These results demonstrate clearly that the silylene–disilene rearrangement by the silyl shift is an efficient process and opens a new way to disilene.

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Synthesis and Structure of the $\{[(C_7H_8)Rh]_5(cis\text{-}Nb_2W_4O_{19})_2\}^{3-}$ Anion

C. J. Besecker and W. G. Klemperer*†

School of Chemical Sciences, University of Illinois
Urbana, Illinois 61801
and Department of Chemistry, Columbia University
New York, New York 10027

V. W. Day*

The Crystalytics Company, Lincoln, Nebraska 68501
and Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588

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The metal tricarbonyl and rhodium pentamethylcyclopentadienyl complexes $[(OC)_3Mn(Nb_2W_4O_{19})]^{3-}$,[1] $[(C_5H_5)Ti(Mo_5O_{18})Mn(CO)_3]^{2-}$,[2] $[(OC)_3Re(Nb_2W_4O_{19})]^{3-}$,[1] and $\{[(CH_3)_5C_5]Rh(Nb_2W_4O_{19})\}^{2-}$ [3] all contain polyoxohexametallate ions bound to organometallic units with a triangle of three contiguous bridging oxygen atoms. In order to extend this family of 18-electron organometallic complexes to more reactive species, we had hoped to prepare the norbornadiene Rh^I complex $[(C_7H_8)Rh(Nb_2W_4O_{19})]^{3-}$. Much to our surprise, however, we have been unable to isolate this complex from the reaction of $[(C_7H_8)Rh(NCCH_3)_2][PF_6]$[4] with equimolar $(cis\text{-}Nb_2W_4O_{19})[(n\text{-}C_4H_9)_4N]_4$.[1] We have isolated instead the $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ anion, a structurally unique complex in which each of two $cis\text{-}Nb_2W_4O_{19}^{4-}$ ions, by utilizing both terminal and bridging oxygens, behaves as a pentadentate, bridging ligand.

Addition of 2.5 equiv of $[(C_7H_8)Rh(NCCH_3)_2](PF_6)$ to 4.0 g of $(cis\text{-}Nb_2W_4O_{19})[n\text{-}C_4H_9)_4N]_4$ in CH_3CN followed by addition of $(C_2H_5)_2O$, filtration of the resulting precipitate, washing with CH_2Cl_2 and $(C_2H_5)_2O$, and drying in vacuo yields 3.6 g of a yellow-orange powder. This powder is crystallized to pure $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_3$,[5] **1**, by cooling a saturated, boiling CH_3CN solution to room temperature. Single crystals marginally suitable for X-ray diffraction studies were obtained only after repeated recrystallization attempts from CH_3CN.

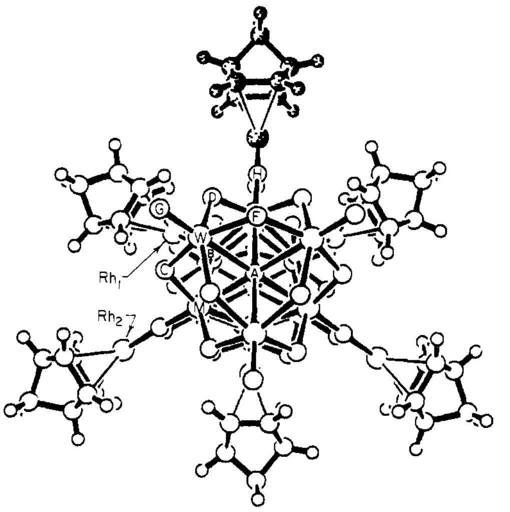

Figure 1. SCHAKAL[7] drawing of the crystallographically disordered $\{[(C_7H_8)Rh]_5(cis\text{-}Nb_2W_4O_{19})_2\}^{3-}$ anion, viewed approximately along a crystallographic C_3 axis. Atoms in the norbornadiene (C_7H_8) units are not labeled. In the remainder of the C_{3h} structure, one member from each set of symmetry-equivalent metal atoms (M, W, Rh_1, Rh_2) and oxygen atoms (A–D, F–H) are labeled. All non-hydrogen atoms were located X-ray crystallographically; hydrogen atom positions were generated by using idealized sp^2 and sp^3 hybridization and a C–H bond length of 0.96 Å. An ordered structure is obtained by removing a Rh_2 norbornadiene unit, one of which is shaded.

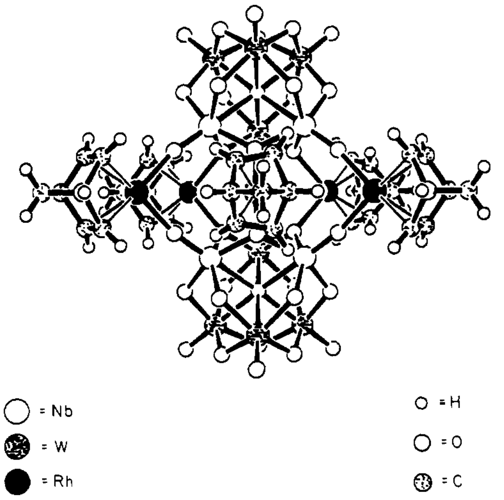

Figure 2. SCHAKAL[7] drawing of the C_{2v} structure proposed for an isolated, ordered $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ anion, viewed along the C_2 axis. The atomic positions are those obtained from the C_{3h} disordered crystal structure and therefore deviate from the proposed C_{2v} symmetry.

X-ray structural analysis[6] revealed that crystals of **1** are composed of discrete $N(n\text{-}C_4H_9)_4^+$ cations and $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ anions in which two $cis\text{-}Nb_2W_4O_{19}^{4-}$ ions are bridged by five $(C_7H_8)Rh^+$ cations. Even though the $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ ions have a maximum possible C_{2v} symmetry, they occupy crystallographic $\bar{6}$-C_{3h} sites in the lattice as a result of crystal packing disorder (see Figure 1). Accordingly, the metal

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† Address correspondence to this author at the University of Illinois.

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(5) Anal. Calcd for $C_{83}H_{148}N_3Nb_4O_{38}Rh_5W_8$: C, 24.00; H, 3.59; N, 1.01; Nb, 8.95, Rh, 12.39; W, 35.42. Found: C, 23.97; H, 3.68; N, 0.99; Nb, 8.97; Rh, 12.32; W, 35.53. $^{13}C\{^1H\}$ NMR (CD_3NO_2, Me_4Si = 0.0, 75.47 MHz, 298 K) δ 61.4, 61.0, 60.7 (d, $^3J_{C\text{-}Rh} \approx 6$ Hz, CH_2), 60.0 (s, NCH_2), 52.0–50.6 (CH and olefinic), 24.9 (s, NCH_2CH_2), 20.8 (s, CH_2CH_3), 14.1 (s, CH_3).

(6) Crystals of **1** are hexagonal, space group $P\bar{6}2C\text{-}D_{3h}^4$ (No. 190) with a = 16.833 (8) Å, c = 27.610 (13) Å, and Z = 2 (d_{calcd} = 2.02 g/cm³; μ_a (Mo K$\bar{\alpha}$) = 8.10 mm^{-1}). Three-dimensional diffraction data (a total of 2600 independent reflections having $2\theta_{Mo K\bar{\alpha}} < 55°$) were collected on a computer-controlled Nicolet P$\bar{1}$ autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full 1° wide ω scans. The structural parameters have been refined to convergence [R (unweighted, based on F) = 0.063 for 932 independent absorption corrected reflections having $2\theta_{Mo K\bar{\alpha}} < 55°$ and $I > 3\sigma(I)$] in cycles of empirically weighted full-matrix least-squares refinement that employed anisotropic thermal parameters for W, Nb, and Rh atoms and isotropic thermal parameters for the remaining non-hydrogen atoms. See paragraph at end of paper regarding supplementary material.

(7) A FORTRAN program for the graphical representation of molecular models written by Dr. Egbert Keller. We are grateful to Dr. Keller for providing a copy of his program.

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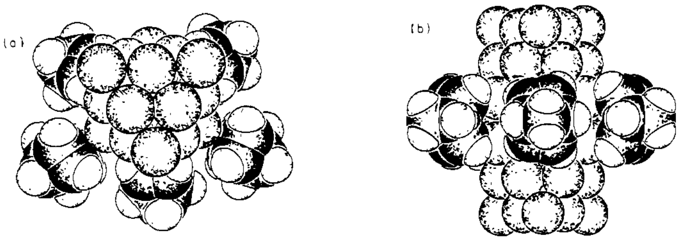

Figure 3. SCHAKAL[7] space-filling drawings of the $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ anion viewed along the same axes employed in Figures 1 and 2. The following atomic radii (Å) were employed: C, 1.7;[9] H, 1.2;[9] O, 1.4;[9] and for metals, 0.0.

sites labeled M in Figure 1 are 67% niobium and 33% tungsten while those labeled W are 100% tungsten. Refinement of occupancies for atoms in the $(C_7H_8)Rh^+$ moieties indicated full occupancy for Rh_1 units and $^2/_3$ occupancy for Rh_2 units resulting from the 3-fold disorder about the crystallographic C_3 axis passing through O_A. The structure of a single, nondisordered $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ anion is proposed in Figure 2. This structure is derived from the structure shown in Figure 1 by first removing a $(C_7H_8)Rh^+$ unit, shaded in Figure 1, and then assigning the Nb atoms to four of the M sites such that C_{2v} anion symmetry is obtained. This assignment is based on the assumption that Nb^V terminal oxygens will be utilized preferentially over W^{VI} terminal oxygens for binding $(C_7H_8)Rh^+$ cations. In this structure, each Rh^I center is bound to only oxygens that are bonded to at least one Nb^V center and completely avoids oxygens bonded only to the W^{VI} centers.

Although the $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ structure is unprecedented, all of its structural features are consistent with well-established inorganic and organometallic structural patterns. The 38 oxygen atoms form six close-packed layers in an ABCCBA sequence. The niobium and tungsten atoms occupy approximately octahedral sites between those layers. Each of the five rhodium atoms is a square-planar, d^8, 16-electron metal center with one pair of cis coordination sites occupied by olefinic C═C bonds and the other pair occupied by oxygen atoms.[8] The $(C_7H_8)Rh^+$ units are oriented relative to the $Nb_2W_4O_{19}{}^{4-}$ ions in such a fashion that effective Rh–O bonding is obtained with minimal weakening of Nb–O and W–O bonds. The 167 (3)° Rh_2–O_H–M angle reflects approximate sp hybridization at O_H and thus minimal interference of Rh_2–O_H bonding with Nb–O_H σ and π bonding. Similarly, the 121 (2)° Rh_1–O_B–M and 117 (2)° M–O_B–M angles reflect approximate sp^2 hybridization at O_B and minimal interference of Rh_1–O_B bonding with M–O_B σ and π bonding. From the viewpoint of nonbonding interactions, the $\{[(C_7H_8)Rh]_5(Nb_2W_2O_{19})_2\}^{3-}$ structure displays a remarkably compact structure (see Figure 3), particularly with regard to contacts between the Rh_1 norbornadiene units and adjacent $Nb_2W_4O_{19}{}^{4-}$ surface oxygens. The potential for realizing shape-selective chemistry at Rh_1 centers is evident.

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Registry No. 1, 83248-21-8; $[(C_7H_8)Rh(NCCH_3)_2](PF_6)$, 83232-01-3; $(cis\text{-}Nb_2W_4O_{19})[n\text{-}(C_4H_9)_4N]_4$, 75005-92-4.

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

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[8] The Rh atom, midpoints of the two olefinic bonds, and two oxygen atoms of each Rh coordination sphere are coplanar to within 0.05 Å; the O–Rh–O angles are 91 (1) and 92 (2)° for Rh_1 and Rh_2, respectively, and the Rh_1–O_B and Rh_2–O_H distances are 2.14 (3) and 2.06 (5) Å, respectively. These parameters are similar to those observed in the analogous $[(C_7H_8)Rh(CH_3CO_2)]_2$ structure: Reis, A. H.; Willi, C.; Siegel, S.; Tani, B. *Inorg. Chem.* **1979**, *18*, 1859.

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Reversible Iron–Nitrogen Migration of Alkyl, Aryl, or Vinyl Groups in Iron Porphyrins: A Possible Passage between σ Fe^{III}(porphyrin)(R) and Fe^{II}(*N*-R)(porphyrin) Complexes

Daniel Mansuy,* Jean-Paul Battioni, Daniel Dupré, and
Eric Sartori

Laboratoire de Chimie de l'Ecole Normale Supérieure
associé au CNRS, 24 rue Lhomond
75231 Paris Cedex 05, France

Genevieve Chottard

Laboratoire de Recherches Physiques
Université P. et M. Curie, Tour 22
75230 Paris Cedex 05, France

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Evidence has been provided for the formation of cytochrome P-450 complexes involving an iron–carbon bond upon metabolic reduction of polyhalogenated compounds[1] and oxidation of 1,3-benzodioxole derivatives.[2] Analogous iron–porphyrin complexes involving either an iron(II)–carbene bond[2,3] or a σ-alkyl–iron(III) bond[4] have been isolated and, most often, fully characterized. It was shown recently that the oxidation of vinylidene carbene–iron porphyrin complexes could lead to *N*-vinyl- and *cis-N,N*-vinylideneporphyrins.[5,6]

The following results are concerned with the reactivity of σ-methyl- (or -vinyl- or -phenyl-) iron(III) porphyrin complexes, and show that their oxidation by $FeCl_3$ leads to the corresponding iron(II) *N*-alkylporphyrin complexes. Moreover, they show that the reverse transfer of the alkyl group from a pyrrole nitrogen atom to the iron, leading from Fe(*N*-R)(porphyrin)(Cl) to Fe(porphyrin)(R) complexes, can be easily obtained upon sodium dithionite reduction of the iron *N*-alkylporphyrin complexes.

Very recently, similar reversible metal–nitrogen migrations of ethyl, ethoxycarbonyl, and phenyl groups in cobalt porphyrins have been described, and their mechanisms have been established.[7] Moreover, transfers of an alkyl group, R, from nitrogen to metal have been reported in the cobalt (R = CH_3[8a] and CH_2COOEt[8b]),

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