a knowledge of that for a cross-reaction, $\Delta S_{12}^{\ddagger}$, with a coreactant having a known activation entropy for self-exchange, $\Delta S_{22}^{\ddagger}$, together with the entropic driving force, ΔS_{12}°. This procedure is most straightforward for cross-reactions having small driving forces (e.g. $K_{12} \lesssim 10^4$) so that $f_{12} \approx 1$ (eq 3), whereupon these quantities are related simply by[4]

$$\Delta S_{12}^{\ddagger} = 0.5(\Delta S_{11}^{\ddagger} + \Delta S_{22}^{\ddagger}) + 0.5\Delta S_{12}^{\circ} \qquad (5)$$

Although experimental activation parameters for such reactions involving $\mathrm{Eu_{aq}}^{3+/2+}$ are sparse, one example is $\mathrm{Eu_{aq}}^{2+}$ oxidation by $\mathrm{V_{aq}}^{3+}$. Inserting the experimental values $\Delta S_{12}^{\ddagger} = -30$ cal deg^{-1} mol^{-1},[5,57] $\Delta S_{22}^{\ddagger}(\mathrm{V_{aq}}^{3+/2+}$ self-exchange) = −25 cal deg^{-1} mol^{-1},[24,57] and $\Delta S_{12}^{\circ} = -11$ cal deg^{-1} mol^{-1} [58] into eq 5 yields a value of $\Delta S_{11}^{\ddagger} = \mathrm{Eu_{aq}}^{3+/2+}$ self-exchange of −25.5 cal deg^{-1} mol^{-1}. Although such negative activation entropies are consistent with nonadiabatic pathways, this value of $\Delta S_{11}^{\ddagger}$ for $\mathrm{Eu_{aq}}^{3+/2+}$ is similar not only to that for $\mathrm{V_{aq}}^{3+/2+}$ but also to those for a number of other aquo and amine couples for which strongly nonadiabatic pathways are unlikely.[4] The observed activation entropies are more likely to be a reflection of the solvent ordering attending the formation of the highly charged encounter complex.[4,8]

The electrochemical reactivities of Eu(III/II) are also in harmony with the above conclusions. Thus, the $\mathrm{Eu_{aq}}^{3+/2+}$ couple exhibits a small rate constant for electrochemical exchange at mercury electrodes, $k^{e}_{ex} = 8 \times 10^{-5}$ cm s^{-1} (corrected for work terms), which is consistent with the rate constants for homogeneous $\mathrm{Eu_{aq}}^{3+/2+}$ reactions on the basis of the Marcus model.[6,47] In addition, the electrochemical reactivity of $\mathrm{Eu_{aq}}^{3+/2+}$ compared to those for other aquo couples is quantitatively consistent with the reactivities of these couples in homogeneous solution.[47] This consistency also extends to activation parameters.[6,54] Large increases in k^{e}_{ex} for Eu(III/II) also occur upon cryptate formation: values of k^{e}_{ex} of ca. 1 cm s^{-1} have been determined for both Eu(2.2.1)$^{3+/2+}$ and Eu(2.2.2)$^{3+/2+}$.[59]

The kinetic effects of encapsulating Eu(III/II) within cryptate cavities has a similarity with the ca. 10^5-fold larger self-exchange rate constant for Co(sep)$^{3+/2+}$ (sep = sepulchrate[60]) compared with that for $\mathrm{Co(en)_3}^{3+/2+}$.[60] The sepulchrate differs structurally from the tris(ethylenediamine) complex in that the ethylenediamine ligands have been "capped" to form a three-dimensional cage, similar to the cryptates.[60] Although the origins of the reactivity differences between Co(sep)$^{3+/2+}$ and $\mathrm{Co(en)_3}^{3+/2+}$ were initially obscured by apparently similar Co–N bond length differences, Δa, in the two couples,[60a] it now appears that the enhanced reactivity of the former couple is chiefly due to a smaller value of Δa and hence ΔG_{is}^{*}.[7]

Taken together, the available evidence therefore suggests that the low reactivities of $\mathrm{Eu_{aq}}^{3+/2+}$ observed in a variety of homogeneous and also heterogeneous environments are predominantly due to large Franck–Condon barriers associated with an increase in the europium–oxygen bond distance and possibly also to an increase in the number of coordinated aquo ligands required to form $\mathrm{Eu_{aq}}^{2+}$ from $\mathrm{Eu_{aq}}^{3+}$. It is clearly desirable to obtain further information on the structural and vibrational properties of lanthanide complexes. Especially in conjunction with theoretical estimates of κ_{el}, such information should allow the factors responsible for the reactivities of $\mathrm{Eu_{aq}}^{3+/2+}$ and other f-electron redox couples to be quantitatively assessed.

Acknowledgment. This work is supported in part by the Air Force Office of Scientific Research. M.J.W. gratefully acknowledges a fellowship from the Alfred P. Sloan Foundation.

Registry No. V, 7440-62-2; Eu, 7440-53-1; $\mathrm{Co(NH_3)_6}^{3+}$, 14695-95-5.

---

(57) Experimental activation entropies $\Delta S^{\ddagger}$ are conventionally evaluated by assuming that the preexponential factor equals kT/h.[21] Strictly speaking, the actual preexponential factor in eq 1, $\kappa_{el}A_n$, should be used instead so that the derived activation entropy refers to the entropy of activation within the encounter complex, ΔS^{*}. Values of A_n close to 1×10^{11} M^{-1} s^{-1} have been conventionally employed on the basis of a simple collisional model;[21] if κ_{el} is taken as unity, this yields $\Delta S^{*} \approx \Delta S^{\ddagger} + 10$ cal deg^{-1} mol^{-1}.[4] However, using a model for A_n based on activation within an encounter complex typically yields[7,21] $A_n \sim 2 \times 10^{12}$ M^{-1} s^{-1}, leading to $\Delta S^{*} \approx \Delta S^{\ddagger} + 2$ cal deg^{-1} mol^{-1}.[4]

(58) ΔS_{12}° obtained from the difference in reaction entropies ΔS_{rc}° for $\mathrm{V_{aq}}^{3+/2+}$ and $\mathrm{Eu_{aq}}^{3+/2+}$ given in ref 18.

(59) Koizumi, N.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *124*, 345.

(60) (a) Sargeson, A. M. *Chem. Br.* **1979**, *15*, 23. (b) Creaser, I. I.; Gene, R. J.; Harrowfield, J. M.; Jerlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.

Contribution from the Evans Chemical Laboratory,
The Ohio State University, Columbus, Ohio 43210

Synthesis, Characterization, and Properties of Manganese Complexes of Macrobicyclic Lacunar Ligands and Their Reactions with Dioxygen Species

NORMAN HERRON and DARYLE H. BUSCH*

Received December 9, 1982

Manganese(II) and -(III) complexes of macrobicyclic ligand systems containing a persistent void in the vicinity of one axial ligation site have been prepared. Synthesis from the appropriate ligand salt is only satisfactorily achieved by using manganese(III) reagents while the manganese(II) complexes are generated by electrochemical reduction of those complexes. Both the +2 and +3 oxidation states are high spin and 5-coordinate, displaying typical magnetic susceptibilities. The manganese(II) complexes react irreversibly with dioxygen to generate the corresponding manganese(III) complex and reduced dioxygen. Depending on solvent, this reduced dioxygen will deprotonate the ligand itself. The manganese(III) complexes display efficient but slow catalase activity while showing no corresponding oxygenation activity toward phenolic substrates.

Introduction

The interaction of manganese complexes with many of the species, in various oxidation states, derived from dioxygen has been extensively investigated and is of both biological[1,2] and industrial[3] importance. For example, with dioxygen itself, reversible binding has been claimed for a number of manganese(II) complexes, with ligands ranging from porphyrins[4] and

---

(1) Keele, B. B.; McCord, J. M.; Fridovich, I. *J. Biol. Chem.* **1970**, *245*, 6176.

(2) Calvin, M. *Rev. Pure Appl. Chem.* **1965**, *15*, 1.

(3) Wieberg, K. B. *Org. Chem. (N.Y.)* **1965**.

(4) Hoffmann, B. M.; Weschler, C. J.; Basolo, F. *J. Am. Chem. Soc.* **1976**, *98*, 5473.

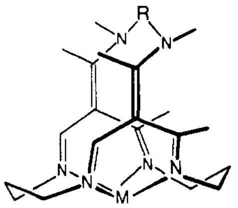


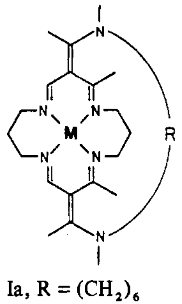
Figure 1. Schematic representation of lacunar macrobicycles emphasizing the presence of a cavity over one axial site of the metal ion.

phthalocyanines[5] through catecholates[6] to tertiary phosphines.[7] In all cases a discreet 1:1 Mn–O_2 adduct is claimed, although such claims have been strongly challenged in the case of the phosphine complexes.[8] Such reversible dioxygen binding is of obvious relevance not only for biochemistry (e.g., photosystem II[9]) but also to industry where facilitated dioxygen transport using stable dioxygen carriers may represent an energy-efficient way of generating dioxygen-enriched air for synthetic fuel applications.[10]

Reaction between singly reduced dioxygen and manganese is biologically important as evidenced by the widespread occurrence of manganese in superoxide dismutases.[11] The dismutation of superoxide is catalyzed by a synthetic manganese complex having quinolato ligands.[12] Valentine has reported that manganese(III) porphyrin complexes are reduced to manganese(II) by superoxide ion[13] and that this product can further react with O_2^- to form a manganese(II) superoxo complex.[13] With doubly reduced dioxygen, the catalase activity of manganese compounds is well-known and this type of reaction has industrial application where manganese inhibitors act as negative catalysts for the peroxide-based autoxidation of alkanes and alcohols.[14] Manganese complexes of porphyrin and phthalocyanine ligands have also recently been shown to possess monoxygenase[15,16] and dioxygenase[17] activity. In particular, a recent report[18] describes the isolation of a (porphyrinato)manganese(V) complex containing a coordinated oxide, generated by reaction of manganese(III) porphyrin with the oxene-transfer reagent iodosylbenzene. This material will catalytically oxidize hydrocarbons in the presence of excess C_6H_5IO.

Our own work with cobalt[19] and iron[20-22] complexes of the lacunar macrobicyclic ligands I (Figure 1) has shown that they are remarkable dioxygen carriers and that a range of small ligands will coordinate to the metal ion within the protected void of the structure. In view of this behavior and the extensive chemistry of manganese–dioxygen systems, we have sought to investigate manganese complexes of structure I and their interaction with oxygen species. We report here the synthesis and characterization of manganese(II) and -(III) complexes of two ligands of structure I and an investigation of their reactions with dioxygen and hydrogen peroxide, looking for O_2 transport and catalase and peroxidase activity. This work constitutes part of our ongoing research into the generation of totally synthetic non-porphyrin metalloprotein models.

I



Ia, R = $(CH_2)_6$
b, R = *m*-xylylene

Experimental Section

Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were recorded on a Perkin-Elmer 283B recording spectrophotometer, and electronic spectra were recorded on a Cary 17D spectrophotometer in 1-cm gastight quartz cells fitted with a gas inlet and bubbling tube as purchased from Precision Cells, Inc., Hicksville, NY. Exposure of solutions of manganese(II) complexes to dioxygen at various partial pressures was achieved by using a series of calibrated rotameters (Matheson, East Rutherford, NJ) to accurately mix dioxygen and dinitrogen standards, followed by passage of the mixture through the quartz bubbling cells. The cell was thermostated (±0.3 °C) using a NesLab constant-temperature circulator with methanol coolant passing through a Varian variable-temperature double-jacketed cell holder. The cell temperature was monitored with a calibrated copper–constantan thermocouple attached to the cell holder itself.

Proton NMR spectra were recorded on a Varian 360-L spectrometer at 60 MHz, and this instrument was used to measure magnetic susceptibilities by the Evans method[23] (acetone reference) at 303 K with Pascal corrections applied. EPR measurements were performed on a Varian E-112 spectrometer in the X band at 9.3 GHz; g values are quoted relative to external dpph ($g = 2.0036$). Samples were run as frozen glasses at 77 K in quartz tubes.

Electrochemical measurements and bulk electrolytic syntheses were performed on a Princeton Applied Research Corp. potentiostat galvanostat, Model 173, equipped with a Model 179 digital coulometer. Current vs. potential curves were recorded on a Houston Instruments Model 2000 X-Y recorder. All measurements were performed in a Vacuum Atmospheres glovebox under an atmosphere of dry, oxygen-free nitrogen. The working electrode for voltammetric curves was a platinum disk, while for bulk electrolyses and coulometry a platinum gauze replaced the disk. Potentials were measured vs. a silver wire dipped in 0.1 M silver nitrate in acetonitrile as reference. The potential of this reference was 0.60 V vs. SHE. The working electrode was spun at 600 rpm by a synchronous motor for the rotating platinum electrode voltamograms (RPE). Peak potentials (E_p) were measured from cyclic voltamograms at 50 mV s^{-1} scan rate. Half-wave potentials ($E_{1/2}$) were taken as the potential at half the height of the RPE voltamogram. The value $|E_{3/4} - E_{1/4}|$ was used as a measure of the reversibility of the couple and was also measured from the RPE voltamogram. All measurements were carried out in solutions con-

---

(5) Lever, A. B. P.; Wilshire, J. P.; Quan, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 3668. Uchida, K.; Naito, H.; Soma, N.; Onishi, T.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1978**, 217.

(6) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 989.

(7) McAuliffe, C. A.; Al-Khateeb, H.; Jones, M. H.; Levason, W.; Minten, K.; McCullough, F. P. *J. Chem. Soc., Chem. Commun.* **1979**, 736.

(8) Brown, R. M.; Bull, R. E.; Green, M. L. H.; Grebenik, J. J.; Martin-Polo, J. J.; Mingos, D. M. P. *J. Organomet. Chem.* **1980**, *201*, 437.

(9) Calvin, M. *Science (Washington, D.C.)* **1974**, *184*, 375.

(10) Stewart, R. F.; Estep, P. A.; Sebastian, J. J. S. *Inf. Circ.—U.S., Bur. Mines* **1959**, *No. 7906*. Adducci, A. J., paper presented at 170th National Meeting of the American Chemical Society, Chicago, IL, Aug 1975. Burke, D. P. *Chem. Week* **1980**, *18* (2), 127.

(11) Fridovich, I. *Adv. Inorg. Biochem.* **1979**, *1*, 67.

(12) Howie, J. K.; Sawyer, D. T. *J. Am. Chem. Soc.* **1976**, *98*, 6698.

(13) Valentine, J. S.; Quinn, A. E. *Inorg. Chem.* **1976**, *15*, 1997. See also: Stein, J.; Fackler, G. J.; McClune, J. A.; Fee, J. A.; Chan, L. T. *Ibid.* **1979**, *18*, 3511.

(14) Zubareva, N. G.; Denison, E. T.; Ablov, A. V. *Kinet. Katal.* **1973**, *14*, 346.

(15) Fauvet, M. P.; Gaudemer, A. *J. Chem. Soc., Chem. Commun.* **1980**, 874.

(16) Willner, I.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Chem. Commun.* **1980**, 964.

(17) Dufour, M. N.; Crumbliss, A. L.; Johnston, G.; Gaudemer, A. *J. Mol. Catal.* **1980**, *7*, 277.

(18) Hill, C.; Shardt, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6374. Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C. *Ibid.* **1980**, *102*, 6375.

(19) Stevens, J. S.; Busch, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 3285.

(20) Busch, D. H.; Zimmer, L. L.; Grzybowski, J. J.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. W.; Christoph, G. G. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5919.

(21) Herron, N.; Busch, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 1236.

(22) Herron, N.; Cameron, J. H.; Neer, G. L.; Busch D. H. *J. Am. Chem. Soc.* **1983**, *105*, 298.

(23) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

taining 0.1 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte.

Conductivity measurements were made in acetonitrile solution using an Industrial Instruments Model RC 16B conductivity bridge with cell constant 0.11 cm^{-1} at 1000 Hz. Gas evolution from catalatic activity of the Mn(III) complexes was monitored by using a mini vacuum line and Texas Instruments precision pressure gauge, Model 145, equipped with a type 1 Bourdon tube capsule, the technique of which has been described earlier.[24] In a typical catalase activity experiment, 2 mL of the Mn(III) catalyst solution in CH_3CN ($\sim 8 \times 10^{-4}$ M) and 20 mL of hydrogen peroxide solution in 97% CH_3CN/H_2O (0.8 M) were placed in separate chambers and attached to the thermostated vacuum line (300.2 K). After thermal and solvent saturation of the vacuum line atmosphere, the catalatic reaction was initiated by vigorous and continuous shaking to mix the two solutions. Oxygen evolution was monitored with both the TI gauge and, as a function of time, with a Hewlett-Packard Model 7101 BM recorder connected to the gauge. Oxygen uptake by the manganese(II) complexes was also monitored by using the same vacuum-line system.

Peroxidase activity of the manganese(III) complexes was monitored by HPLC in the following manner. A 20-mg portion of Mn(III) catalyst and 200 mg of substrate were weighed into a flask and dissolved in 2 mL of CH_3CN. A 20-mL portion of H_2O_2 solution ($\sim$0.8 M) in water was added and the reaction stirred for 30 min. After this time, the solution was acidified with concentrated H_2SO_4 and extracted with 5 × 2 mL portions of diethyl ether. The ether extracts were combined and rotovapped at room temperature, and the product was taken up in 10 mL of methanol for HPLC analysis using a Du Pont Instruments Model 841 liquid chromatograph equipped with a 50-cm C_{18} reverse-phase column and photometer detector at 254 nm.

Synthesis. Both of the lacunar ligands were prepared from the pure nickel(II) complexes[25,26] as HPF_6 derivatives as previously described. All manipulations and preparations of manganese(II) and synthesis of manganese(III) complexes were carried out in a Vacuum Atmospheres glovebox under oxygen-free nitrogen. All chemicals were reagent grade and used without further purification; all solvents were dried and distilled under N_2 before use.

Chloro(2,3,10,11,13,19-hexamethyl-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-$\kappa^4 N$)manganese(III) Hexafluorophosphate, [MnCl((CH$_2$)$_6$(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (Mn(III)-Ia). A 3.00-g sample (3.3 mmol) of the ligand salt[26] [H_4((CH_2)$_6$(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)]Cl(PF_6)$_3$ was slurried in 10 mL of CH_3CN, and to this was added a solution of 1.55 g (4.4 mmol) tris(2,4-pentanedionato)manganese(III) in 5 mL of acetonitrile. The deep red-brown solution was stirred and warmed for 45 min and then pumped to dryness. Washing with toluene removed any unreacted Mn(acac)$_3$, and a sandy brown powder remained. Recrystallization from acetonitrile/ethanol gave 1.73 g (64%) of dark red crystals. Anal. Calcd for $C_{26}H_{44}N_6MnClP_2F_{12}$: C, 38.00; H, 5.36; N, 10.23; Mn, 6.69; Cl, 4.3. Found: C, 38.21; H, 5.51; N, 10.21; Mn, 6.50; Cl, 4.51.

Chloro(2,3,11,12,14,20-hexamethyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-1,5,7,9(28),12,14,19,21,26-nonaene-$\kappa^4 N$)manganese(III) Hexafluorophosphate, [MnCl((*m*-xylylene)(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (Mn(III)-Ib). A procedure identical with that described above using the ligand salt[27] [H_4((*m*-xylylene)(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)]Cl(PF_6)$_3$ yields a deep brown microcrystalline material (58%). Anal. Calcd for $C_{28}H_{40}N_6MnClP_2F_{12}$: C, 39.99; H, 4.80; N, 9.99; Mn 6.52; Cl, 4.22. Found: C, 39.99; H, 4.97; N, 10.12; Mn, 6.26; Cl, 4.11.

Chloro(2,3,10,11,13,19-hexamethyl-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-$\kappa^4 N$)manganese(II) Hexafluorophosphate, [MnCl((CH$_2$)$_6$(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)]PF$_6$ (Mn(II)-Ia). A 0.5-g sample of the corresponding Mn(III) complex was dissolved in acetronitrile containing 0.1 M $N(CH_3)_4PF_6$. The solution was stirred and electrolyzed with a platinum gauze at −0.7 V vs. Ag^0/Ag^+ under an atmosphere of oxygen-free nitrogen. Reduction proceeded smoothly over a period of $\sim$30 min after which time a total of 58.3 C (99%) had passed and the solution had lightened from deep red-brown to a deep orange. The solution was isolated and pumped to dryness to give a bright orange powder. Extensive repeated recrystallizations from acetonitrile/ethanol in an attempt to remove the $N(CH_3)_4PF_6$ electrolyte yielded large red crystals in 39% yield. Despite the recrystallization, the isolated product still contained 2.8% by weight of the electrolyte as evidenced by the analysis. Anal. Calcd for $MnC_{26}H_{44}N_6ClPF_6$: C, 46.19; H, 6.56; N, 12.43. Found: C, 45.55; H, 6.63; N, 12.12. Calcd with 2.8% by weight of $N(CH_3)_4PF_6$: C, 45.52; H, 6.53; N, 12.26.

(2,3,11,12,14,20-Hexamethyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-1,5,7,9(28),12,14,19,21,26-nonaene-$\kappa^4 N$)manganese(II) Hexafluorophosphate, [Mn((*m*-xylylene)(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (Mn(II)-Ib). A procedure identical with that above yielded light orange crystals after repeated recrystallization (35%). Anal. Calcd for $MnC_{28}H_{40}N_6P_2F_{12}$: C, 41.75; H, 5.01; N, 10.43; Mn, 6.82. Found: C, 41.96; H, 5.32; N, 10.67; Mn, 6.63.

Results and Discussion

Synthesis and Characterization. Despite numerous attempts, synthesis aimed at the direct production of manganese(II) complexes were all unsatisfactory, leading to ill-characterized materials polluted with unreacted reagents. Synthetic schemes involving reaction of ligand salt with manganese(II) acetate or manganese(II) trifluoromethanesulfonate[27] using acetate or triethylamine as base under nitrogen in anhydrous media were attempted. While undoubtedly the synthesis yielded some of the desired product, as shown by electrochemistry, the very low affinity of manganese(II) for the macrobicyclic ligands I is evident and reminiscent of previous reports of similar attempted syntheses,[27] in particular the synthesis of manganese porphyrin species.[28]

Manganese porphyrin species may be prepared by reaction of manganese(III) salts with the porphyrin ligand followed by reduction to manganese(II). Adopting a similar approach for the present complexes proved very successful. Simple warming of Mn^{III}(acac)$_3$ with the ligand salts of I in dry acetonitrile leads to readily isolable pure manganese (III) complexes. The acac$^-$ ligands act as the base that is required to deprotonate the ligand salt. Manganese(III) acetate may also be used, but yields are lower and purification procedures are more difficult. Of particular interest is the persistence of the chloro ligand in these manganese(III) species. Chloride originates with the ligand salt, which is its only source in the reaction. Yet, despite its stoichiometric presence and the large excess of coordinating solvent, it remains bound in the isolated materials. Conductivity studies in acetonitrile give Onsager plots[29] (Ia, slope = 607 Ω^{-1} mol$^{1.5}$ cm$^{3.5}$), which show that the chloride ion remains bound in solution with the complex presumably being 5-coordinate square pyramidal.[20] However, addition of silver ion does produce a white precipitate, so the chloride ion may be removed by more extreme measures. This behavior is extremely reminiscent of the corresponding iron species where a chloride ion seems tenaciously bound in anhydrous media.[20,21]

The brown crystalline manganese(III) complexes have clean sharp infrared spectra that are very similar to those of the corresponding iron(III) species. Visible spectra of the complexes contain a single fairly sharp Gaussian band in the 450–800-nm region, and the spectra are discussed below. The magnetic moments of complexes Ia and Ib were measured by the method of Evans in deuterionitromethane and gave values of 4.85 and 4.89 μ_B, respectively, indicating high-spin d^4 configurations. Such a magnetic configuration is predicted to give observable NMR signals,[30] and indeed such signals may

---

(24) Melnyk, A. C.; Kildahl, N. K.; Rendina, A. R.; Busch, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 3232.

(25) Busch, D. H.; Olszanski, D. J.; Stevens, J. C.; Schammel, W. P.; Kojima, M.; Herron, N.; Zimmer, L. L.; Holter, K. A.; Mocak, J. *J. Am. Chem. Soc.* **1981**, *103*, 1942.

(26) Busch, D. H.; Jackels, S. C.; Callahan, R. W.; Grzybowski, J. J.; Zimmer, L. L.; Kojima, M.; Olszanski, D. J.; Schammel, W. P.; Stevens, J. C.; Holter, K. A.; Mocak, J. *Inorg. Chem.* **1981**, *20*, 2834.

(27) Bryan, P. S.; Dabrowiak, J. C. *Inorg. Chem.* **1975**, *14*, 296.

(28) Stults, B. R.; Day, V. W.; Tasset, E. L.; Marianelli, R. S. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1259.

(29) Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587.

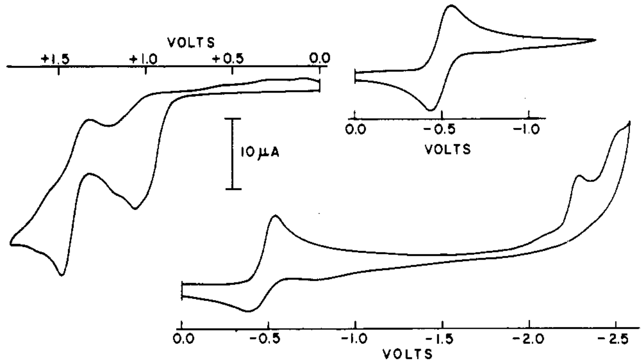


Figure 2. Redox processes for Mn(III)-Ia by cyclic voltammetry (n-Bu_4NBF_4 supporting electrolyte, $Ag/AgNO_3$ (0.1 M) reference electrode, Pt-disk electrode, 0.05 V s^{-1} scan rate, $T = 22$ °C under N_2, in acetonitrile solution, [Mn] $\simeq 2 \times 10^{-3}$ M).

be seen in the ^1H NMR spectrum of Mn(III)-Ib although they are extremely broad (line width >200 Hz) and are shifted considerably downfield (discernible peaks at ~55, ~37, ~28 ppm) at 303 K. Perhaps surprisingly, a rather good EPR signal is observed for frozen solutions of the manganese(III) complexes. A broad isotropic signal centered at $g = 2.04$ and split into an ill-resolved sextet $A_{Mn} \approx 108$ G by hyperfine coupling to the manganese nucleus ($I = {}^5/_2$) is observed at 77 K in dimethyl sulfoxide solvent.

The electrochemical behavior of the Mn(III) species is exemplified in Figure 2. Very good redox couples are observed for the II/III conversion in CH_3CN, the data being $E_{1/2} = -0.5$ V and $|E_{3/4} - E_{1/4}| = 75$ mV for ligand Ia and $E_{1/2} = -0.45$ V and $|E_{3/4} - E_{1/4}| = 82$ mV for Ib. No other redox waves are detected in the +0.9 → -2.0 V region. These potentials are very similar to, but slightly more negative than, those of the corresponding iron(II/III) couple at -0.4 and -0.39 V for Ia and Ib, respectively. Coulometry of the Mn(III) complex Ia indicated that the wave at -0.5 V corresponded to a one-electron process and was indefinitely reversible.

The electrochemical data above, and in particular the excellent behavior during controlled-potential electrolysis for coulometry, suggested that electrochemistry was a good way to effect a reductive synthesis of the elusive manganese(II) complexes of structure I, especially since chemical reductions with $NaBH_4$ had proven unsatisfactory. Taking the manganese(III) complex and performing bulk reductive electrolysis in acetonitrile solution at -0.7 V resulted in a color change from deep red brown to deep orange as the predicted quantity of electrical energy was passed. Isolation of the manganese(II) complex from the reduced solution was hampered by the presence of the large quantities of $N(CH_3)_4PF_6$ supporting electrolyte; however, repeated recrystallizations proved largely effective in generating pure, large orange crystals of the Mn(II) complexes. The isolated complexes are oxygen sensitive (see below), and all operations must be carried out in an inert atmosphere.

The manganese(II) complexes isolated as solids have different compositions, as indicated by analyses. Mn(II)-Ia crystallizes as the chloro hexafluorophosphate salt whereas Ib crystallizes as a bis(hexafluorophosphate) salt. The reason for the difference is unclear, but the difference may simply represent a switch in relative solubilities due to crystal packing. The infrared spectra of both complexes are very sharp and almost identical with those of the corresponding nickel(II) species. The most striking change between the IR spectra of the +3 and +2 complexes is that in the Mn(III) species the imine C=N and C=C stretching region is split into two well-resolved bands at 1535 and 1610 cm^{-1} (Ia) whereas in the Mn(II) complex this feature is a single absorption centered on 1575 cm^{-1}. The visible spectra of the complexes are essentially featureless, the orange color being derived from the tail of an intense charge-transfer band in the near-UV region (see below).

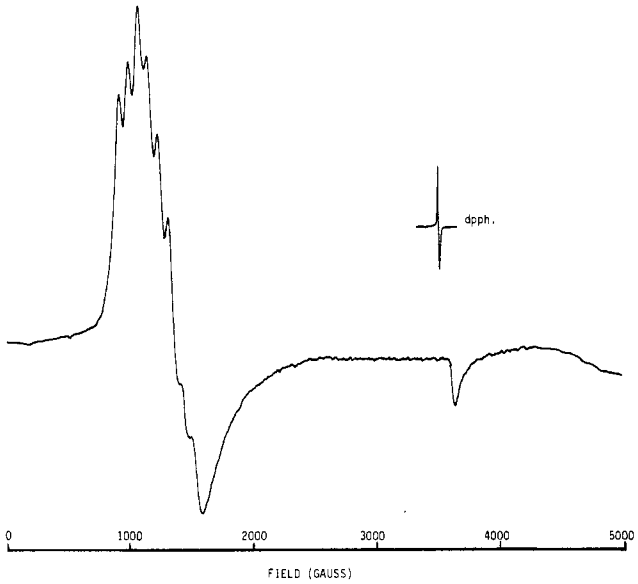


Figure 3. EPR spectrum of Mn(II)-Ib, with dpph as external reference at $g = 2.0036$.

Table I. EPR Parameters for Mn(II) Complexes of Ligand I

complex	g_x	A_x, G	g_y	A_y, G	g_z	E/D^a	% rhomb^a
Ia	6.45	65	5.56	69	1.99	0.019	5.75
Ib	6.48	62	5.63	65	1.99	0.020	5.94

^{a} E/D = ratio of rhombicity to zero-field splitting, and % rhomb is the percentage rhombicity, both as defined in ref 32.

The Evans method magnetic moments of the Mn(II) complexes in deuterionitromethane at 303 K are 5.75 and 5.66 μ_B for Ia and Ib, respectively and, although a little low, are consistent with a high-spin ($S = {}^5/_2$) d^5 configuration. As expected, for such a configuration no ^1H NMR signals could be detected in the -100 → 200 ppm range due to the potent relaxation properties of high-spin d^5 Mn(II). EPR spectra of these complexes are, however, readily observed and are typical[31] of a rhombically distorted high-spin d^5 system with a large value of the zero-field splitting parameter, D, $D >> 0.3$ cm^{-1} (the X-band microwave quantum) (Figure 3). The absorptions are split by hyperfine coupling to the manganese nucleus, and the spectra are tabulated in Table I.

Reaction of Manganese(II) with Dioxygen. The manganese(II) complexes of structure I are, as noted above, sensitive to dioxygen. Orange solutions in either Me_2SO or CH_3CN turn deep red upon exposure to the air. This reaction was followed by visible spectroscopy (Figure 4) by exposing an acetonitrile solution (293 K) containing 1.5 M pyridine axial base to pure oxygen and observing the visible spectrum as a function of time. A very slow reaction proceeds as a simple Gaussian band increases at 511 nm (Mn(II)-Ib). Flushing the oxygenated solution with dinitrogen and even freeze-pump-thaw cycles fail to reverse this spectral change, indicating that either an extremely tightly bound dioxygen adduct is formed or, more likely, simple autoxidation of the manganese(II) complex is taking place. Three sets of experiments prove that it is indeed the latter that is occurring but with an

---

(30) LaMar, G. N. In "NMR of Paramagnetic Molecules"; Lamar, G. N., Horrocks, W. D., Holm, R. H., Eds.; Academic Press: New York, 1973.

(31) Dowsing, R. D.; Gibson, J. F.; Goodgame, M.; Hayward, P. J. *J. Chem. Soc. A* **1969**, 187.

(32) Palmer, G. *Adv. Inorg. Biochem.* **1980**, *2*, 153.

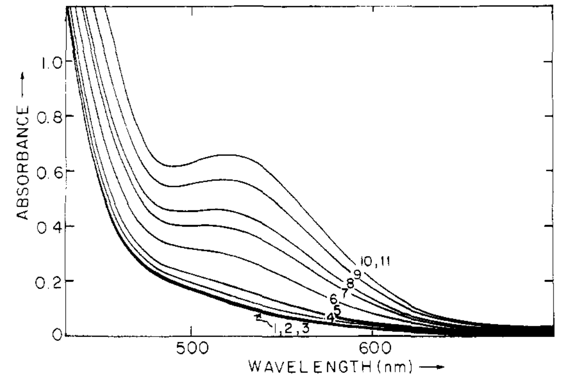


Figure 4. Irreversible interaction of O_2 with Mn(II)-Ib as indicated by electronic spectra in 1.5 M pyridine/acetonitrile at 20 °C ([Mn^{II}] = 2.85×10^{-4} M). Exposure times to O_2 are (1) 0 s, (2) 180 s, (3) 500 s, (4) 1000 s, (5) 1500 s, (6) 3000 s, (7) 4000 s, (8) 5000 s, (9) 7000 s and (10, 11) 8500 s, with additional N_2 bubbling for 3600 s. At lower temperatures, the reaction is much slower but the curves are identical in shape.

Table II. Visible Spectroscopic Parameters for Mn(II) and Mn(III) Complexes with I in Me_2SO

complex	λ_{max}, nm	ϵ, dm^3 mol^{-1} cm^{-1}
Mn(III)-Ia	493	4679
Mn(III)-Ia + KO_2	511	2309
Mn(II)-Ia + O_2	511	2254
Mn(III)-Ib	501	2418
Mn(III)-Ib + KO_2	517	1346
Mn(II)-Ib + O_2	518	1258

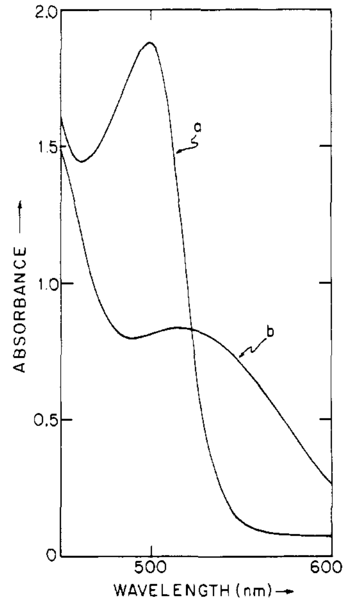
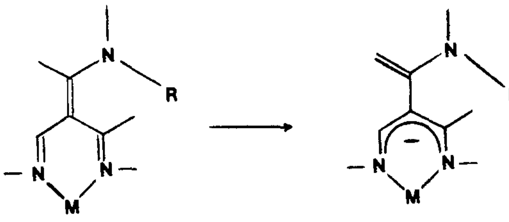


Figure 5. Electronic spectra of (a) Mn(III)-Ib in Me_2SO (7.9×10^{-4} M) and (b) Mn(II)-Ib in Me_2SO after exposure to pure O_2 for 3 h (6.7×10^{-4} M). Both were run at 20 °C vs. Me_2SO reference.

Scheme I



interesting complexity of mechanism.

First, exposure of a deuterionitromethane solution of manganese(II) Ia or Ib to dioxygen for 1 h results in a fall in the magnetic moment of the complex (Evans method) from 5.75 to 4.97 μ_B for Ia and from 5.66 to 4.76 μ_B for Ib. These changes closely correspond to conversion from an $S = {}^5/_2$ to an $S = 2$ system and are most readily interpreted as a Mn(II) to Mn(III) oxidation. The EPR spectral changes accompanying exposure of the Mn(II) solution to dioxygen also suggest conversion to Mn(III) as a spectral feature at $g \approx 2.04$ and $A_{Mn} \approx 110$ G grows as the Mn(II) signal disappears. This $g \approx 2.04$ feature is essentially identical with that of the genuine Mn(III) complex as reported above.

Second, the stoichiometry of the reaction with dioxygen was examined by using an oxygen-filled mini vacuum line to measure the pressure changes as the reaction proceeds. The data show that 0.32 ± 0.10 mol of oxygen/mol of manganese(II) present is consumed. Simple one-electron oxidation of Mn(II) → Mn(III) would give an O_2:Mn(II) ratio of 0.25 if all of the oxygen's oxidizing power is used to oxidize the manganese. Certainly the data is inconsistent with the formation of a 1:1 dioxygen adduct.

While the above data strongly indicate that the reaction with dioxygen involves simple oxidation to manganese(III), the changes in visible spectra are superficially inconsistent with this interpretation. Figure 5 shows that a spectrum of a genuine sample of Mn(III)-Ib is entirely different from that for the reaction product formed between O_2 and Mn(II). The explanation for the apparent conflict comes from the following set of experiments as tabulated in Table II. Addition of excess potassium superoxide, dissolved in dimethyl sulfoxide,[33] to a Me_2SO solution of the manganese(III) complex results in a dramatic change in the visible spectrum—the solution turns red and the absorption maximum moves 18 nm to longer wavelength while decreasing to half the intensity. This spectrum is then quantitatively the same as that generated by exposure of the same Mn(II) complex to O_2. The function served by the superoxide ion appears to be simply to act as a powerful base capable of deprotonating the ligand. That superoxide is a potent base in anhydrous media is well documented,[34] and it is also well-known that the ligands of type I are readily deprotonated at the acidic methyl group as in Scheme I.[25,26] This deprotonation clearly has a dramatic effect on the metal ion environment and as such would be expected to markedly affect the chromophore.

In order to confirm this interpretation, strong bases such as triethylamine were added to the Mn(III) complexes and they induced identical changes that could be quantitatively reversed by reprotonation with acid (HCl). The reaction between O_2 and the manganese(II) complexes appears, therefore, to involve simple oxidation to manganese(III) and superoxide followed by deprotonation of the manganese(III) complex by the superoxide ion and its disproportionation to peroxide. Unfortunately, at no time has there been any evidence for the intermediacy of a discrete manganese–dioxygen adduct, and indeed it is quite possible that the whole reaction proceeds via an outer-sphere electron transfer, which would be consistent with the slow kinetics.

Reaction of Manganese(III) with Peroxide. Both manganese(III) complexes react smoothly with hydrogen peroxide in acetonitrile solution. Oxygen evolution was monitored over a period of 30 min at which time the moles of dioxygen released per mole of catalyst were 125 ± 5 for Ia and 36 ± 3 for Ib. At this time the oxygen evolution was essentially

---

(33) Valentine, J. S. In "Biochemical and Clinical Aspects of Oxygen"; Caughey, W. S., Ed.; Academic Press: New York, 1979; p 659.

(34) Lee-Ruff, E. *Chem. Soc. Rev.* **1977**, *6*, 195; Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393.

complete for Ia but still continued for Ib. The initial rates of the reaction measured from the slope of the evolution curve were 6.9 ± 10^{-3} and 1.9 × 10^{-3} mol of O_2/s for Ia and Ib, respectively, and these compare with a value of 8.4 × 10^{-2} mol of O_2/s for an effective catalase model compound of iron(III)[24] under the same conditions. Clearly, the manganese complexes are efficient disproportionation catalysts, but their rate of reaction is much slower than that of iron(III) catalase analogues.

In the case of iron(III) catalase models, or iron(III) heme units in general, catalase activity is frequently coupled with peroxidase activity either via generation of free oxy radical species during disproportionation or through the intermediacy of a high oxidation state iron oxo species.[24] Since the present manganese species display slow catalase activity, they were tested for peroxidase behavior by introducing an oxidizable substrate, phenol or 2,6-dimethylphenol, to the catalase experiments. In all cases, after workup of the reaction mixture, the only organic species recovered and detected was unreacted phenol in almost quantitative yield. This result is in marked contrast to results with the corresponding iron(III) complexes of structure I, where in addition to catalase activity catalytic conversion of phenol to quinone proceeds with moderate efficiency. It therefore appears that, if the disproportionation of peroxide does proceed via a high oxidation state metallo-oxo species, then in the case of manganese this species is incapable of phenol oxidation, and this may indicate that it has enhanced stability over the more reactive iron species.[18] As such, the manganese systems may offer a fruitful line of investigation toward elucidation of the potent oxidizing species of the natural heme oxygenases such as peroxidase or cytochrome P-450. This and experiments related to oxene atom transfer from reagents such as iodosylbenzene or metaperiodate are topics of continuing investigation in these laboratories.

Acknowledgment. The support of the National Institutes of Health is gratefully acknowledged.

Registry No. Mn(III)-Ia, 87306-40-9; Mn(II)-Ia, 87306-44-3; Mn(III)-Ib, 87306-42-1; Mn(II)-Ib, 87306-46-5; $[H_4((CH_2)_6(MeNEthi)_2Me_2[16]tetraeneN_4)]Cl(PF_6)_3$, 87318-57-8; $[H_4((m\text{-xylylene})(MeNEthi)_2Me_2[16]tetraeneN_4)]Cl(PF_6)_3$, 87306-47-6; tris(2,4-pentanedionato)manganese(III), 14284-39-0; oxygen, 7782-44-7; hydrogen peroxide, 7722-84-1; potassium superoxide, 12030-88-5.

Contribution from the Departments of Chemistry and Physics,
The University of Texas at Austin, Austin, Texas 78712

Ferrocenyl-Substituted Phosphenium Cations and Phosphide Anions

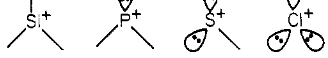
S. G. BAXTER, R. L. COLLINS, A. H. COWLEY,* and S. F. SENA

Received February 16, 1983

The phosphorus(III) chloride $Fc(Me_2N)PCl$ (**6**) (Fc = ferrocenyl) was prepared by the reaction of Me_3SiNMe_2 with $FcPCl_2$ (**5**). Treatment of Fc_2PCl (**4**), **6**, or **5** with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 solution results in tetrachloroaluminate salts of the phosphenium ions $[Fc_2P]^+$ (**7**), $[Fc(Me_2N)P]^+$ (**8**), or $[Fc(Cl)P]^+$ (**9**), respectively. ^{31}P, ^{27}Al, and ^1H NMR data are reported for all three salts, and the formulation of **7** as a ferrocenyl compound was confirmed by ^{57}Fe Mössbauer spectroscopy. No evidence for $[FcP]^{2+}$ formation was found when **5** was treated with excess Al_2Cl_6. The Lewis acidity of **7** was demonstrated by reaction with n-Bu_3P, which results in the adduct $[n\text{-}Bu_3PPFc_2]^+[AlCl_4]^-$ (**10**). The iron carbonyl complex $(Fc_2PCl)Fe(CO)_4$ (**11**) was prepared by the reaction of **4** with $Fe_2(CO)_9$ in n-hexane. Treatment of **11** with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 solution affords the coordinated phosphenium ion complex $[Fc_2PFe(CO)_4]^+[AlCl_4]^-$ (**12**). ^{57}Fe Mössbauer data for **12** suggest that the phosphenium ion occupies an axial site of the iron trigonal bipyramid. Reduction of **4** with $LiAlH_4$ in Et_2O affords the secondary phosphine Fc_2PH (**13**), which can be lithiated to Fc_2PLi (**14**) with n-BuLi. Treatment of **14** with D_2O produced Fc_2PD (**15**). The diphosphine Fc_2PPFc_2 (**16**) can be prepared via the reaction of **4** with K, Mg, or sodium naphthalenide in THF.

Introduction

Two-coordinate phosphorus cations (phosphenium ions) represent a relatively new class of compounds that have attracted significant recent attention.[1] Featuring six valence electrons, phosphenium ions constitute part of an isoelectronic series that extends from silicenium[2] to chloronium[3] ions:



At the inception of this work, all isolable unligated phosphenium ions featured at least one conjugatively stabilizing amido substituent.[1,4] Our primary goal was to synthesize phosphenium ions with only P–C bonds. Since the ferrocenyl (Fc) group has proved to be highly effective for stabilizing positive charge, particularly in the realm of carbocation chemistry,[5] we were encouraged to undertake the synthesis of ferrocenyl-substituted phosphenium ions.[6] In passing, we note thate since starting this program, we have discovered $[(Me_5C_5)PR]^+$, R = t-Bu, and $(Me_3Si)_2CH$, a different class of carbon-based phosphenium ion.[7] Furthermore, in a historical vein we should note the pioneering work of Dimroth and co-workers[8] on the

---

* To whom correspondence should be addressed at the Department of Chemistry.

(1) For early work in this area, see: (a) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534. (b) Hutchins, R. O.; Maryanoff, B. E. *J. Org. Chem.* **1972**, *37*, 3475. (c) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046. (d) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Ibid.* **1977**, *16*, 994. For a review, see: (e) Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789. For developments since 1980, see: (f) Baxter, S. G.; Cowley, A. H.; Mehrotra, S. K. *J. Am. Chem. Soc.* **1981**, *103*, 5572. (g) Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 2916.

(2) Silicenium ions have so far defied all attempts at isolation. For reviews, see: (a) Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1. (b) O'Brien, D. H.; Hairson, T. J. *Organomet. Chem. Rev., Sect. A* **1971**, *7*, 95. See also: (c) Cowley, A. H.; Cushner, M.; Riley, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 624. (d) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485.

(3) For a thorough discussion of halonium ions, the reader is referred to: Olah, G. A. "Halonium Ions"; Wiley: New York, 1975.

(4) There is one instance of a ligated MeO-substituted phosphenium ion (however, free phosphenium ions of the type $(RO)_2P^+$ have not been isolated): (a) Muetterties, E. L.; Kirner, J. F.; Evans, W. J.; Watson, P. L.; Abdel-Meguid, S. S.; Tavanaiepour, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1056. (b) Choi, H. W.; Gavin, R. M.; Muetterties, E. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1085. (c) Day, V. W.; Tavanaepour, I.; Abdel-Meguid, S. S.; Kirner, J. F.; Goh, L.-Y.; Muetterties, E. L. *Inorg. Chem.* **1982**, *21*, 657.

0020-1669/83/1322-3475$01.50/0