Inorg. Chem. **1987**, *26*, 4389–4391

strain of cyclotrisilane compared with that of cyclotetrasilane. The strong hyperconjugation mechanism is due to energetically low lying antibonding orbitals. In other words the quasi-metallic character[14] in the cyclosilanes comes to the fore. A ring strain analysis of **1** and **2** via isodesmic and homodesmic reactions gives energies comparable to those of the carbon analogues. However, in contrast to the latter, ring condensation of silicon compounds is exothermic. The effect of through-bond interaction in fused four-membered ring systems remains to be established. According to our qualitative analysis one expects a rather strong central bond for persila[2.2.2]propellane. Detailed ab initio investigations on the latter structure as well as persila[2.2.0]hexane are currently under investigation.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. We thank Dr. M. Schindler and U. Welz for help in the computations, which were performed on the Cyber 205 computer at the Ruhr-Universität Bochum. W.W.S. also thanks Prof. Weidenbruch (Universität Oldenburg) for valuable exchange of information.

Registry No. 1, 98721-26-7; 3, 110698-79-8.

Notes

Contribution from UA CEA/CNRS 331, IRDI/DESICP/DPC,
CEA, CEN/SACLAY 91191, Gif S/Yvette, France,
and Laboratoire de Chimie Moléculaire,
UA CNRS 426, Parc Valrose, 06034 Nice, France

Pulse Radiolysis: A New Way To Study Molecular Oxygen Activation. Application to a Vanadium Complex, $VCl_3(4\text{-pic})_3$

Brigitte Le Motais,[†] Anne-Marie Koulkes-Pujo,*[†]
and Liliane G. Hubert-Pfalzgraf[‡]

Received November 7, 1986

Biological oxygen carriers transport and store dioxygen in living systems. They are characterized by their ability to bind O_2 reversibly, generally through a low-valent metal atom such as iron(II) in hemoglobin or myoglobin[1] or vanadium(III) or -(IV) in haemovanadin[2] (a protein found in the 1.5–2 N H_2SO_4 solution existing in the vacuoles of Ascidiidae blood cells). In order to better understand the mechanism of this fundamental O_2-carrying process, synthetic metal compounds able to add molecular oxygen reversibly were studied. This approach has given rise to a great deal of research,[3] especially with group 9 and group 10 metal derivatives such as the Vaska complex $Ir(PPh_3)_2(CO)Cl$.[4] Little has been done, however, with synthetic oxygen carriers containing early transition elements, although coordination of molecular oxygen, sometimes reversible, has been observed for some titanium(III),[5] vanadium(III),[6] and niobium(IV)[7] adducts, with nitrogen donors, often porphyrines.

Investigating the radiolytic behavior of group 5 metal compounds (vanadium, niobium, tantalum) in nonaqueous solvents (acetonitrile, dichloromethane), as a route to low-valent derivatives,[8-10] we noticed that after oxygenation of $VCl_3(4\text{-pic})_3$ (4-pic = $4\text{-}CH_3C_5H_4N$), the initial vanadium(III) compound could be recovered by radiolysis in oxygen-free acetonitrile. The experimental data (IR, EPR, and absorption spectra and gas analysis), as well as the characteristics of the radiolytic experiments, led us to suggest the formation in solution of a dimeric vanadium–dioxygen adduct, with a coordinated superoxide like O_2^-. Nevertheless, the oxovanadium(IV) species $VOCl_2(4\text{-pic})_2$ represents the final and only isolable metallic species.

Experimental Section

All manipulations were performed under vacuum or dry argon, using Schlenk tube and vacuum-line techniques. Solvents and 4-picoline were purified by standard methods.[11] $VCl_3(4\text{-pic})_3$ was synthesized according to the literature.[12] This complex being very moisture-sensitive, its oxygenation reaction was carried out on a vacuum line by bubbling O_2, previously dried over a P_2O_5 column, into its acetonitrile or dichloromethane solution.

The concentrations of the solutions (typically 2×10^{-3} mol·dm^{-3}) were so chosen that, in radiolysis experiments, the solute modification occurs by an indirect effect, i.e. by reaction with the transient species produced in the irradiated solvent.

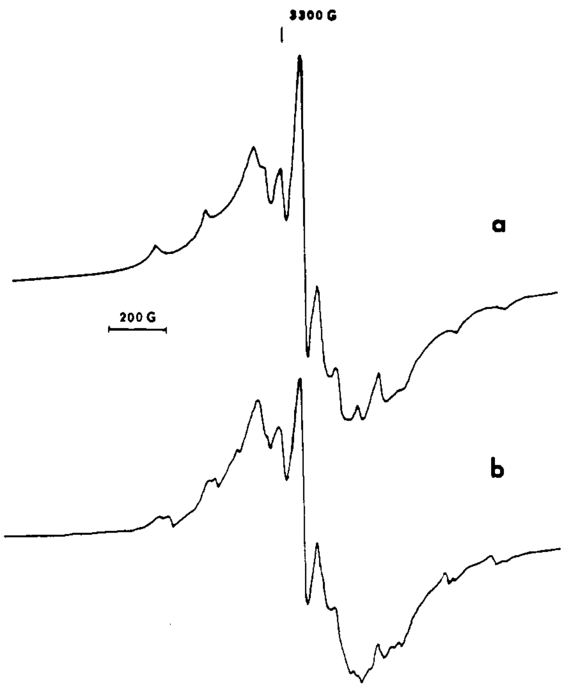


Figure 1. EPR spectra in frozen acetonitrile (173°K) of (a) $VCl_3(4\text{-pic})_3$; (b) $VCl_3(4\text{-pic})_3$–dioxygen adduct.

Time-resolved experiments were performed with a Febetron 707 apparatus, delivering 1.8-MeV electron pulses of 30 ns base pulse duration and (3–5) × 10^{18} eV·g^{-1} dose. The concentrations of the intermediates

---

* To whom correspondence should be addressed.

[†] IRDI/DESICP/DPC.

[‡] UA CNRS 426.

(1) Rifkind, J. M. In *Bioinorganic Chemistry*; Eichhorn, G. L., Ed.; Elsevier: New York, 1973.

(2) Carlisle, D. B. *Proc. R. Soc. London, B* **1968**, *171*, 31.

(3) Summerville, D. A.; Jones, R. D.; Hoffman, B. M.; Basolo, F. *J. Chem. Educ.* **1979**, *56*, 157. Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139 and references therein.

(4) Vaska, L. *Science (Washington, D.C.)* **1963**, *140*, 809. Vaska, L.; Chen, L. S. *J. Chem. Soc., Chem. Commun.* **1971**, 1080.

(5) Marchon, J. C.; Latour, J. M.; Borehaim, C. J. *J. Mol. Catal.* **1980**, *7*, 227. Cotton, R.; Premovic, P.; Stanadal, L.; West, P. *J. Chem. Soc., Chem. Commun.* **1980**, 863.

(6) Swinehart, J. H. *J. Chem. Soc., Chem. Commun.* **1971**, 1443.

(7) Richard, P.; Guilard, R. *J. Chem. Soc., Chem. Commun.* **1983**, *1454*. Matsuda, Y.; Sakamoto, S.; Koshima, H.; Murakami, Y. *J. Am. Chem. Soc.* **1985**, *107*, 6415.

(8) Koulkes-Pujo, A. M.; Le Motais, B.; Hubert-Pfalzgraf, L. G. *J. Chem. Soc., Dalton Trans.* **1986**, 1741.

(9) Koulkes-Pujo, A. M.; Le Motais, B.; Hubert-Pfalzgraf, L. G. *Radiat. Phys. Chem.* **1987**, *29*, 21.

(10) Tsunoda, M.; Hubert-Pfalzgraf, L. G.; Riess, J. G. *Inorg. Chim. Acta* **1981**, *52*, 231.

(11) Riddick, J. A.; Bunger, W. B. *Techniques of Chemistry*: *Organic Solvents*, 3rd ed.; Wiley Interscience: New York, 1970; Vol. 2.

(12) Rupp, H. A. *Z. Anorg. Allg. Chem.* **1970**, *377*, 105.

0020-1669/87/1326-4389$01.50/0

thus created in the solvent were generally (4–6) × 10^{-5} mol·dm^{-3}. The detection system has been previously described.[13]

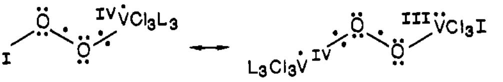
The γ-radiolysis experiments were carried out with a ^{60}Co γ-source, delivering a dose rate of 2 × 10^{16} eV·g^{-1}·min^{-1}. Absorption spectra of the γ-irradiated solutions were measured with a Beckman Acta IV spectrophotometer. EPR spectra were obtained on a Bruker ER-200D spectrometer. Microanalyses were performed by the Centre de Microanalyses of the CNRS.

Results and Discussion

The oxygenation reaction of the complex $VCl_3(4\text{-pic})_3$ in acetonitrile or dichloromethane solutions results in a progressive change of the solution color from purple to pale green. The uptake of dioxygen is almost quantitative, and this process is readily reversed by gentle warming in vacuo, more slowly (i.e. in a few days) at room temperature. Its kinetics have already been explored by Halko and Swinehart on the related derivative $VCl_3(py)_3$ in pyridine.[14]

This experiment points out that $VCl_3(4\text{-pic})_3$ is able to coordinate molecular oxygen without being irremediably oxidized. The nature of this reversible vanadium–O_2 binding can be estimated from the value of the O–O stretching frequency observed in the IR spectrum of the adduct. This value, which we found equal to 1070 cm^{-1}, is in the range expected for dimeric compounds containing a bound dioxygen in a reduced superoxide-like state, O_2^-.[3]

We therefore suggest that the dioxygen adduct of $VCl_3(4\text{-pic})_3$ can be mixed-valence species with the following structure:



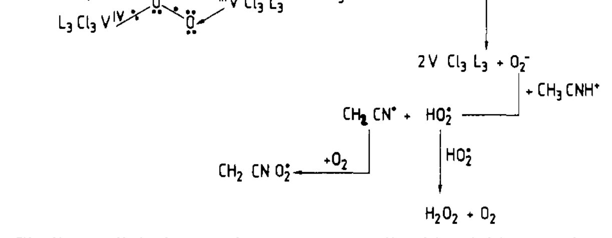
L = 4-pic

This structure is in agreement with that established for the oxygenation product of the analogous rhodium(III) derivative $[Rh(4\text{-pic})_4Cl_2]^+$, which is also a binuclear complex presenting a superoxide-like coordinated O_2:[15] $[(4\text{-pic})_4ClRhO_2RhCl(4\text{-pic})_4]^{3+}$.

The EPR spectrum of the vanadium–dioxygen compound investigated in frozen acetonitrile is only slightly modified with respect to $VCl_3(4\text{-pic})_3$ (Figure 1). Conversely, the corresponding electronic spectrum differs significantly from that of $VCl_3(4\text{-pic})_3$ (Figures 2 and 3). It presents, indeed, two bands at 335 and 750 nm, which may be attributed, as for the previously mentioned rhodium–O_2 complex, to two charge-transfer transitions $\pi_h^*(O_2) \rightarrow d_\sigma^*(V)$ and $d_\pi(V) \rightarrow \pi_v^*(O_2)$ (π_h^* and π_v^* designating respectively the O_2 horizontal and vertical antibonding orbitals, relative to the plane containing the metal–dioxygen moiety).[16] The similitude of the spectroscopic data of the vanadium dioxygen adduct in CH_2Cl_2 and CH_3CN solutions suggests that acetonitrile is not involved in the coordination sphere. Both the electronic and EPR spectra of $VCl_3(4\text{-pic})_3$ were recovered when the adduct deoxygenated.

The dimeric vanadium(III) μ-oxo derivatives $(THF)_3Cl_2VO\text{-}VCl_2(THF)_3$ has previously been described.[17] However, attempts to isolate the labile vanadium–oxygen adduct from the solution invariably led to the obtaining of $VOCl_2(4\text{-pic})_2$, characterized by microanalysis, EPR ($\langle g \rangle$ = 1.98; $\langle A \rangle$ = 102.5 G at room temperature (Figure 4)), and infrared spectroscopy (strong absorption band at 974 cm^{-1}, assigned to a terminal oxo bond). The formation of this stable vanadyl species appears to be favored by moisture.

Additional support for the dimeric structure of the labile vanadium–dioxygen adduct was nevertheless accessible through radiolysis experiments. The radiolysis technique allows the generation, in a deoxygenated solvent S, of transient reductive and oxidative species, such as e^-_s, S^-, or S^+, which may then react with a low-concentration solute. Surprisingly, we observed that γ-irradiation in oxygen-free acetonitrile could completely reverse the oxygenation reaction of $VCl_3(4\text{-pic})_3$. In this case, the restoration of the initial vanadium(III) complex is initiated by the radical anions CH_3CN^-, radiolytically formed in the solvent.[17] Pulse radiolysis experiments have indeed established the fact that the decay rate of CH_3CN^- is increased proportionally to the concentration of the vanadium–dioxygen compound. These radical anions attack the complex upon its O_2 moiety and lead to its dissociation into $VCl_3(4\text{-pic})_3O_2$ and $[VCl_3(4\text{-pic})_3]^-$, identified by its absorption spectrum.[9] These last two species promptly react together by a second-order kinetic process (k = 3 × 10^{10} mol^{-1}·dm^3·s^{-1}), which gives O_2^- and restores the initial $VCl_3(4\text{-pic})_3$ complex with a radiolytic yield G equal to 1.8 ± 0.2. This value, measured at the end of the formation process of $VCl_3(4\text{-pic})_3$, is twice as large as $G(CH_3CN^-)$ (i.e. 1.03)[18] and therefore clearly indicates the dimeric structure of the vanadium–dioxygen adduct investigated. As for the superoxide anion O_2^- generated simultaneously with $VCl_3(4\text{-pic})_3$, it probably reacts with the other radiolytically produced transient species CH_3CNH^+, giving new radicals $CH_2CN^\bullet$ and $HO_2^\bullet$, which finally lead to alkylperoxide $O_2CH_2CN^\bullet$ and hydrogen peroxide H_2O_2 (since no gaseous oxygen is detected by gas chromatography). Disproportionation of $HO_2^\bullet$ has previously been reported to be a rapid and thermodynamic favorable process.[19] The following scheme is proposed (L = 4-pic):



Similar radiolysis experiments were realized in dichloromethane, but the results were quite different: they led to the precipitation of the blue-green vanadyl derivative $VOCl_2(4\text{-pic})_2$, due to an oxidation of $[VCl_3(4\text{-pic})_3]_2O_2$ by the radical cations $CH_2Cl_2^{\bullet+}$,

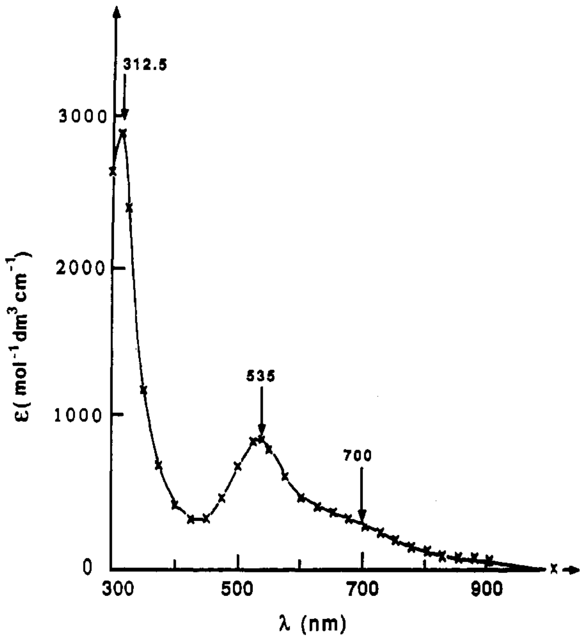


Figure 2. Electronic absorption spectrum of $VCl_3(4\text{-pic})_3$ in CH_3CN solution.

---

(13) Tran Thi, T. H.; Koulkes-Pujo, A. M. *J. Phys. Chem.* **1983**, *87*, 1166.
(14) Halko, D. J.; Swinehart, J. H. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1589.
(15) Addison, A. W.; Gillard, R. D. *J. Chem. Soc. A* **1970**, 2523.
(16) Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348.
(17) Chandrasekhar, P.; Bird, P. H. *Inorg. Chem.* **1984**, *23*, 3677.
(18) Bell, I. P.; Rodgers, M. A. J.; Burrows, H. D. *J. Chem. Soc., Faraday Trans.* **1977**, *73*, 3.
(19) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393.

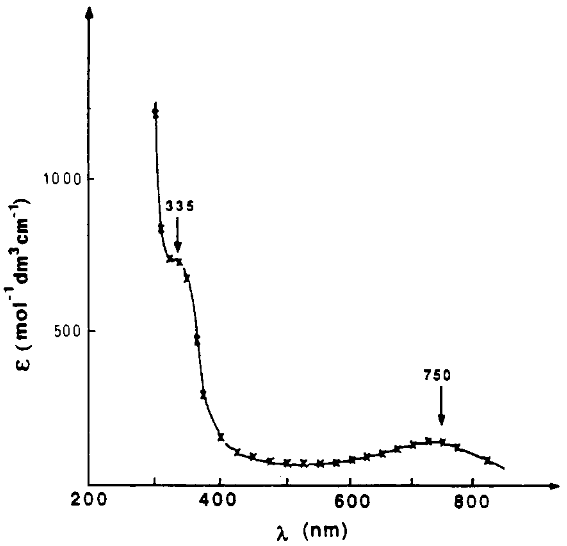


Figure 3. Electronic absorption spectrum of $[VCl_3(4\text{-pic})_3]_2O_2$ in CH_3CN and CH_2Cl_2 solutions.

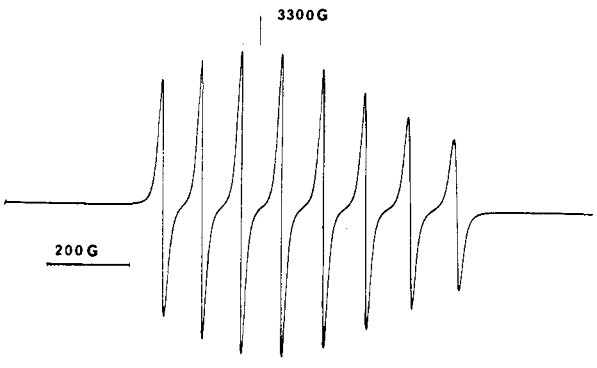


Figure 4. EPR spectrum of $VOCl_2(4\text{-pic})_2$ in acetonitrile at room temperature.

without any oxygen liberation (no reducing species is produced in pulse-radiolyzed pure CH_2Cl_2, the $CH_2Cl_2^{\bullet -}$ radical anion being quickly transformed into Cl^- and $CH_2Cl^\bullet$).

We showed that the vanadium(III) complex $VCl_3(4\text{-pic})_3$ is able to coordinate molecular oxygen according to a dimeric superoxo mode and ascertained our hypothesis by radiolysis experiments. This radiolysis technique therefore appears to be suitable for determining the structures of oxygen-carrying compounds and even giving an insight into their mechanism.

Acknowledgment. We thank M. Postel and G. Folcher for fruitful discussions and J. Potier for his technical assistance in Febetron experiments.

Registry No. $VCl_3(4\text{-pic})_3$, 107333-90-4; $[VCl_3(4\text{-pic})_3]_2O_2$, 111005-83-5; O_2, 7782-44-7; CH_3CN, 75-05-8; CH_2Cl_2, 75-09-2; $VOCl_2(4\text{-pic})_3$, 52593-61-0.

Contribution from the Department of Chemistry,
State University of New York at Buffalo,
Buffalo, New York 14214

Aerobic Oxidation of Cyclohexene with a Phosphine-Ruthenium(II)-Aquo Catalyst

Randolph A. Leising and Kenneth J. Takeuchi*

Received July 8, 1987

The activation of molecular oxygen by transition-metal complexes, with a focus on organic substrate oxidation, is a topic of much current research.[1-16] In particular, the reductive activation of dioxygen is characteristic of the widely occurring hemoprotein cytochrome P-450,[17-20] where the catalytic organic substrate oxidation cycle of cytochrome P-450 has been suggested to include a high-valent iron-oxo intermediate as the active oxidant. In this regard, many transition-metal complexes have been studied as organic substrate oxidizers, including cobalt,[21-23] copper,[24] chromium,[25-29] iron,[30-35] manganese,[36-42] and ruthenium[43-46] complexes.

---

(1) Collman, J. P.; Kubota, M.; Hosking, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 4809-4811.
(2) Cenini, S.; Fusi, A.; Capparella, G. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 127-131.
(3) Ochiai, E. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 453-457.
(4) Hanzlik, R. P.; Williamson, D. *J. Am. Chem. Soc.* **1976**, *98*, 6570-6573.
(5) Ledlie, M. A.; Allum, K. G.; Howell, I. V.; Pitkethly, R. C. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1734.
(6) Nishinaga, A.; Tomita, H.; Shimizu, T.; Matsuura, T. *Fundamental Research in Homogeneous Catalysis*; Ishii, Y., Tsutsui, M., Eds.; 1978; Vol. 2.
(7) Veprek-Siska, J. *Acta Biol. Med. Ger.* **1979**, *38*, 357-361.
(8) (a) Tabushi, I.; Koga, N. *J. Am. Chem. Soc.* **1979**, *101*, 6456-6458. (b) Tabushi, I.; Yazaki, A. *J. Am. Chem. Soc.* **1981**, *103*, 7371-7373. (c) Tabushi, I.; Kodera, M.; Yokoyama, M. *J. Am. Chem. Soc.* **1985**, *107*, 4466-4473. (d) Tabushi, I.; Kodera, M. *J. Am. Chem. Soc.* **1986**, *108*, 1101-1103.
(9) Chin, D.-H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 5945-5947.
(10) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981.
(11) (a) Martell, A. E. *New Front. Organomet. Inorg. Chem., Proc. China-Jpn.-U.S.A. Trilateral Semin., 2nd, 1982* **1984**, 309-320. (b) Wang, X.-Y.; Montekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1984**, *23*, 271-275.
(12) Mansuy, d.; Fontecave, M.; Bartoli, J. *J. Chem. Soc., Chem. Commun.* **1983**, 253-254.
(13) (a) Riley, D. P.; Shumate, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 3179-3184. (b) Oliver, J. D.; Riley, D. P. *Inorg. Chem.* **1984**, *23*, 156-158. (c) Riley, D. P. *Inorg. Chim. Acta* **1985**, *99*, 5-11.
(14) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790-5792.
(15) Che, C.-M.; Leung, W.-H.; Poon, C.-K. *J. Chem. Soc., Chem. Commun.* **1987**, 173.
(16) Bilgrien, C.; Davis, S.; Drago, R. S. *J. Am. Chem. Soc.* **1987**, *109*, 3786-3787.
(17) (a) Ullrich, V. *Angew. Chem., Int. Ed. Engl.* **1972**, *8*, 701-712. (b) Ullrich, V. *Top. Curr. Chem.* **1979**, *83*, 67-104.
(18) Sato, R.; Omura, T. *Cytochrome P-450*; Academic: New York, 1978.
(19) White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *49*, 315-356.
(20) Guengerich, F. P.; MacDonald, T. L. *Acc. Chem. Res.* **1984**, 17, 9-16.
(21) (a) Nishinaga, A. *Chem. Lett.* **1975**, 273-276. (b) Nishinaga, A.; Tomita, H. *J. Mol. Catal.* **1980**, *7*, 179-199.
(22) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 265-272.
(23) Herron, N.; Chavan, M. Y.; Busch, D. H. *J. Chem. Soc., Dalton Trans.* **1984**, *8*, 1491-1494.
(24) Tai, A. F.; Margerum, L. D.; Valentine, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 5006-5008.
(25) Sharpless, K. B.; Flood, T. C. *J. Am. Chem. Soc.* **1971**, *93*, 2316-2318.
(26) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613-7615.
(27) Nill, K. H.; Wasgestian, F.; Pfeil, A. *Inorg. Chem.* **1979**, *18*, 564-567.
(28) Buchler, J. W.; Lay, K. L.; Castle, L.; Ulrich, V. *Inorg. Chem.* **1982**, *21*, 842-844.
(29) Creager, S. E.; Murray, R. W. *Inorg. Chem.* **1985**, *24*, 3824-3828.
(30) (a) Groves, J. T.; Van Der Puy, M. *J. Am. Chem. Soc.* **1974**, *96*, 5274-5275. (b) Groves, J. T.; Nemo, T. E.; Meyers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032-1033. (c) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786-5791. (d) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7834-7836.
(31) Chang, C. K.; Kuo, M. *J. Am. Chem. Soc.* **1979**, *101*, 3413-3414.
(32) Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 6123-6125.
(33) Smith, J. R. L.; Sleath, P. R. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1009-1016.
(34) Herron, N.; Zimmer, L. L.; Grzybowski, J. J.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. W.; Cameron, J. H.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 6585-6596.