N]_2[II]$), in which the Sb atom caps a closed Fe_3 triangle and donates its lone pair of electrons to an external $Fe(CO)_4$ unit. $[Et_4N]_2[Sb_2Fe_3(CO)_{17}]$ is observed as a minor product of this reaction. $[Et_4N]_2[II]$ crystallizes in the monoclinic centrosymmetric space group $P2_1/c$ with $a = 13.805$ (6) Å, $b = 18.934$ (9) Å, $c = 15.295$ (6) Å, $\beta = 97.76$ (6)°, $Z = 4$, and $V = 3961$ (3) Å³. The ¹H NMR spectrum shows a singlet at $\delta = -19.74$ ppm for the hydride ligand. When $[Et_4N]_2[II]$ is treated with an additional 1 equiv of trifluoromethanesulfonic acid, $[Et_4N][H_2SbFe_4(CO)_{13}]$ ($[Et_4N][III]$) is formed. $[Et_4N][III]$ crystallizes in the triclinic centrosymmetric space group $P\bar{1}$ with $a = 12.714$ (2) Å, $b = 14.342$ (2) Å, $c = 8.970$ (2) Å, $\alpha = 99.57$ (1)°, $\beta = 105.27$ (1)°, $\gamma = 82.34$ (1)°, $Z = 2$, and $V = 1549.0$ (4) Å³. The ¹H NMR spectrum shows a singlet at $\delta = -22.63$ ppm for the hydride ligands. The cluster structure is virtually identical with that of $[II]^{2-}$ with an extra bridging H ligand. When treated with 1 equiv of $TiCl_3$ or $SbCl_5$, $[Et_4N]_3[I]$ produces $[Et_4N]_2[CISbFe_3(CO)_{12}]$ ($[Et_4N]_2[IV]$), in which Sb is tetrahedrally bound to one Cl^- and three $Fe(CO)_4$ units, as determined by X-ray diffraction at -80 °C: $[Et_4N]_2[IV] \cdot 0.5CH_2Cl_2$, monoclinic centrosymmetric space group $C2/c$ with $a = 29.30$ (1) Å, $b = 18.500$ (6) Å, $c = 16.844$ (6) Å, $\beta = 119.58$ (2)°, $Z = 8$, and $V = 7942$ (6) Å³.

Introduction

Recent studies involving the incorporation of heavy main-group elements into transition-metal clusters have led to a number of exciting molecules with unexpected structure and bonding patterns.^{1,2} Notable examples are $[(\mu_3, \eta^2-E_2)\{W(CO)_5\}_3]$ [$E = As, Sb, Bi$] with very short E-E distances and electron deficient EM_3 molecules like $[CpMn(CO)_2]_3As$,⁶ $[Cr(CO)_5]_2[Mn(CO)_5]As$,⁷

$[Cr_2(CO)_9][Mn(CO)_5]As$,⁷ $[Mn(\eta^5-C_5H_4Me)(CO)_2]_3Te$,⁸ and $[Et_4N]_2[EF_3(CO)_{12}]^{2-}$ ($E = Pb, Sn$).⁹ In $[(\eta^5-C_5H_5)Mo]_2-[\mu, \eta^4-As_5]$ ¹⁰ a planar As_5 ring is capped on opposite sides by two $[\eta^5-CpMo]$ fragments. The structure of $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]^{11}$

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