

observed for the $\{\text{Fe}_2\text{O}\}^{4+}$, $\{\text{Fe}_2\text{O}(\text{O}_2\text{CR})_2\}^{2+}$, and $\{\text{Fe}_2\text{O}(\text{O}_2\text{P}(\text{OR})_2)_2\}^{2+}$ cores.^{4,6,16}

In conclusion, the novel asymmetric $\{\text{Fe}_2\text{O}\}^{7+}$ core has been synthesized by the route given in eq 1. The resulting isosceles triangle of iron atoms has antiferromagnetic exchange and ground-state magnetic properties quite different from those of the extensively studied basic iron carboxylates.^{15,18} These results provide valuable insight into the relationships that occur between magnetic and structural properties of polynuclear iron-oxo complexes and should facilitate the study of such units in biological systems such as ferritin.

Acknowledgment. This work was supported by National Institutes of Health Grant GM-32134 from the National Institute of General Medical Sciences. Magnetic measurements and some computations were made at the SQUID magnetometer facility of the Francis Bitter National Magnet Laboratory. We thank Drs. R. B. Frankel and G. C. Papaefthymiou for helpful discussions and Drs. E. C. Theil and N. D. Chasteen for preprints of articles describing their work.

Registry No. 1- $2\text{C}_6\text{H}_6$, 96998-70-8.

Supplementary Material Available: Atomic positional and thermal parameters for compound 1- $2\text{C}_6\text{H}_6$ (2 pages). Ordering information is given on any current masthead page.

(18) Dziobkowski, C. T.; Wroblewski, J. T.; Brown, D. B. *Inorg. Chem.* **1981**, *20*, 671-678 and references cited therein.

Cleavage of Ruthenium and Osmium Porphyrin Dimers: Formation of Organometallic Ruthenium Porphyrin Complexes and Highly Reduced Metalloporphyrin Species

J. P. Collman,* P. J. Brothers, L. McElwee-White, E. Rose, and L. J. Wright

Department of Chemistry, Stanford University
Stanford, California 94305

Received January 29, 1985

Early reports on naturally occurring and synthetic metalloporphyrins focused on heteroatom donors (N, P, O, S) or CO coordinated to the metal. More recently, a small number of metalloporphyrin complexes containing metal-carbon bonds in the axial coordination sites have been reported. These include alkyl, acyl, carbene, vinyl, vinylidene, and acetylene species. Hydride complexes have also been prepared.¹

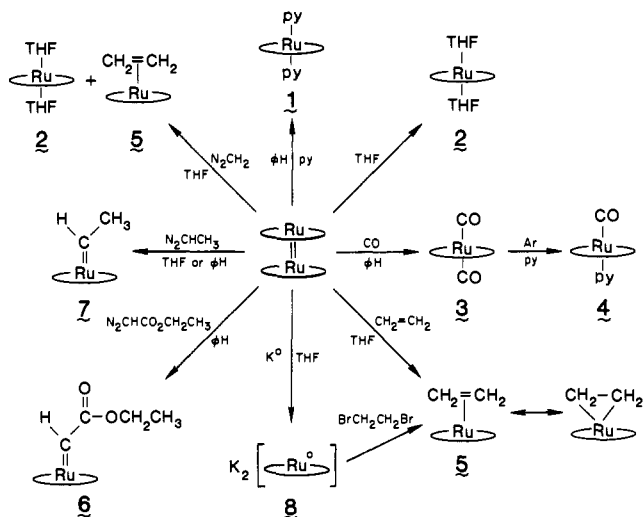
We recently described the characterization of the double-bonded porphyrin dimers $[\text{M}(\text{Por})]_2$ ($\text{M} = \text{Ru}, \text{Os}$; $\text{Por} = \text{OEP}, \text{TTP}$).^{2,3} In the presence of any potentially coordinating ligand, these dimers are cleaved to form $\text{M}(\text{Por})\text{L}_2$ species. Formation of the complexes $\text{Ru}(\text{TTP})\text{L}_2$ ($\text{L} = \text{py}$, **1**; THF , **2**; CO , **3**) is illustrated in Scheme I. Preparations of these products by independent routes have been described in the literature.⁴⁻⁷

(1) (a) Abeysekera, A. M.; Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V. *J. Chem. Soc., Perkin Trans. 1* **1977**, 36-44. (b) Abeysekera, A. M.; Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1395-1403. (c) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869-3870. (d) Ogoshi, H.; Setsune, J.-I.; Nanbo, Y.; Yoshida, Z.-I. *J. Organomet. Chem.* **1978**, *159*, 329-339. (e) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302-303. (f) De Cian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1850-1851. (g) Chan, Y. W.; Renner, M. W.; Balch, A. L. *Organometallics* **1983**, *2*, 1888-1889. (h) Mansuy, D. *Pure Appl. Chem.* **1980**, *52*, 681-690.

(2) (a) Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500-3510. (b) Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7684-7688.

(3) Abbreviations: Por = porphyrinato dianion unspecified; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; TPP = 5,10,15,20-tetraphenylporphyrinato dianion; TTP = 5,10,15,20-tetra-*p*-tolylporphyrinato dianion; py = pyridine; THF = tetrahydrofuran.

Scheme I



Treatment of a THF solution of $[\text{Ru}(\text{Por})]_2$ ($\text{Por} = \text{OEP}, \text{TTP}$) with ethylene (5 min at room temperature), followed by purging with Ar and recrystallization from THF/ROH ($\text{R} = \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2$) yields the novel organometallic metalloporphyrin ethylene complex $\text{Ru}(\text{Por})(\text{CH}_2=\text{CH}_2)$.⁸ The coordinated ethylene in $\text{Ru}(\text{TTP})(\text{CH}_2=\text{CH}_2)$ (**5**) gives rise to a singlet at -4.06 ppm in the ^1H NMR spectrum. The integrated intensities indicate that there is one ethylene present per Ru porphyrin moiety. The upfield shift of 9 ppm (relative to free ethylene) can be attributed to the porphyrin ring current effect. The ^1H NMR spectrum remains unchanged at -85°C . In the presence of ethylene, no coordinated olefin is observed by ^1H NMR indicating fast exchange on the NMR time scale. We are currently investigating the reaction of the dimers with other olefins.

The ease with which the ruthenium dimer can be cleaved upon treatment with neutral donor ligands suggested that reaction with a neutral carbene precursor " $:\text{CRR}'$ " might lead to carbene complexes of the form $\text{Ru}(\text{Por})(\text{CRR}')$. A vinylidene complex, $\text{Ru}(\text{TPP})(\text{C}=\text{C}(p\text{-C}_6\text{H}_4\text{Cl})_2)$, had been prepared by insertion of Ru into a free base porphyrin already containing the carbene moiety bridged between two pyrrole nitrogen atoms.¹⁸

(4) (a) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015-3024. (b) Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J.; Gallucci, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7030-7032.

(5) Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151-5163. $\text{Ru}(\text{TTP})(\text{THF})_2$ NMR ($\text{THF}-d_6$, 300 MHz) H_β 8.17 (s), H_α , H_m 7.94 (d), 7.49 (d), CH_3 2.63 (s) ppm. $\text{Ru}(\text{OEP})(\text{THF})_2$ NMR ($\text{THF}-d_6$, 300 MHz) H_{meso} 9.29 (s), CH_2CH_2 3.87 (q), CH_2CH_3 1.83 (t) ppm.

(6) Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1975**, *97*, 235-236. $\text{Ru}(\text{TTP})(\text{CO})_2$ NMR (C_6D_6 , 300 MHz) H_β 9.05 (s), H_α , H_m 8.08 (d), 7.24 (d), CH_3 2.39 (s) ppm. The complex was identified by IR and NMR spectroscopy in the presence of excess CO.

(7) Little, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 8583-8590.

(8) (a) The ethylene complex can be formulated either as a $\text{Ru}(\text{IV})$ metalloacyclopropane or as a $\text{Ru}(\text{II})$ ethylene π complex. We use the latter formulation. $\text{Ru}(\text{TTP})(\text{CH}_2=\text{CH}_2)$ NMR ($\text{THF}-d_6$, 300 MHz) H_β 8.37 (s), H_α , H_m 7.95 (d), 7.49 (br d), CH_3 2.64 (s), CH_2CH_2 -4.06 (s) ppm; NMR (C_6D_6 , 300 MHz) H_β 8.81 (s), H_α , H_α , H_m , H_m 8.19 (d), 8.04 (d), 7.30 (d), 7.25 (d), CH_3 2.39 (s), CH_2CH_2 -3.54 (s) ppm; MS (DEI), m/z $[\text{M}]^+$ 798; $[\text{M} - \text{CH}_2\text{CH}_2]^+$ (base peak) 770; UV-vis (THF) λ_{max} (log ϵ), 408 (5.23), 504 (4.21), 524 (sh) nm. Anal. Satisfactory C, H, N for $\text{Ru}(\text{TTP})(\text{CH}_2=\text{CH}_2)\cdot\text{THF}$. One equivalent of THF observed by ^1H NMR in C_6D_6 . $\text{Ru}(\text{OEP})(\text{CH}_2=\text{CH}_2)$ NMR ($\text{THF}-d_6$, 300 MHz) H_{meso} 9.63 (s), CH_2CH_3 3.94 (q), CH_2CH_2 1.84 (t), CH_2CH_2 -4.78 (s) ppm; MS (NDCI), m/z $[\text{M}]^+$ (base peak) 662; $[\text{M} - \text{CH}_2\text{CH}_2]^+$ 634; UV-vis (THF) λ_{max} (log ϵ), 388 (5.12), 497 (sh), 520 (4.28), 543 (sh) nm. (b) A complex claimed on the basis of an electronic spectrum to be a ruthenium OEP ethylene complex is mentioned in the secondary literature. However, this species was neither isolated nor characterized. James, B. R.; Addison, A. W.; Cairns, M.; Dolphin, D.; Farrell, N. P.; Paulson, D. R.; Walker, S. *Fundam. Res. Homogeneous Catal.* **1979**, *3*, 751-772.

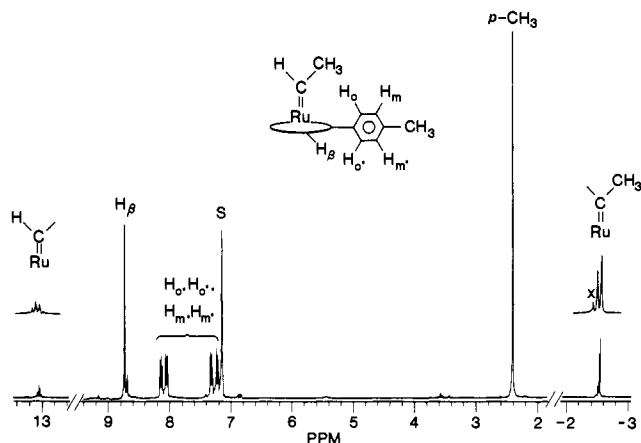


Figure 1. NMR spectrum (C_6D_6 , 300 MHz) of $Ru(TTP)(CHCH_3)$.

When $[Ru(TTP)]_2$ is treated with a slight excess of $N_2CHCO_2CH_2CH_3$ in benzene at room temperature the carbene complex $Ru(TTP)(CHCO_2CH_2CH_3)$ (6) is produced.⁹ The ethyl triplet and quartet resonances each appear ca. 1 ppm upfield from those in free ethyl diazoacetate. The carbene proton resonance is observed at 13.43 ppm, within the range for the proton in complexes of the form $M=C(H)R$.¹⁰ The eight β -pyrrolic protons appear as a singlet, indicating that the carbene complex has axial symmetry on the NMR time scale at room temperature. An electronic barrier to rotation would not be expected since either of the symmetry equivalent metal d_{xz} or d_{yz} orbitals can participate in the π -bonding.

Treatment of a benzene or THF solution of the dimer with a stream of nitrogen containing diazoethane produces the ethylidene complex $Ru(TTP)(CHCH_3)$ (7).¹¹ The 1H NMR spectrum of this complex in C_6D_6 is shown in Figure 1. The ethylidene ligand gives rise to a doublet at -2.55 ppm for the methyl group and a quartet at 13.03 ppm for the carbene proton. Irradiation of the quartet at 13.03 ppm causes the doublet at -2.55 ppm to collapse to a singlet. The phenyl protons on the *p*-tolyl substituents on the porphyrin appear in the 1H NMR as four distinct doublets, indicating inequivalence of the two sides of the porphyrin plane. When the ethylidene complex is generated in THF solution a small amount of the ethylene complex 5 is observed by 1H NMR, suggesting that some rearrangement of the ethylidene fragment may have occurred. The carbene complexes described herein are the first such metalloporphyrin species to contain a proton on the carbene carbon atom.

These results implied that reaction with diazomethane might lead to a methylene complex " $Ru(TTP)(CH_2)$ ". However, when CH_2N_2/N_2 is bubbled through a THF solution of $[Ru(TTP)]_2$ a methylene species is not observed. Instead, 1H NMR shows the reaction products to be a 1:1 mixture of the ethylene complex 5 and $Ru(TTP)(THF)_2$ (2), as shown in Scheme I. The bimolecular coupling of $M=CH_2$ fragments to form $M(CH_2=CH_2)$ and $M(solvato)$ species is not unprecedented.¹² The stoichiometry of the reaction observed here is consistent with such a process, although as yet we have no direct evidence for the involvement of $Ru=CH_2$ intermediates.

(9) We prefer the formulation generally adopted for late-transition-metal carbene complexes; in this case Ru(II) bonded to a formally neutral carbene fragment. $Ru(TTP)(CHCO_2CH_2CH_3)$ NMR (C_6D_6 , 300 MHz) H_β 8.78 (s), H_α , H_m 8.13 (d), 8.07 (d) 7.33 (d), 7.24 (d), $PhCH_3$ 2.40 (s), CH 13.43 (s), CH_2CH_3 2.53 (q), CH_2CH_3 0.14 (t) ppm; UV-vis (C_6H_6) λ_{max} (log ϵ), 408 (4.96), 529 (4.02) nm.

(10) (a) Marsella, J. A.; Foltling, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596-5598. (b) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31-C36.

(11) $Ru(TTP)(CHCH_3)$ NMR (C_6D_6 , 300 MHz) H_β 8.73 (s), H_α , H_m 8.14 (d), 8.05 (d), 7.33 (d), 7.23 (d), $Ph-CH_3$ 2.39 (s), $CHCH_3$ 13.03 (q), $CHCH_3$ -2.55 (d) [$J(CHCH_3) = 6$ Hz] ppm; MS (NDCl), m/z [M^-] 798, [$M - CHCH_3$] $^-$, base peak 770; UV-vis (C_6H_6) λ_{max} (log ϵ), 395 (4.82), 421 (4.97), 527 (4.14) nm.

(12) (a) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811-5819. (b) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577-6578.

A second class of neutral carbene precursors is the Wittig reagents $Ph_3P=CRR'$, which have been successfully used to transfer a carbene moiety to a transition metal.¹³ We are currently investigating the utility of such species as reagents for the preparation of ruthenium porphyrin carbene complexes.

The magnetic properties and formal metal-metal double bond of the $[M(Por)]_2$ dimer can be satisfactorily modeled by an MO scheme in which the HOMO's and LUMO's are derived from metal d orbitals.² The presence of the half empty π^* and empty σ^* orbitals implies that reduction of the dimer by a total of four electrons would result in a net bond order of zero and is consistent with cleavage of the dimer to form two zerovalent dianionic monomers.

$[Ru(Por)]_2$ (Por = OEP, TTP), when stirred with Na/K alloy in THF for 30 min, or K metal in THF for several hours, gives a suspension of a violet-black precipitate, which is decanted from the reducing agent. This insoluble, highly air-sensitive material has been characterized on the basis of its subsequent reactivity as the ruthenium(0) porphyrin dianion $K_2[Ru(Por)]$. For example, treatment of $K_2[Ru(TTP)]$ (8) with 1,2-dibromoethane in THF yields the same ethylene complex 5 that was formed independently in the reaction of $[Ru(TTP)]_2$ with ethylene (Scheme I).

The osmium dimer $[Os(TTP)]_2$ can be reduced under the same conditions to yield the sparingly soluble green salt $K_2[Os(TTP)]$. The 1H NMR spectrum of this complex is consistent with a diamagnetic species and indicates that the plane of symmetry which contains the porphyrin is retained.¹⁴ The reactions of the ruthenium and osmium dianions are the subject of another publication.¹⁵

Acknowledgment. We thank Andrew Duxbury and Stephen Frank for some assistance with porphyrin syntheses. Financial support for this work was provided by the National Institutes of Health Grant GM17880-14 and the National Science Foundation Grant CHE83-18512. NMR spectra were recorded on an instrument supported by the National Science Foundation Grant CHE81-09064.

(13) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43-51.

(14) $K_2[Os(TTP)]$ NMR (THF- d_8 , 300 MHz) H_β 8.93 (s), H_α , H_m 7.91 (d), 7.33 (d), CH_3 2.50 (s) ppm.

(15) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E., unpublished results.

Zirconium Cluster Compounds Stabilized by Interstitial Atoms

Robin P. Ziebarth and John D. Corbett*

Department of Chemistry, Iowa State University
Ames, Iowa 50011

Received April 8, 1985

A prolific cluster chemistry has been discovered for electron-poorer zirconium analogues of the traditional $(Nb,Ta)_6X_{12}^{n+}$ clusters (X = Cl, Br, some I, $n = 2, 3, 4$)^{1,2} where a second-period element Be, B, C, or N within each cluster now contributes both strong Zr-interstitial (int) bonding and additional electrons. The results of an extensive study of Zr-Cl-int systems to explore the breadth and variety of this chemistry has given the results summarized in Table I according to the structural framework, i.e., without regard to interstitial atoms and cations. All compounds except $Zr_6Cl_{14}B$ are obtained in greater than 90% yield as red-brown powders or reddish-black, well-faceted gemlike crystals by stoichiometric reactions of Zr powder, $ZrCl_4$, and, as appro-

(1) Schäfer, H.; Schnering, H.-G. *Angew. Chem.* **1964**, *76*, 833.

(2) Wells, A. F. "Structure Inorganic Chemistry", 5th ed., pp. 432-437, Clarendon Press: Oxford, England 1984; pp. 432-437.

(3) Guthrie, D. H.; Corbett, J. D. *Inorg. Chem.* **1982**, *21*, 3290.

(4) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.*, submitted for publication.

(5) Bauer, D.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1968**, *361*, 259.

(6) Imoto, H.; Simon, A., unpublished results.