

this motion by increased tipping: the angles defined by Fe-N_{1m}-C_{1m2} and by Fe-N_{1m}-C₁₋₅ increase their asymmetry upon oxygenation (in I, 132.1 (8) and 126.3 (7)°, respectively; in II, 135.0 (6) and 123.5 (5)°). The angle made between the Fe-N_{1m} vector and the twofold axis normal to the porphyrinato plane decreases from 9.6 to 7.1° upon oxygenation. Small, but complex, changes in the crystal packing also are observed upon oxygenation. In both I and II the solvate ethanol is hydrogen bonded to the N-H part of the 2-MeIm ligand.

Caution must be exercised in making comparisons between these model systems and hemoproteins, particularly with regard to cooperativity in hemoglobin.⁶ The "pickets", intermolecular interactions, and, most notably, the hindrance afforded by a 2-MeIm ligand have no exact biological parallel. Nonetheless, the deoxy structure, I, with the sterically demanding 2-MeIm ligand remains a plausible model for the restraint⁶ of T state deoxy hemoglobin (the low affinity form). The oxy structure, II, should not be compared with R state oxyhemoglobin (the high affinity form): the 2-MeIm ligand of II can never be unrestrained (as are "relaxed" oxyhemoproteins⁶ or Fe(O₂)(TpvPP)(1-MeIm)⁸). However, complex II may be a simple analogue of T state oxyhemoglobin. The Fe-N_{1m} bond length is the same in complexes I, II, and also Fe(O₂)(TpvPP)(1-MeIm); significantly it is the Fe-O bond length which has lengthened in II, a result of importance in protein stereochemistry. In contrast, the T state NO adduct of hemoglobin has the Fe-N_{1m} bond ruptured.¹¹ This difference between NO and O₂ may reflect their relative binding and trans-labilizing properties.

Recent solid-gas measurements^{3,12} on I and its desolvated form show O₂ affinities less than that found for Fe(TpvPP)(1-MeIm), which are consistent with the lengthened Fe-O bond in I and reflect the axial base restraint. Surprisingly the presence of solvate ethanol has a large influence on the solid state O₂ binding of Fe(TpvPP)(2-MeIm): with it, O₂ binds weakly and with no site-site interaction;¹² without it, O₂ binds strongly and with cooperativity.³ Further structural and ligand binding studies of Fe(TpvPP)(1,2-dimethylimidazole), which has no solvate, may delineate the effects of crystal forces and hydrogen bonding in these systems.

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References and Notes

- J. L. Hoard in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, pp 317-380; J. L. Hoard, personal communication.
- Abbreviations: TpvPP, *meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrinato; TPP, *meso*-tetraphenylporphyrinato; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole. Following Hoard's notation¹: N_p, porphyrinato nitrogen atom, N_m, coordinated imidazole nitrogen atom; Fe-Ct, displacement of the iron atom from the least-squares plane of the porphyrinato nitrogen atoms; Fe-P_c, corresponding displacement from the 24-atom porphyrinato plane; Ct-N_p, radius of the porphyrin "hole". Doming is defined as the difference between Fe-Ct and Fe-P_c.
- J. P. Collman, J. I. Brauman, E. Rose, and K. S. Suslick, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 1052 (1978).
- Compound I crystallizes, as the monoethanol solvate, in space group C₂_v^h-C2/c with unit cell parameters a = 18.871 (11), b = 19.425 (13), c = 18.434 (11) Å; β = 91.48 (3)°; V = 6755.0 Å³; Z = 4. A total of 4176 unique reflections was collected on a Picker FACS-I automatic diffractometer using graphite-monochromatized Mo Kα radiation. Compound II was obtained by exposure of crystals of I to O₂ saturated with ethanol. The space group is unaltered and unit cell parameters change only slightly (a = 18.864 (5), b = 19.451 (5), c = 18.287 (5) Å; β = 91.45 (2)°; V = 6707.0 Å³; Z = 4). Ni-filtered Cu Kα radiation was used to collect 5183 unique reflections. The b axis is normal to the porphyrinato plane. Except for the 2-MeIm ligand and ethanol solvate, which were refined as rigid groups, all nonhydrogen atoms were assigned anisotropic thermal parameters; hydrogen atoms were located and included as fixed contributions to F_o. The final structural models for I and II assume C₂ molecular symmetry and are described by 373 and 396 variables, respectively; full-matrix least-squares refinement on all data (including F_o² < 0) led to R indices on F² of 0.142 and 0.120; conventional R indices on F for data having F_o² > 3σ (F_o²) are 0.086 and 0.083. The usual solution, refinement, and analysis programs were employed (see, for example, J. M. Waters and J. A. Ibers, *Inorg. Chem.*, **16**, 3273 (1977)).
- Comparison of the structures of the deoxy complex, Fe(TPP)(2-MeIm), with the oxy complex, Fe(TpvPP)(1-MeIm)(O₂),⁸ is necessarily indirect because of the differing axial bases.
- For a recent review, see M. F. Perutz, *Br. Med. Bull.*, **32**, 195 (1976).
- J. P. Collman, J. I. Brauman, K. M. Doxsee, T. R. Halbert, and K. S. Suslick, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 564 (1978); J. P. Collman, J. I. Brauman, K. M. Doxsee, T. R. Halbert, S. E. Hayes, and K. S. Suslick, *J. Am. Chem. Soc.*, **100**, 2761 (1978).
- G. B. Jameson, G. A. Rodley, W. T. Robinson, R. R. Gagne, C. A. Reed, and J. P. Collman, *Inorg. Chem.*, **17**, 850 (1978); J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Natl. Acad. Sci., U.S.A.*, **71**, 1326 (1974).
- See, for example, W. T. Robinson and G. A. Rodley, *Nature*, **235**, 438 (1972); G. B. Jameson, W. T. Robinson, and G. A. Rodley, *J. Chem. Soc., Dalton Trans.*, **191** (1978); R. S. Gall and W. P. Schaefer, *Inorg. Chem.*, **15**, 2758 (1976); A. Avdeef and W. P. Schaefer, *J. Am. Chem. Soc.*, **98**, 5153 (1976).
- This would tend to dispel the slight reservations expressed⁷ about the accuracy of the Fe-O separation for Fe(O₂)(TpvPP)(1-MeIm).
- M. F. Perutz, S. V. Kilmartin, K. Nagai, A. Szabo, and S. R. Simon, *Biochemistry*, **15**, 378 (1976); J. C. Maxwell and W. S. Caughey, *ibid.*, **15**, 388 (1976).
- K. S. Suslick, Ph.D. Thesis, Stanford University, 1978.

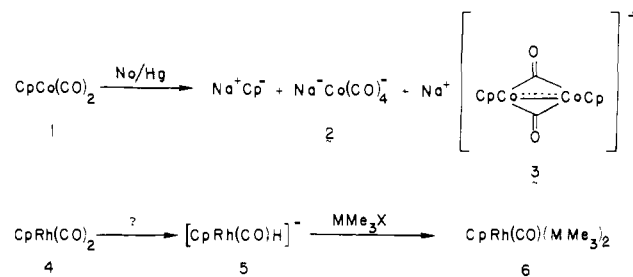
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Chemical Reduction of η⁵-Cyclopentadienyldicarbonylrhodium. Crystal and Molecular Structure of an Anionic Trinuclear Rhodium Cluster with "Semi-Triple-Bridging" Carbonyl Ligands

Sir:

Reduction of CpCo(CO)₂ (1, Cp ≡ η⁵-C₅H₅) with sodium amalgam leads¹ to the formation of sodium tetracarbonylcobaltate (2) and the binuclear cobalt radical anion 3. Reduction



of the rhodium analogue, 4, takes a different course.² In an attempt to understand the differences between these two reactions, we have reexamined the rhodium reduction. We report our results, which include the isolation and X-ray structure determination of an unusual product formed in this process.

Reduction of 4 with sodium amalgam in tetrahydrofuran (THF) was reported² to give a solution "with properties characteristic of its containing [η⁵-C₅H₅Rh(CO)H]⁻". This assignment was made on the basis of an IR absorption at 1892 cm⁻¹ and formation of complexes 6 upon treatment of the reduction solution with MMe₃X derivatives (M = Ge, Sn). In our hands, treatment of an 0.08 M solution of 4 in THF with 1.5 molar equiv of 0.3% Na/Hg for 3-5 h caused disappear-

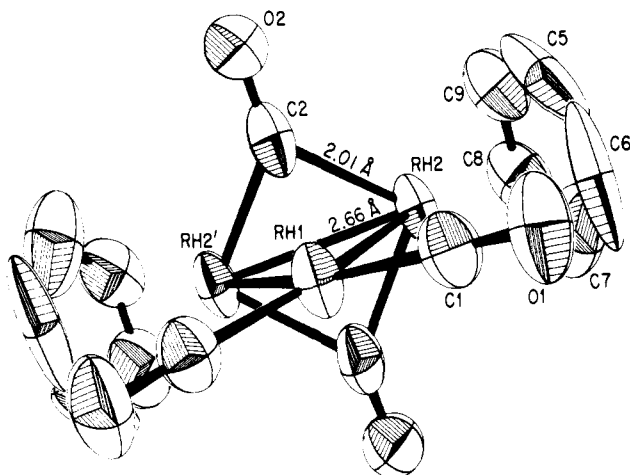


Figure 1. ORTEP drawing of $[\text{Cp}_2\text{Rh}_3(\text{CO})_4]^-$ with selected bond distances indicated. The molecule lies on a crystallographic twofold axis of symmetry; two asymmetric units contain one PPN^+ cation, one $\text{Cp}_2\text{Rh}_3(\text{CO})_4^-$ anion, and one THF molecule. The Rh-1-Rh-2-C-2 bond angle is 61.4° ; the dihedral angle between the Rh_3 plane and Rh-2-Rh-2'-C-2 plane is 77.5° .

ance of starting material and appearance of the earlier-reported² strong IR absorption at 1892 cm^{-1} . However, weaker bands in this region were also observed at 1860, 1910, 1973, and 2035 cm^{-1} . Furthermore, the solution exhibited three absorptions at lower frequency (1658 , 1693 , and 1730 cm^{-1}).

Using techniques similar to those described for the corresponding cobalt reduction,¹ we have succeeded in isolating salts of two different anions from this solution. The first, isolated in 14% yield as its $(\text{PPh}_3)_2\text{N}^+$ (PPN^+) salt, exhibits one band in the IR at 1892 cm^{-1} . The complex is diamagnetic but has no ^1H NMR; it is therefore clearly not $\text{PPN}^+ \mathbf{5}$. The sodium salt is responsible for the three bands in the initial reduction solution seen at 1860, 1892, and 2035 cm^{-1} . In intensity and shape these are identical with the bands reported³ for $\text{Na}^+\text{-Rh}(\text{CO})_4^-$, and we have therefore assigned the tetracarbonylrhodate structure (**7**) to this anion.

Assignment of structure to the second complex (isolated in 60% yield) was more difficult. As the (presumably contact ion paired^{1,4}) sodium salt, it was responsible for the three low-frequency bands in the IR. The PPN^+ salt exhibited a single low-frequency carbonyl absorption as well as two high-frequency bands (1693 , 1910 , and 1973 cm^{-1}). This material is diamagnetic and exhibits a single sharp line in the ^1H NMR in the cyclopentadienyl region ($\delta\ 5.20$ ppm in acetone- d_6). Its structure is therefore clearly different from that of the dimeric radical anion **3** isolated in the corresponding cobalt reduction.

Crystals of the second complex suitable for an X-ray diffraction study were obtained by slow diffusion (through a coarse frit) of hexane into a THF solution of the PPN^+ salt at room temperature; in this way, the material was collected as brown-orange plates.⁵ The salt crystallizes in the monoclinic system with the following crystal data: $a = 12.134$, $b = 25.323$, $c = 15.707\text{ \AA}$; $\alpha = \gamma = 90^\circ$; $\beta = 91.22^\circ$; space group $C2/c$; $z = 4$. The density was measured as 1.594 g cm^{-3} by flotation in $\text{CCl}_4/\text{CBr}_4$ ($\rho_{\text{calcd}} = 1.598$). Single-crystal diffraction data were collected out to 50° on a Syntex P2₁ automated diffractometer using monochromatic $\text{Mo K}\alpha$ radiation at room temperature; the structure was determined using 4602 reflections. A three-dimensional Patterson map was employed in locating the rhodium atoms. A three-dimensional Fourier map revealed the locations of all nonhydrogen atoms in the asymmetric unit, except for those in a tetrahydrofuran molecule incorporated in the crystal. Anisotropic full-matrix

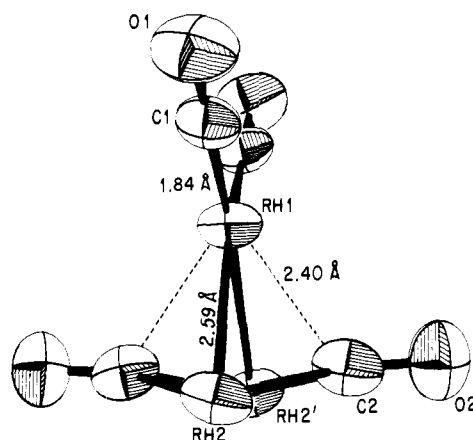
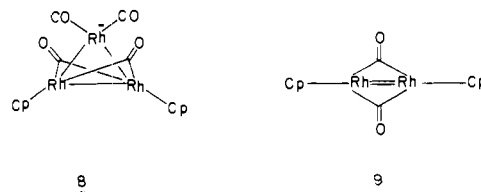


Figure 2. Slightly skewed edge-on view of rhodium triangle in $[\text{Cp}_2\text{Rh}_3(\text{CO})_4]^-$ (Cp rings omitted for clarity).

least-squares refinement followed by a difference Fourier map revealed the THF molecule, situated in a crystal void. Positions of the hydrogen atoms were calculated and not refined. Subsequent refinement of all coordinates in one full matrix and all anisotropic parameters and the scale factor in a second full matrix converged to a final $R_1 = 0.053$, $R_2 = 0.010$, goodness of fit = 1.57 for the 2502 reflections with $(F_{\text{obsd}})^2 \geq 3\sigma$.

Figure 1 shows an ORTEP drawing of the final structure of this anion (**8**). A complete list of bond distances and angles for $\text{PPN}^+ \mathbf{8}$ follows this article in the microfilm edition of the journal; a few important bond distances are shown in Figure 1. If we locate the single negative charge *formally* on the unique metal atom, **8** may be thought of as an adduct of $\text{Rh}(\text{CO})_2^-$ and $[\text{CpRh}(\text{CO})]_2$ (**9**); i.e., the highly unsaturated $\text{Rh}(\text{CO})_2^-$ fragment is coordinated in a "carbene-like" sense to the rhodium-rhodium double bond. Alternatively (and



perhaps more directly connected with the mechanism of formation of this complex and its relationship to **3**; see below), the cluster can be thought of as a "radical coupling" product formed by interaction of paramagnetic fragments $[\text{CpRh}(\text{CO})]_2^-$ and $\text{Rh}(\text{CO})_2^-$. In any case, the result is a trinuclear cluster containing three rhodium-rhodium bonds of essentially single-bond length.

A particularly interesting feature of the structure (see Figure 2) is that coordination of the $\text{Rh}(\text{CO})_2^-$ fragment has apparently induced the two bridging carbonyls to lean *toward* the unique rhodium atom, rather than away from it, as might have been expected on simple steric grounds. The C-2-Rh-1 distance is 2.40 \AA . At the same time, the oxygen atoms in the bridging carbonyl are bent slightly *away* from the third rhodium (i.e., the angle between the Rh-2-Rh-2'-C-2 plane and the C-2-O-2 axis is 170°). This interaction is reminiscent of a number of cases in which formally terminal CO groups have been found to "lean" toward unsaturated metal centers, thus becoming "semi-bridging" carbonyl ligands.⁶ In the case of **8** two CO groups, which are already symmetrically bridging two metal atoms, are coordinated weakly to a third. Perhaps "semi-triple-bridging" is an appropriate structural description for this type of interaction (cf. Figure 3). Its appearance in this molecule is a nice confirmation of Cotton's suggestion⁶ that unsymmetrical bridging provides a mechanism for transferring excess negative charge to less electron-rich areas of a molecule.

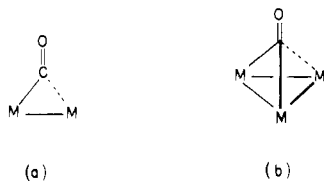
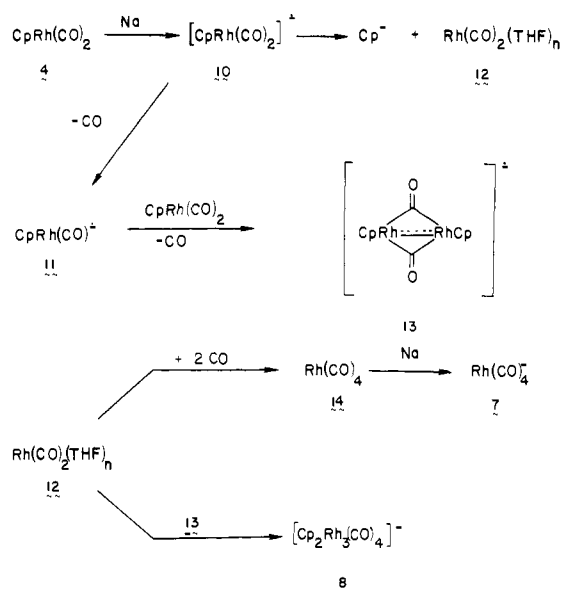


Figure 3. Schematic drawings of (a) a semi-bridging CO group; (b) a "semi-triple-bridging" CO group.

Scheme I



In complex **8**, three things reinforce this type of interaction: (a) the pseudo-square-planar configuration about the unique rhodium atom, (b) its coordinative unsaturation, and (c) the fact that Rh-I formally carries the molecule's negative charge.

We offer the route outlined in Scheme I as a working hypothesis for the mechanism of formation of **7** and **8**. As in the cobalt case, we assume that initial reduction to radical anion **10** is followed by competing CO loss (giving **11**) and loss of the cyclopentadienyl ring (leading to a (probably highly solvated) $\text{Rh}(\text{CO})_2$ fragment (**12**)). Complex **11** reacts with a second molecule of starting material, again followed by CO loss, to give radical anion **13**. Complex **13** is apparently more reactive than **3** and, instead of terminating the reaction at this stage, undergoes "radical coupling" with **12**; this leads to the isolated trinuclear cluster **8**. The alternative fate of **12** again parallels the cobalt reduction, giving **7** via coordination of CO and further reduction.

Carbonylation of **8** occurs unusually rapidly, leading cleanly to $\text{Rh}(\text{CO})_4^-$ and $\text{CpRh}(\text{CO})_2$ (no reaction between CO and **3** occurs in 24 h). It seems likely that this process involves initial dissociation, giving $\text{Rh}(\text{CO})_4^-$ and **9**. By analogy to the corresponding doubly bonded cobalt dimer,^{7,8} **9** should react immediately with CO, leading to **4**, as is observed.

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Supplementary Material Available. Three tables, listing interatomic distances and angles, fractional coordinates, and intensity data (26 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) N. E. Schore, C. S. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 1781 (1977).
- (2) (a) R. Hill and S. A. R. Knox, *J. Organomet. Chem.*, **84**, C31 (1975); (b) R. Hill and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 2622 (1975).
- (3) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 21 (1969).
- (4) M. Darensbourg, H. Barros, and C. Borman, *J. Am. Chem. Soc.*, **99**, 1647 (1977).
- (5) Crystals identical with those used for the X-ray study were shown to have an IR spectrum identical with those obtained by large-scale recrystallization from THF/hexane.
- (6) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 1233 (1974), and references cited there.
- (7) N. E. Schore, C. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **98**, 7436 (1976).
- (8) W.-S. Lee and H. H. Brintzinger, *J. Organomet. Chem.*, **127**, 87 (1977).
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Polyoxoanion Supported Organometallics: Synthesis and Characterization of $\alpha\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{PW}_{11}\text{O}_{39})]^{4-}$

Sir:

Solid oxide supported organometallic compounds of the early transition elements have been studied extensively during the past 20 years as catalysts for a variety of hydrocarbon transformations.¹⁻³ These catalysts not only provide the practical advantages of heterogeneous catalysts relative to homogeneous systems with regard to product isolation and catalyst stability, but in many cases also provide activity which far exceeds that of their homogeneous analogues. The factors responsible for this enhanced activity remain obscure owing to the difficulty of characterizing surface-bound species. We have therefore sought the isolation of organometallic compounds bound to the surfaces of soluble oxide clusters with the hope that these species might provide insights into the factors responsible for the reactivity of solid oxide supported analogues. We report here the synthesis and characterization of $\alpha\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{PW}_{11}\text{O}_{39})]^{4-}$, the first polyoxoanion supported organometallic complex.

The $\alpha\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{PW}_{11}\text{O}_{39})]^{4-}$ ion (see Figure 1) was selected as an initial synthetic objective since several of its structural features are preceded. This ion is related to the well-characterized $\text{PW}_{12}\text{O}_{40}^{3-}$ ion⁴ by substitution of a $[\text{W}^{\text{VI}}\text{O}]^{4+}$ subunit with $[\text{Ti}^{\text{IV}}(\eta^5\text{-C}_5\text{H}_5)]^{3+}$. Similar substitution of a $[\text{W}^{\text{VI}}\text{O}]^{4+}$ unit in the $\text{PW}_{12}\text{O}_{40}^{3-}$ anion by inorganic cations has been demonstrated to yield stable complexes.⁵⁻⁷ $[\text{Ti}^{\text{IV}}(\eta^5\text{-C}_5\text{H}_5)]^{3+}$ was chosen as an organometallic subunit for three reasons. First, Ti^{IV} has a 0.745 Å crystal radius⁸ which is almost identical with the 0.74 Å crystal radius⁸ for W^{VI} , indicating that Ti^{IV} is geometrically well suited for W^{VI} substitution in the $\text{PW}_{12}\text{O}_{40}^{3-}$ structure. Second, Ti^{IV} has a vast oxygen chemistry,⁹ assuring the thermodynamic stability of $\text{Ti}^{\text{IV}}\text{-O}$ bonds. Finally, the $[\text{Ti}^{\text{IV}}(\eta^5\text{-C}_5\text{H}_5)]^{3+}$ unit has been thoroughly characterized in a large number of organometallic compounds and can be easily identified using routine spectroscopic techniques.¹⁰

Synthesis of the desired complex is accomplished by allowing $\alpha\text{-}[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{H}_3\text{PW}_{11}\text{O}_{39}$ to react with $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3$ in 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$. Recrystallization of the crude reaction product from $(\text{CH}_3)_2\text{CO}/\text{C}_6\text{H}_5\text{CH}_3$ yields pure $\alpha\text{-}[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{-}$