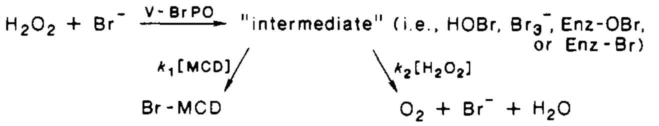
O_2/min at 0.095 M Br^-), reflecting the larger oxidation potential of iodide. Figure 1B shows that a solution of H_2O_2 and Br^- at pH 6.5 does not produce O_2, despite the favorable potential, and Figure 1A demonstrates that a solution of H_2O_2 is stable with respect to disproportionation under the conditions of these experiments.

Figure 2 shows a profile of the rate of MCD bromination (Figure 2A) and the rate of dioxygen formation (Figure 2B), both in the presence of 47.5 μM MCD catalyzed by V-BrPO. The rate of dioxygen formation catalyzed by V-BrPO, 10.0 μM/min, is identical with the rate of MCD bromination, 10.5 μM/min at 40–95 μM [MCD] (see Table I). Moreover, the maximum rate of O_2 formation is independent of the presence of MCD, since the rate of O_2 formation in the absence of MCD is 10.4 μM/min. That the ratio of the rate of MCD bromination to dioxygen formation is 1.05 ± 0.05 suggests that both reactions proceed through a common intermediate, which in analogy to FeHeme-BrPO may be an enzyme-bound OBr^- moiety, an enzyme-bound Br moiety, HOBr, or Br_3^-. Any of these can react with MCD to give the brominated product or with another 1 equiv of H_2O_2 to produce O_2 and Br^- at rates much faster than that for the production of the intermediate.[7,10,14,15] Chloride ($\leq$0.5 M) does not affect the rate of MCD bromination nor the O_2-formation rate, although fluoride inhibits both reactions.

This is the first report of halide-dependent catalase activity for V-BrPO. This feature is shared with Fe_{NH}-BrPO, which is reported to have equivalent rates of MCD bromination and oxygen evolution in the halide-dependent catalase reaction,[9] but is distinctly different from the FeHeme haloperoxidases and many other FeHeme peroxidases, which have appreciable catalase activities in the absence of halide ion.[7,11] The identical rates of MCD bromination and Br^--assisted O_2 formation and the lack of O_2 formation in the absence of bromide suggest the possible mechanism



$$H_2O_2 + Br^- \xrightarrow{\text{V-BrPO}} \text{"intermediate" (i.e., HOBr, } Br_3^-\text{, Enz-OBr, or Enz-Br)}$$
$$\text{"intermediate"} \xrightarrow{k_1[\text{MCD}]} \text{Br-MCD}$$
$$\text{"intermediate"} \xrightarrow{k_2[H_2O_2]} O_2 + Br^- + H_2O$$

During the bromination of MCD, a slow rate of O_2 formation is evident in Figure 2B, although, this rate is 80–95% less than the rate of O_2 formation in the absence of MCD or after all MCD is consumed. Even at much higher MCD concentrations (i.e., up 250 μM), the rate of O_2 formation is not completely shut off, indicating that k_1[MCD] competes with $k_2[H_2O_2]$ for reaction with the "intermediate". V-BrPO also catalyzes the bromination of uracil or cytosine, forming the 5-bromo derivatives,[16] although neither uracil nor cytosine is an efficient substrate, even at 10 mM concentrations, since dioxygen evolution (i.e., $k_2[H_2O_2]$) is concomitant with bromination (i.e., k_1[pyrimidine]).

In conclusion, we have shown that, unlike FeHeme haloperoxidases, V-BrPO cannot catalyze the direct disproportionation of H_2O_2 in the absence of bromide or iodide. The catalase activity of FeHeme haloperoxidases may be a consequence of the electron-transfer function of the FeHeme moiety since $Heme^+Fe^{IV}{=}O$ can oxidize H_2O_2, leading to direct catalase activity, or oxidize Br^-, leading to bromination and Br^--assisted catalase reactivity. We are continuing our investigation of the role of the vanadium(V) ion to determine whether V-BrPO functions as an electron-transfer catalyst or a Lewis acid catalyst of bromide oxidation by hydrogen peroxide.

Abbreviations: 2-chloro-5,5-dimethyl-1,3-dimedone, MCD; bromoperoxidase, BrPO; chloroperoxidase, ClPO.

Acknowledgment. A.B. gratefully acknowledges grants from the National Science Foundation (DMB87-16229), the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Committee on Research of the UCSB Academic Senate, and the American Cancer Society, Junior Faculty Research Award (JFRA-216).

Department of Chemistry
University of California
Santa Barbara, California 93106

Richard R. Everett
Alison Butler*

Received September 14, 1988

---

(14) Kanofsky, J. R. *J. Biol. Chem.* **1984**, *259*, 5596.

(15) Griffin, B. W. *Biochem. Biophys. Res. Commun.* **1983**, *116*, 873.

(16) Formation of 5-bromocytosine was confirmed by electron impact mass spectral analysis and by comparison of R_f values from thin-layer chromatography.

General Synthetic Route to the Dirhenium Octahydrides $Re_2H_8(PR_3)_4$ from the Triply Bonded Complexes $Re_2Cl_4(PR_3)_4$. An Unexpected Structure for the Complex $Re_2H_8(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$)

The so-called "agno-hydrides" of rhenium were first described in detail by Chatt and Coffey in 1969 and formulated as $[ReH_x(PR_3)_2]_2$ ($x < 7$ and PR_3 = PEt_2Ph, PPh_3).[1] Later work by Bau et al.[2] identified these complexes as having the novel hydrido-bridged structure $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$. The most commonly used method for the synthesis of these complexes and the more recently prepared dimethylphenylphosphine derivative $Re_2H_8(PMe_2Ph)_4$[3] involves the thermal decomposition of the corresponding mononuclear heptahydride complexes $ReH_7(PR_3)_2$ (i.e., the original Chatt and Coffey procedure).[4-8] Subsequently, the isolation of $Re_2H_8(PMe_3)_4$ has been reported,[9] although its synthesis involves a different recipe. In view of the novel chemistry that is now being uncovered for dirhenium polyhydride complexes,[10-13] we have sought to devise a simple synthetic methodology that would be suitable for an extensive range of phosphine ligands and so provide a single uniform synthetic strategy for $Re_2H_8(PR_3)_4$. We can now report the successful development of such a route for PR_3 = PMe_3, PEt_3, P-*n*-Pr_3, PMe_2Ph, PEt_2Ph, $PMePh_2$, $Ph_2PCH_2PPh_2$ (dppm), and $Ph_2PCH_2CH_2PPh_2$ (dppe)

---

(1) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963.

(2) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

(3) Green, M. A. Ph.D. Thesis, Indiana University, 1982. This source provides details of the synthesis of $Re_2H_8(PMe_2Ph)_4$, a complex whose chemistry has been examined in detail by Professor K. G. Caulton and his group.

(4) An excellent alternative high-yield synthesis of $Re_2H_8(PPh_3)_4$ involves the reaction of the quadruply bonded dirhenium(III) complexes $(n\text{-}Bu_4N)_2Re_2Cl_8$ or $Re_2Cl_6(PPh_3)_2$ with $NaBH_4$ and PPh_3 in ethanol.[5] The photolysis of $ReH_5(PR_3)_3$ and $ReH_7(PR_3)_2$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph) gives $Re_2H_8(PR_3)_4$, along with other products,[6,7] while the chemical oxidation of anionic $K[ReH_6(PMePh_2)_2]$ leads to $Re_2H_8(PMePh_2)_4$.[8] However, these latter reactions have not yet been developed into useful synthetic procedures.

(5) Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2674.

(6) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695.

(7) Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1981**, *214*, 221.

(8) Bruno, J. W.; Caulton, K. G. *J. Organomet. Chem.* **1986**, *315*, C13.

(9) Lyons, D.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1985**, 587.

(10) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2319.

(11) (a) Allison, J. D.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 163. (b) Allison, J. D.; Cotton, F. A.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1984**, *23*, 159.

(12) (a) Boyle, P. D.; Johnson, B. J.; Alexander, B. D.; Casalnuovo, J. A.; Gannon, P. R.; Johnson, S. M.; Larka, E. A.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1987**, *26*, 1346. (b) Moehring, G. A.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 1861.

(13) (a) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 5137. (b) Sutherland, B. R.; Ho, D. M.; Huffman, J. C.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 135. (c) Westerberg, D. E.; Sutherland, B. R.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1988**, *110*, 1642.

0020-1669/89/1328-0395$01.50/0

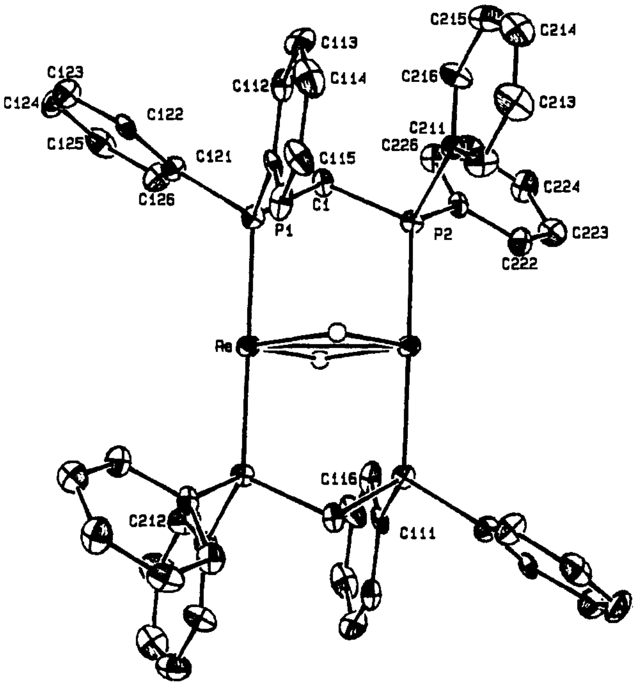


Figure 1. ORTEP view of the structure of $Re_2H_8(\mu\text{-dppm})_2$. The thermal ellipsoids are drawn at the 50% probability level. The probable positions of the bridging hydrido ligands are shown as circles of arbitrary radius. Important bond lengths (Å) and angles (deg) are as follows: Re–Re = 2.933 (1), Re–P(1) = 2.358 (3), Re–P(2) = 2.389 (3), P(1)–C(1) = 1.83 (1), P(2)–C(1) = 1.84 (1); Re–Re–P(1) = 87.64 (8), Re–Re–P(2) = 92.33 (7), P(1)–Re–P(2) = 164.1 (1). The P(1)–Re–Re–P(2) torsional twist angle (χ) = 15.9 (1)°.

that should be easily adaptable for use with many other phosphine ligands.

The synthetic procedure involves the use of dirhenium compounds that already contain the desired $[(R_3P)_2ReRe(PR_3)_2]$ architecture, namely, the triply bonded dirhenium(II) phosphine complexes $Re_2Cl_4(PR_3)_4$ (PR_3 represents a monodentate phosphine or half of a bidentate phosphine).[14] The reaction between $Re_2Cl_4(PR_3)_4$ and $LiAlH_4$ in glyme at room temperature for 12–24 h, followed by hydrolysis of the reaction mixture with deoxygenated H_2O and workup,[15] gives the pure crystalline orange octahydride complexes in yields generally of 30–50%.[16] These reactions probably proceed through the intermediacy of aluminohydride complexes.[17] Note that a mechanism involving the thermolysis of a $ReH_7(PR_3)_2$ intermediate[1] is not favored as a major pathway because of the mild reaction conditions that are used.[18]

While there is ample evidence for the close identity in structure of $Re_2H_8(PR_3)_4$ (PR_3 = monodentate phosphine),[19,20] the complexes $Re_2H_8(dppe)_2$ and $Re_2H_8(dppm)_2$ offer the opportunity for some important structural variations. The former complex probably contains chelating dppe ligands as evidenced by its $^{31}P\{^1H\}$ NMR spectrum (C_6D_6), which shows a singlet at δ +53.1, a chemical shift which is characteristic of a five-membered ring formed by chelating phosphines bound to rhenium.[21] Its ^1H NMR spectrum (CD_2Cl_2) displays a pentet at δ −6.62 (J_{P-H} = 9.5 Hz) which achieves coalescence at ≃−80 °C. An interesting reaction is the conversion of this complex into $Re_2H_4(dppe)_3$ in 55% yield upon its reaction with dppe (2 equiv) in THF at room temperature.[22]

The conversion of $Re_2Cl_4(\mu\text{-dppm})_2$[14b] into $Re_2H_8(dppm)_2$ occurs with retention of the intramolecularly bridging dppm ligands as evidenced by a crystal structure determination of this complex (Figure 1).[23] The molecules have crystallographically imposed $\bar{1}$ symmetry. The most remarkable features of this structure are (1) a Re–Re distance (2.933 (1) Å) that is ca. 0.4 Å longer than in $Re_2H_8(PEt_2Ph)_4$[2] and $Re_2H_8(PMe_3)_4$[9] and (2) a P–Re–P angle (164.1 (1)°) that is much larger than the corresponding angles of ca. 103–105° that characterize the derivatives containing monodentate phosphines.[2,9] Although we were unable to locate the terminal hydride ligands in this structure determination, we found evidence for a bridging hydride ligand in a difference Fourier map. Isotropic refinement on this assumption led to rather long Re–H(1) distances of 2.0 (1) and 2.1 (1) Å. While we cannot be certain that we have correctly located this pair of hydride ligands, nonetheless, we are confident that this structural conclusion is correct based upon the other structural features of this complex and the striking differences that exist between it and $Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4$. The presence of eight hydride ligands was confirmed by measurement of the ^{31}P 2DJ NMR spectrum of this complex (CD_2Cl_2), in which selective coupling to the hydride ligands occurs. This spectrum (available in the supplementary material) appears as a binomial nonet centered at δ +34.5 (J_{P-H} = 11.9 Hz). Like other dirhenium octahydrides, $Re_2H_8(dppm)_2$ displays a pentet for the Re–H resonance (at δ −6.20 with J_{P-H} ≃ 11 Hz) in its ^1H NMR

---

(14) (a) Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 1987. (b) Ebner, J. R.; Tyler, D. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 833.

(15) A typical procedure is as follows. A quantity of $Re_2Cl_4(PMe_3)_4$ (0.534 g, 0.65 mmol) is mixed with an excess of $LiAlH_4$ (0.397 g, 10.46 mmol) and deoxygenated glyme (20 mL) and the mixture stirred under N_2 at room temperature for 17 h. The resulting gray suspension is slowly hydrolyzed by using a deoxygenated H_2O (5 mL)/glyme (15 mL) mixture and then is stirred with gentle warming for an additional 4 h and filtered through Celite under N_2, and the filtrate is stripped to dryness under vacuum. The residue is extracted into benzene and filtered, the filtrate again stripped to dryness, and the residue purified by precipitation from methanol/deoxygenated H_2O; yield 0.150 g (34%). Anal. Calcd for $C_{12}H_{44}P_4Re_2$: C, 21.04; H, 6.49. Found: C, 20.58; H, 6.56. The other products are generated in a similar fashion, with the exception that for the dppm derivative THF was used as the reaction solvent. Some differences exist in the final purification step.

(16) The one exception is $Re_2H_8(PEt_3)_4$, which was isolated as a pure solid in only 10% yield after removal of some $ReH_7(PEt_3)_2$ and $ReH_5(PEt_3)_3$ contaminants. Anal. Calcd for $C_{24}H_{68}P_4Re_2$: C, 33.78; H, 8.05. Found: C, 33.56; H, 8.36.

(17) Barron, A. R.; Wilkinson, G. *Polyhedron* **1986**, *5*, 1897.

(18) Interestingly, we find that the reaction of the dirhenium octahydride complexes with additional $LiAlH_4$, followed by the usual workup procedure,[15] affords complexes of the type $ReH_7(PR_3)_2$. This strongly supports the conclusion that the thermolysis of $ReH_7(PR_3)_2$ "intermediates" is not leading to $Re_2H_8(PR_3)_4$ in our systems.

(19) The close similarity in the properties (spectroscopic and electrochemical) of these complexes implies that they possess similar structures in solution. The ^1H NMR spectral properties of the PMe_3, PMe_2Ph, PEt_2Ph, and $PMePh_2$ derivatives agree well with literature data,[1,2,6,7,9] and the ^1H NMR spectra of the previously unreported PEt_3 and P-*n*-Pr_3 complexes (C_6D_6) show pentets at δ −7.35 and δ −7.31 (J_{P-H} ≃ 10 Hz), respectively. The $^{31}P\{^1H\}$ spectra (C_6D_6) show a singlet for all the complexes. Note that the cyclic voltammograms of all these complexes (recorded in 0.1 M Bu_4NPF_6–CH_2Cl_2) resemble closely those reported previously for $Re_2H_8(PPh_3)_4$ and $Re_2H_8(PEt_2Ph)_4$.[11a]

(20) In addition to the neutron diffraction structure of $Re_2H_8(PEt_2Ph)_4$,[2] there is mention[9] of a preliminary X-ray crystal structure determination on $Re_2H_8(PMe_3)_4$ that has confirmed the essential isostructural nature of these two compounds.

(21) Anderson, L. B.; Bakir, M.; Walton, R. A. *Polyhedron* **1987**, *6*, 1483.

(22) Root, D. R.; Fanwick, P. E.; Walton, R. A. Unpublished work.

(23) Red crystals of $Re_2H_8(dppm)_2$, which were grown by the diffusion of methanol into a solution of this complex in benzene, are monoclinic, space group $P2_1/n$, with a = 12.962 (3) Å, b = 12.002 (8) Å, c = 14.979 (4) Å, β = 112.30 (2)°, V = 2156 (3) Å^3, Z = 2, d_{calc} = 1.770 g/cm^3. X-ray data were collected at −145 °C on a 0.14 × 0.11 × 0.06 mm crystal for 3988 independent reflections having $4 < 2\theta < 50°$ on an Enraf-Nonius diffractometer using graphite-crystal-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection and reduction methods are the same as described elsewhere.[24] An empirical absorption correction was applied,[25] but no correction for extinction was made. The Re, P, and C atoms were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[26] Positions for phenyl ring hydrogen atoms were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. The final residuals were R = 0.048 (R_w = 0.057) for 2470 data with $I > 3.0\sigma(I)$.

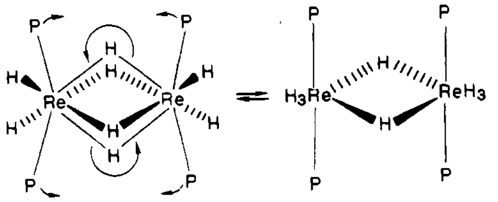
(24) Fanwick, P. E.; Harwood, W. S.; Walton, R. A. *Inorg. Chim. Acta* **1986**, *122*, 7.

(25) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.

(26) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. *Ibid.*; Table 2.2B.

spectrum (CD_2Cl_2). This feature broadens with some loss in structure but is otherwise unchanged upon cooling to -70 °C.

We suggest that the structure of $Re_2H_8(dppm)_2$ can be considered to represent a distortion from $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$ in which an opening up of the P-Re-P angles (constrained here to do so by the nature of the bridging dppm ligands), and a concomitant lengthening of the Re-Re bond is accompanied by a conversion of two of the bridging Re-H-Re units to terminal Re-H bonds. Such a low energy "concertina-like" process (see below) may well be the origin of the fluxionality of this class of molecule as a whole.



A final point of interest is the implication that the long Re-Re bond, coupled with the observed diamagnetism of the dppm complex, accords with the presence of a Re-Re single bond and, most likely, only a 16-electron count for the Re centers. Formally, at least, the dramatic Re-Re bond shortening that accompanies conversion to the $Re(\mu\text{-}H)_4Re$ structure is consistent with an 18-electron count and a Re≡Re bond. Further studies of the reaction and structural chemistry of these complexes are under way, especially those involving the dppe and dppm derivatives.

Acknowledgment. Support from the National Science Foundation, through Grant Nos. CHE85-06702 and CHE88-07444 to R.A.W. and Grant No. CHE86-15556 for the purchase of the MicroVAX II computer and diffractometer, is gratefully acknowledged. We also thank the National Institutes of Health (Grant No. RR-01077) and the National Science Foundation (Grant No. 8714258) for funds for the purchase of the NMR spectrometers.

Supplementary Material Available: Listing of atomic positional parameters, a figure showing the $Re_2(\mu\text{-}H)_2P_4$ core of $Re_2H_8(dppm)_2$ as viewed down the Re-Re bond axis, and a figure showing the ^{31}P 2DJ NMR spectrum of $Re_2H_8(dppm)_2$ (4 pages). Ordering information is given on any current masthead page.

Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Phillip E. Fanwick
Dawn R. Root
Richard A. Walton*

Received October 27, 1988

Articles

Contribution from the Department of Chemistry,
Oberlin College, Oberlin, Ohio 44074

Chromium, Molybdenum, and Tungsten Zerovalent Complexes of the Nitrogen Chelating Ligand 2-(Phenylazo)pyridine (2-PAP), Including Air-Stable *cis*-$M(CO)_2(2\text{-PAP})_2$ and $M(2\text{-PAP})_3$

Martin N. Ackermann,* Carolyn R. Barton, Charles J. Deodene, Elizabeth M. Specht, Sarah C. Keill, William E. Schreiber, and Hidong Kim

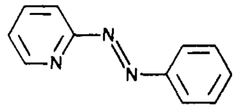
Received June 20, 1988

The reaction of 2-(phenylazo)pyridine (2-PAP) with $M(CO)_4$(norbornadiene), $M(CO)_3(CH_3CN)_3$, or $M(CO)_6$ provides $M(CO)_4(2\text{-PAP})$ (M = Cr, Mo, W), *cis*-$M(CO)_2(2\text{-PAP})_2$ (M = Mo, W), and $M(2\text{-PAP})_3$ (M = Cr, Mo, W) as air-stable solids. All compounds are diamagnetic except $Cr(2\text{-PAP})_3$, for which μ_{eff} is ~1.1 μ_B at ambient temperature. In $M(CO)_4(2\text{-PAP})$ and *cis*-$M(CO)_2(2\text{-PAP})_2$ the CO stretching frequencies are unusually high for complexes of a chelating nitrogen ligand. Compared to the frequency for uncoordinated 2-PAP, the N═N stretching frequency is lowered by 61-136 cm^{-1} in the complexes with the magnitude of the decrease following the order $M(CO)_4(2\text{-PAP})$ > *cis*-$M(CO)_2(2\text{-PAP})_2$ > $M(2\text{-PAP})_3$. Cyclic voltammetry shows that the first oxidation occurs at relatively high potentials in these complexes. ^1H and ^{13}C NMR data suggest that the *cis*-$M(CO)_2(2\text{-PAP})_2$ and $M(2\text{-PAP})_3$ complexes may each exist in a single isomeric form. The ^{95}Mo chemical shifts increase by 900-1200 ppm for each pair of CO's replaced by 2-PAP in $Mo(CO)_6$; the shift of +1502 ppm for $Mo(2\text{-PAP})_3$ is over 1000 ppm more positive than any previously reported for a Mo(0) compound. The complexes are compared to those of other chelating nitrogen ligands. It is concluded that 2-PAP is a poor σ donor but a very good π acceptor toward low-valent metal centers.

Introduction

Reactions of diazenes (azo compounds) with metal carbonyls have provided a rich variety of complexes.[1] A simple but most often adopted mode of coordination of the diazene linkage is through σ donation by one of the nitrogen atoms to a metal center. In this mode diazenes also can participate in π bonding through use of the vacant N═N π* molecular orbital. Evidence, such as lowering of the N═N stretching frequency upon coordination, indicates that simple diazenes have modest π-acceptor ability in low-oxidation-state metal complexes.[2]

As part of our continuing interest in diazenes as ligands, we were attracted to the chelating ligand 2-(phenylazo)pyridine (2-PAP). Because of reports that 2-PAP behaves as a strong π acceptor toward a variety of metal ions such as Ru(II),[3,4] Os(II),[5]



2-(phenylazo)pyridine, 2-PAP

---

(1) (a) Albini, A.; Kisch, H. *Top. Curr. Chem.* **1979**, *65*, 105. (b) Carty, A. J. *Organomet. Chem. Rev. A* **1972**, *7*, 191. (c) Kilner, M. *Adv. Organomet. Chem.* **1972**, *105*, 115.

(2) (a) Ackermann, M. N.; Willett, R. M.; Englert, M. H.; Barton, C. R.; Shewitz, D. B. *J. Organomet. Chem.* **1979**, *175*, 205. (b) Ackermann, M. N.; Dobmeyer, D. J.; Hardy, L. C. *J. Organomet. Chem.* **1979**, *182*, 561. (c) Ackermann, M. N.; Hardy, L. C.; Xiao, Y. Z.; Dobmeyer, D. J.; Dunal, J. A.; Felz, K.; Sedman, S. A.; Alperovitz, K. F. *Organometallics* **1986**, *5*, 966.

(3) (a) Krause, R. A.; Krause, K. *Inorg. Chem.* **1980**, *19*, 2600. (b) Krause, R. A.; Krause, K. *Inorg. Chem.* **1982**, *21*, 1714.

(4) (a) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 2246. (b) Goswami, S.; Chakravarty, A.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 602. (c) Goswami, S.; Mukherjee, R.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 2285. (d) Ghosh, P.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1985**, 361. (e) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 2737.

0020-1669/89/1328-0397$01.50/0 © 1989 American Chemical Society