tance, 2.507 (1) Å, on the other hand, is quite long.[15] The long P(1′)–Mn interactions occur approximately perpendicular to the $P_2(t\text{-BuN})_2$ rings while the short interactions are more in-plane. In this regard the P(1), P(2), Mn, C(1), C(2), and C(4) atoms nearly lie in a plane that is perpendicular to the C(3)–Mn–P(1′) vector.[16] The Mn–CO bond distances, Mn–C(1) = 1.842 (4) Å, Mn–C(2) = 1.831 (5) Å, Mn–C(3) = 1.822 (5) Å, and Mn–C(4) = 1.850 (4) Å offer some evidence for the differing donor qualities of P(2) and P(1′) sites. The Mn–C(4) distance is long and trans to the short Mn–P(2) distance while Mn–C(3) is short and trans to the long Mn–P(1′) distance.

The infrared spectrum (benzene) of **4** shows four bands in the terminal carbonyl stretching region, 2043, 1995 (s), 1960 (s), and 1943 (m) cm^{-1}, which is consistent with local C_s symmetry for the *cis*-$Mn(CO)_4$ P_2 fragment. The $^{31}P\{^1H\}$ NMR spectrum (H_3PO_4 reference) shows two resonances at 345 [P(1), P(1′)] and 0.9 ppm [P(2), P(2′)], and no P(1)–P(2) coupling has been resolved. The spectrum is consistent with two uniquely differing phosphorus environments as found in the crystal structure determination. The $^{13}C\{^1H\}$ NMR spectrum (Me_4Si reference) shows two resonances at 56.8 (J_{PNC} = 9 Hz, $(CH_3)_3C$) and 31.1 ppm ($(CH_3)_3C$).

The process by which **4** is formed appears to be complex. Sodium chloride appears with some CO evolution at −78 °C followed by additional CO evolution and $Mn_2(CO)_{10}$ generation at THF reflux. Accompanying color and spectroscopic changes suggest formation of at least three species prior to the appearance of **4**, and these are under study at this time. It appears that this complex offers a starting point for a new family of main-group–transition-metal clusters whose chemistry should be intriguing.

Acknowledgment. R.T.P. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The authors also acknowledge NSF Grants CHE 78-2921, CHE 80-07979, and CHE 81-10536, which facilitated the purchases of the X-ray diffractometer, FTIR spectrometer, and mass spectrometer. We also thank Dr. D. Wrobleski for obtaining several early ^{31}P NMR spectra at Los Alamos National Laboratory.

Registry No. **1**, 24335-35-1; **4**, 93841-99-7; $NaMn(CO)_5$, 13859-41-1.

Supplementary Material Available: Details of the crystal structure determination and listings of crystal structure data, positional parameters, anisotropic thermal parameters, bond distances, bond angles, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of New Mexico
Albuquerque, New Mexico 87131

Donn A. DuBois
Eileen N. Duesler
Robert T. Paine*

Received November 1, 1984

---

(14) Some typical Mn-phosphine Mn–P distances: $[Mn(CO)_4PEt_3]_2$, 2.247 (7) Å;[14a] $ClMn(CO)_4(PPh_3)$, 2.398 (4) Å;[14b] $(CO)_4Mn(H)(PPh_2)Mn(CO)_4$, 2.284 (6) Å;[14c] $[Ph_4P][Mn(CO)_4PPh_3]$, 2.248 (2) Å.[14d] (a) Bennett, M. J.; Mason, R. *J. Chem. Soc. A* **1968**, 75. (b) Vahrenkamp, H. *Chem. Ber.* **1971**, *104*, 449. (c) Doedens, R. J.; Robinson, W. T.; Ibers, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 4323. (d) Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1980**, *19*, 159.

(15) This distance is longer than the Mn–P distances found in several manganese phosphides,[12] 2.36–2.41 Å.

(16) Deviations (Å) from this approximate plane: P(1), +0.029; P(2), −0.070; Mn, 0.130; C(1), −0.041; C(2), 0.041; C(4), −0.006. Nitrogen atom deviations: N(1), 0.453; N(2), 0.186.

Articles

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Cobaltocene Reductions of Multiply Bonded Dirhenium Complexes: Isolation, Characterization, and Reactivity Studies of $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(O_2CR)_4Cl_2]$, $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(PR_3)_2]$, and $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_5(PR_3)_3]$

KIM R. DUNBAR and R. A. WALTON*

Received June 4, 1984

The quadruply bonded dirhenium(III) complexes $Re_2Cl_6(PR_3)_2$ (PR_3 = PEt_3, P-*n*-Pr_3, $PMePh_2$, $PEtPh_2$) and $Re_2(O_2CR)_4Cl_2$ (R = C_3H_7, CMe_3, Ph) are reduced by cobaltocene in acetone to give the paramagnetic salts $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(PR_3)_2]$ and $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(O_2CR)_4Cl_2]$, respectively, complexes which are derivatives of the Re_2^{5+} core. The cobaltocene reduction of $Re_2Cl_5(PMePh_2)_3$ to give $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3]$ and its oxidation to $[Re_2Cl_5(PMePh_2)_3]PF_6$ by $NO^+PF_6^-$ have also been accomplished. These results demonstrate that mixed halide–phosphine complexes of Re_2^{n+} (n = 6, 5, 4) exhibit the most extensive redox chemistry of any class of multiply bonded dimetal species. The nonredox substitution chemistry of $[Re_2Cl_6(PR_3)_2]^-$ with PR_3 and of $[Re_2Cl_5(PR_3)_3]^-$ with PR_3 has been shown to lead to the formation of $Re_2Cl_5(PR_3)_3$ and $Re_2Cl_4(PR_3)_4$, respectively.

Introduction

The redox properties of compounds that possess multiple metal–metal bonds are developing into an important facet of the chemistry of this class of molecules.[1] Dirhenium complexes have proved especially interesting because of their ability to undergo multiple-electron oxidations or reductions without disruption of the dimetal unit. One such example is that of the net four-electron reduction of the Re(IV) anion $[Re_2Cl_9]^-$, possessing a Re–Re triple bond ($\sigma^2\pi^4$ configuration), to give the Re(II) complex $Re_2Cl_4(PEt_3)_4$, also possessing a formal bond order of 3 ($\sigma^2\pi^4\delta^2\delta^{*2}$).[2] Previous studies on the electrochemistry of $Re_2X_4(PR_3)_4$ and $Re_2X_4(LL)_2$ (X = Cl, Br, I; LL = 1,2-bis(diphenylphosphino)ethane or 1-(diphenylphosphino)-2-(diphenylarsino)ethane)[3,4] led to the discovery of a novel series of coupled electrochemical–chemical reactions and the isolation of the paramagnetic monocations of these complexes.[5-7] More recently,[8] the isolation and

---

(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; see also references therein.

(2) Hertzer, C. A.; Walton, R. A. *Inorg. Chim. Acta* **1977**, *22*, L10.

(3) Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 1987.

(4) Ebner, J. R.; Tyler, D. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 833.

structural determination of the series $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_n$ (n = 0, 1, 2) have allowed for a direct measurement and interpretation of the variation of M–M bond length with change in formal bond order.

A logical and important extension of this simple electron-transfer chemistry is to those species that possess accessible, electrochemically and chemically reversible reductions. With this objective in mind, we have been developing the use of cobaltocene as a clean one-electron-transfer reagent for the preparation of anionic multiply bonded dimetal species and have recently been successful in preparing the diosmium species $[Os_2(O_2CR)_4Cl_2]^-$ (R = C_2H_5, C_3H_7) and $[Os_2(hp)_4Cl_2]^-$ (Hhp is 2-hydroxypyridine).[9] In the present report we describe the synthesis and characterization of salts of anions of the types $[Re_2Cl_6(PR_3)_2]^-$, $[Re_2Cl_5(PR_3)_3]^-$, and $[Re_2(O_2CR)_4Cl_2]^-$ and compare their properties with those of other isoelectronic dirhenium(III,II) and dirhenium(II,II) species.

Experimental Section

Starting Materials. The complexes of the types $Re_2Cl_6L_2$ (L = PEt_3, P-n-Pr_3, $PEtPh_2$, $PMePh_2$),[3] $Re_2Cl_5(PMePh_2)_3$,[3] and $Re_2(O_2CR)_4Cl_2$ (R = n-Pr, t-Bu, Ph)[10] were prepared according to standard literature procedures. The phosphine ligands, the carboxylic acids, and cobaltocene were obtained from commercial sources and used without further purification. Solvents were dried and freshly distilled under nitrogen prior to use.

Reaction Procedures. All reactions were carried out in a dry nitrogen atmosphere with standard vacuum-line techniques. Schlenk-ware was used for the isolation of the cobaltocene salts of the carboxylate anions.

A. Reactions of $Re_2Cl_6(PR_3)_2$ with Cobaltocene. (i) $Re_2Cl_6(PEt_3)_2$. In a typical reaction, $Re_2Cl_6(PEt_3)_2$ (0.24 g, 0.30 mmol) was dissolved in 20 mL of dry, freshly distilled acetone to which was added 1 equiv of cobaltocene (0.056 g, 0.30 mmol) via a side-arm addition tube. The reaction solution was stirred at room temperature for 15 min and then chilled to 0 °C for 1 h. The resulting dark green solid was filtered off, washed with acetone followed by diethyl ether, and dried in vacuo; yield 0.18 g (60%). Anal. Calcd for $C_{22}H_{40}Cl_6CoP_2Re_2$: C, 26.15; H, 3.99. Found: C, 26.17; H, 3.98.

(ii) $Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2$. A mixture comprising $Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2$ (0.25 g, 0.28 mmol) and cobaltocene (0.052 g, 0.28 mmol) was added to 10 mL of acetone at 0 °C. The lower reaction temperature was necessary in this instance to prevent decomposition of the product, which is quite soluble in most solvents, unlike its other phosphine analogues. The green-brown solution was stirred for 10 min and reduced in volume to approximately 3 mL. A gray-green solid was filtered off, and the resulting filtrate was treated with diethyl ether to produce additional product. The combined solids were washed with diethyl ether and dried in vacuo; yield 0.21 g (69%). Anal. Calcd for $C_{28}H_{52}Cl_6CoP_2Re_2$: C, 30.72; H, 4.79. Found: C, 30.91; H, 4.48.

(iii) $Re_2Cl_6(PMePh_2)_2$. Stoichiometric quantities of $Re_2Cl_6(PMePh_2)_2$ (0.15 g, 0.152 mmol) and cobaltocene (0.029 g, 0.15 mmol) were suspended in 10 mL of acetone. The reaction solution was stirred at room temperature for 1 h to give a pale yellow solution and a tan precipitate. The product was collected by filtration, washed with copious amounts of acetone, and dried in vacuo; yield 0.13 g (74%). Anal. Calcd for $C_{36}H_{36}Cl_6CoP_2Re_2$: C, 36.81; H, 3.09. Found: C, 36.52; H, 2.92.

(iv) $Re_2Cl_6(PEtPh_2)_2$. With the use of a procedure similar to that in section A(i), $Re_2Cl_6(PEtPh_2)_2$ (0.30 g, 0.296 mmol) and cobaltocene (0.57 g, 0.30 mmol) were stirred for 0.5 h at room temperature in 20 mL of acetone. The solution was chilled to 0 °C, and a quantity of pale green solid was collected, washed with acetone, and dried in vacuo; yield 0.332 g (93%). Anal. Calcd for $C_{38}H_{40}Cl_6CoP_2Re_2$: C, 37.94; H, 3.35. Found: C, 37.84; H, 3.50.

B. Reactions of $Re_2Cl_5(PMePh_2)_3$. (i) Reaction with Cobaltocene. A mixture of $Re_2Cl_5(PMePh_2)_3$ (0.155 g, 0.135 mmol) and cobaltocene (0.026 g, 0.137 mmol) was suspended in 10 mL of acetone and stirred for 0.5 h. The resulting orange-brown solid was filtered off under nitrogen, and the orange filtrate was reduced in volume to yield additional product. The solids were washed with diethyl ether and vacuum dried; combined yield 0.130 g (72%). Anal. Calcd for $C_{49}H_{49}Cl_5CoP_3Re_2$: C, 43.94; H, 3.69. Found: C, 44.25; H, 4.12.

(ii) Reaction with Nitrosonium Hexafluorophosphate. A quantity of $Re_2Cl_5(PMePh_2)_3$ (0.150 g, 0.130 mmol) was suspended in 5 mL of freshly distilled acetonitrile to which was added 0.23 g of $NOPF_6$. The solution immediately turned a deep purple color, with concomitant precipitation of a purple-gray solid. A quantity of KPF_6 was added to aid the precipitation of the salt. The reaction mixture was chilled to 0 °C, and the product was collected by filtration, washed with ethanol and then diethyl ether, and dried under reduced pressure; yield 0.13 g (76%). Anal. Calcd for $C_{39}H_{39}Cl_5F_6P_4Re_2$: C, 36.16; H, 3.03. Found: C, 35.81; H, 2.82.

C. Reactions of the Cobaltocenium Salts. (i) Preparation of $Re_2Cl_5(PEt_3)_3$. A mixture of $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(PEt_3)_2]$ (0.10 g, 0.099 mmol) and triethylphosphine (0.1 mL) was dissolved in 15 mL of CH_2Cl_2, and the solution was stirred for 5 min at room temperature, during which time its color changed from dark green to bright olive green. The solvent was distilled off under reduced pressure, and the resulting residue was extracted with acetone and recrystallized from acetone–diethyl ether; yield 0.07 g (78%). The product was identified by means of its ESR spectral and electrochemical properties through a comparison with those exhibited by an authentic sample of $Re_2Cl_5(PEt_3)_3$.[6]

(ii) Preparation of $Re_2Cl_4(PMePh_2)_4$. $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3]$ (0.20 g, 0.170 mmol) and $PMePh_2$ (0.8 mL) were dissolved in 15 mL of CH_2Cl_2, and the mixture was stirred at room temperature for 3 h. The green solution was reduced in volume, and ethanol was added to precipitate the product. A cyclic voltammogram of the crude solid revealed that it was a mixture and that one of the minor components was $Re_2Cl_5(PMePh_2)_3$. The latter product was removed by extraction into acetone. The remaining light green insoluble solid was recrystallized from dichloromethane–diethyl ether at 0 °C; yield 0.12 g (55%). Anal. Calcd for $C_{52}H_{52}Cl_4P_4Re_2$: C, 47.49; H, 3.99. Found: C, 47.35; H, 3.55.

D. Reduction of $Re_2(O_2CR)_4Cl_2$ by Cobaltocene To Give $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(O_2CR)_4Cl_2]$. (i) n-Butyrate (R = C_3H_7). $Re_2(O_2CC_3H_7)_4Cl_2$ (0.20 g, 0.25 mmol) and 1 equiv of cobaltocene (0.05 g, 0.25 mmol) were added to 6 mL of acetone, and the mixture was stirred for 10 min at room temperature. The insoluble light green solid was filtered off under nitrogen and washed with acetone and diethyl ether; yield 0.170 g (70%). Anal. Calcd for $C_{26}H_{38}Cl_2CoO_8Re_2$: C, 31.84; H, 3.90. Found: C, 32.15; H, 3.78.

(ii) Pivalate (R = CMe_3). A small quantity of $Re_2(O_2CCMe_3)_4Cl_2$ (0.164 g, 0.193 mmol) was stirred for 1 h at 0 °C in a solution containing 0.037 g of cobaltocene in 10 mL of acetone. The pale green insoluble product was collected under nitrogen, washed with acetone, and dried in vacuo; yield 0.123 g (62%). Anal. Calcd for $C_{30}H_{46}Cl_2CoO_8Re_2$: C, 34.72; H, 4.47. Found: C, 35.37; H, 4.59.

(iii) Benzoate (R = Ph). A mixture of $Re_2(O_2CC_6H_5)_4Cl_2$ (0.20 g, 0.22 mmol) and cobaltocene (0.042 g, 0.22 mmol) was suspended in 10 mL of acetone and stirred under nitrogen for 20 min at 0 °C. The resulting mustard-colored solid was filtered off, washed with acetone, and dried in vacuo; yield 0.18 g (73%). Although the spectroscopic and electrochemical properties of this product confirmed its identity, a satisfactory microanalysis could not be obtained. Anal. Calcd for $C_{38}H_{30}Cl_2CoO_8Re_2$: C, 40.86; H, 2.71. Found: C, 39.13; H, 2.84.

E. Preparation of Complexes of the Type $Re_2Cl_6(PR_3)_2$. In spite of the well-characterized nature of this class of complex,[1,3] details of the preparative recipes that maximize the product yields and avoid contamination by $Re_2Cl_5(PR_3)_3$ and $Re_2Cl_4(PR_3)_4$ impurities are not readily available. This oversight is corrected herein, where we give the conditions that we recommend be used. In all instances, the identities and purities of the products were confirmed by their spectral and electrochemical properties.[3,6]

(i) Triethylphosphine. In a typical reaction 0.50 g (0.44 mmol) of $(n\text{-}Bu_4N)_2Re_2Cl_8$, 20 mL of methanol, 0.5 mL of concentrated HCl, and 0.80 mL of PEt_3 were stirred under nitrogen for 4 h at 0 °C. The resulting insoluble green precipitate was filtered off and washed with methanol; yield 0.263 g (77%). The unrecrystallized product was found to be pure upon examination of its electrochemical properties.

(ii) Tri-n-propylphosphine. In a procedure essentially identical with that in section E(i), reagents in the stated proportions were stirred for

---

(5) Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 991.

(6) Brant, P.; Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 4424.

(7) Brant, P.; Glicksman, H. D.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 3202.

(8) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.

(9) Tetrick, S. M.; Coombe, V. T.; Heath, G. A.; Stephenson, T. A.; Walton, R. A. *Inorg. Chem.*, in press.

(10) Cotton, F. A.; Oldham, C.; Robinson, W. R. *Inorg. Chem.* **1966**, *5*, 1798.

Table I. Spectroscopic and Conductivity Data for Cobaltocenium Salts of Dirhenium Complexes

complex	medium[a]	electronic abs max,[b] nm	conductivity,[c] Ω^{-1} cm^2 mol^{-1}
$[(C_5H_5)_2Co][Re_2Cl_6(PEt_3)_2]$	CH_2Cl_2	1525 (1200), 715 (400)	120
$[(C_5H_5)_2Co][Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2]$	CH_2Cl_2	1450 (1000), 715 (430)	115
$[(C_5H_5)_2Co][Re_2Cl_6(PEtPh_2)_2]$	CH_2Cl_2	1475 (1000), 715 (400)	118
$[(C_5H_5)_2Co][Re_2Cl_6(PMePh_2)_2]$	CH_2Cl_2	1475 (1100), 710 (410)	123
$[(C_5H_5)_2Co][Re_2(O_2CC_3H_7)_4Cl_2]$	NM	715	127
	CH_3CN	710 (100), 380 (6000)	
$[(C_5H_5)_2Co][Re_2(O_2CCMe_3)_4Cl_2]$	NM	700	118
	CH_3CN	690 (100), 400 (6000)	
$[(C_5H_5)_2Co][Re_2(O_2CC_6H_5)_4Cl_2]$	NM	760	115
	CH_3CN	745 (140)	

[a] The solution spectra were run under anaerobic conditions in a specially designed quartz cell. Nujol mulls (NM) were prepared under N_2, and their spectra were run as diffuse reflectance spectra. [b] Extinction coefficients are given in parentheses. [c] Conductivity measurements were done on 1×10^{-3} M acetonitrile solutions.

2.5 h at room temperature; yield 0.28 g (77%).

(iii) Tri-*n*-butylphosphine. Typically, 1.0 g (0.88 mmol) of $(n\text{-}Bu_4N)_2Re_2Cl_8$, 1.2 mL of $P\text{-}n\text{-}Bu_3$, 20 mL of methanol, and 15 drops of concentrated HCl were stirred under nitrogen for 3 h at 0 °C. The resulting crude solid was filtered off and dissolved in diethyl ether, the solution filtered, and the product reprecipitated by addition of methanol to the filtrate; yield 0.662 g (76%).

(iv) Methyldiphenylphosphine. $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.50 g, 0.44 mmol), 0.6 mL of $PMePh_2$, 25 mL of methanol, and 1 mL of concentrated HCl were stirred at room temperature for 0.5 h. The resulting olive green precipitate was filtered off, washed with methanol, and dried in vacuo; yield 0.41 g (95%).

(v) Ethyldiphenylphosphine. In a procedure similar to that in section E(iv), 0.40 g of $(n\text{-}Bu_4N)_2Re_2Cl_8$, 0.3 mL of $PEtPh_2$, 20 mL of methanol, and 0.5 mL of HCl were stirred at room temperature for 0.5 h; yield 0.30 g (86%).

(vi) Dimethylphenylphosphine. A quantity of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.50 g, 0.44 mmol) was stirred under nitrogen for 5 h in a solution of 25 mL of methanol, 0.5 mL of concentrated HCl, and 0.6 mL of PMe_2Ph. The green solid was removed by filtration and washed with methanol followed by diethyl ether; yield 0.349 g (93%).

F. Preparation of $Re_2Cl_5(PEt_3)_3$. A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.30 g, 0.26 mmol), 0.6 mL of PEt_3, 15 mL of methanol, and 0.3 mL of concentrated HCl was stirred for 5 min at room temperature and subsequently chilled for 1 h at 0 °C. A green solid (0.02 g) was filtered off, and cyclic voltammetry revealed that it was a mixture of $Re_2Cl_4(PEt_3)_4$ and $Re_2Cl_5(PEt_3)_3$. The volume of the solution was reduced under nitrogen, and addition of diethyl ether precipitated 0.15 g (55%) of green product, which was identified as $Re_2Cl_5(PEt_3)_3$ on the basis of its spectroscopic and electrochemical properties.[6]

Physical Measurements. Electrochemical measurements were made in dichloromethane or acetonitrile solvents that contained 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values were determined as $(E_{p,a} + E_{p,c})/2$ and are referenced to the saturated potassium chloride calomel electrode (SCE) at room temperature. Voltammetric experiments were performed with a Bioanalytical System, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B X-Y recorder. Conductivity measurements were performed on 1×10^{-3} M acetonitrile solutions with use of an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. Electronic absorption spectra were recorded as CH_2Cl_2 or CH_3CN solutions on Cary 17 (region 1800–900 nm) and IBM 9420 UV-visible spectrophotometers. X-Band ESR spectra of dichloromethane solutions were recorded at −160 °C with use of a Varian E-109 spectrometer.

Analytical Procedures. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results and Discussion

a. Preparation and Reactivity of the Complexes $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(PR_3)_2]$ (PR_3 = PEt_3, $P\text{-}n\text{-}Pr_3$, $PMePh_2$, $PEtPh_2$). The neutral species $Re_2Cl_6(PR_3)_2$ possess a very accessible, electrochemically reversible one-electron reduction in the potential range +0.1 to −0.15 V vs. SCE.[6] We find that these complexes can be reduced chemically using acetone solutions of cobaltocene to produce the salts $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(PR_3)_2]$. Although the use of other solvents such as dichloromethane and tetrahydrofuran was investigated, none were as satisfactory as acetone in yielding products of suitable purity. The derivatives where PR_3 = $PMePh_2$ or $PEtPh_2$ were the most insoluble of the complexes that we isolated, a property that aided their stability. Solutions of these complexes are rather air sensitive, certainly more so than are the solids, and so must be handled under a nitrogen or argon atmosphere.

The electronic absorption spectra of these salts show a fairly intense band at ~1500 nm (Table I) that is readily assignable to the $\delta \rightarrow \delta^*$ transition of the Re_2^{5+} core.[1,11-13] X-Band ESR spectral studies on CH_2Cl_2 glasses (in CH_2Cl_2 at −160 °C) of all four complexes show that they are characterized by broad signals centered at ~2700 G, in accord with the spectral features reported previously[6,8,14] for dirhenium phosphine complexes containing the Re_2^{5+} core. In fact, solutions of one of the anions reported in this work, i.e. $[Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2]^-$, were generated electrochemically in an earlier study,[6] and its ESR spectrum was recorded (see Figure 1A of ref 6). This spectrum is identical with that of the chemically generated anion as is present in $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2]$. For all four complexes, the $g_\perp$ values are estimated to be ca. 2.40 with values of $A_\perp$ on the order of 75–100 G. From the spacing of the two lines at lowest fields, $A_\parallel$ is found to be ~350 G, and on the basis of an 11-line spectrum that arises from the coupling to two equivalent rhenium nuclei (i.e. $4(5/2) + 1 = 11$), $g_\parallel \simeq 2.2$. These values agree nicely with those reported in the earlier studies.

Solutions of these complexes in acetonitrile possess conductivities (Λ_M = 115–125 Ω^{-1} cm^2 mol^{-1}) that are consistent with their being 1:1 electrolytes (Table I). The electrochemical properties of these complexes were investigated by the technique of cyclic voltammetry, and the half-wave potentials vs. SCE for 0.2 M TBAH–dichloromethane solutions are presented in Table II. All the cobaltocenium salts possess a reduction at $E_{1/2} \simeq -0.90$ V vs. SCE, representing the couple $Co(C_5H_5)_2^+ + e^- \rightleftharpoons Co(C_5H_5)_2$, the presence of which serves as a means of monitoring the success of the reduction. On the basis of a consideration of the relative peak currents associated with this couple and any that arise from the dirhenium unit, the approximate stoichiometry of the resulting complex can easily be ascertained. The $[Re_2Cl_6(PR_3)_2]^-$ anions each exhibit a one-electron oxidation with $E_{1/2}$ values between +0.06 and −0.12 V vs. SCE. For sweep rates (v) ranging from 50 to 400 mV/s, the ratio $i_p/v^{1/2}$ was found to be constant and $i_{p,a}/i_{p,c} \approx 1$, in accord with diffusion control. The potential separation between anodic and cathodic peaks, ΔE_p, was ~100 mV for sweep rates of 200 mV/s. With our cell configuration, these properties are consistent with a reversible electron-transfer process.[15] These complexes also exhibit a second reduction at quite

---

(11) Ebner, J. R.; Walton, R. A. *Inorg. Chim. Acta* **1975**, *14*, L45.

(12) Cotton, F. A.; Fanwick, P. E.; Gage, L. D.; Kalbacher, B.; Martin, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 5648.

(13) Bursten, B. E.; Cotton, F. A.; Fanwick, P. E.; Stanley, G. G.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 2606.

(14) Cotton, F. A.; Pedersen, E. *J. Am. Chem. Soc.* **1975**, *97*, 303.

Table II. Cyclic Voltammetric Data for Dichloromethane Solutions of Dirhenium Complexes[a]

complex	$E_{1/2}(\text{ox})_2$	$E_{1/2}(\text{ox})_1$	$E_{1/2}(\text{red})_1$[b]	$E_{1/2}(\text{red})_2$
$[(C_5H_5)_2Co][Re_2Cl_6(PEt_3)_2]$		−0.06	−0.90	−1.15[c]
$[(C_5H_5)_2Co][Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2]$		−0.12	−0.90	−1.30[c]
$[(C_5H_5)_2Co][Re_2Cl_6(PMePh_2)_2]$		+0.06	−0.93	−0.97
$[(C_5H_5)_2Co][Re_2Cl_6(PEtPh_2)_2]$		0.00	−0.95[d]	−0.95[d]
$[(C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3]$	+0.51	−0.62	−0.89	
$[Re_2Cl_5(PMePh_2)_3]PF_6$			+0.50	−0.64
$Re_2Cl_4(PMePh_2)_4$	+0.90	−0.19		
$[(C_5H_5)_2Co][Re_2(O_2CC_3H_7)_4Cl_2]$		−0.35	−0.95	
$[(C_5H_5)_2Co][Re_2(O_2CCMe_3)_4Cl_2]$		−0.44	−0.95	
$[(C_5H_5)_2Co][Re_2(O_2CC_6H_5)_4Cl_2]$		−0.31	−0.93	

[a] $E_{1/2}$ values in volts vs. SCE; Pt-bead electrode in dichloromethane with 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. [b] With the exception of the complexes $[Re_2Cl_5(PMePh_2)_3]PF_6$ and $Re_2Cl_4(PMePh_2)_4$, these values are for the $[(\eta^5\text{-}C_5H_5)_2Co]^+ + e^- \rightleftharpoons [(\eta^5\text{-}C_5H_5)_2Co]$ couple. [c] $E_{p,c}$ value; $i_{p,c}/i_{p,a} \neq 1$. [d] Overlap of couples associated with the cation and anion.

negative potentials, with $E_{1/2}$ values ranging from −0.90 to −1.30 V vs. SCE. This process is associated with the reduction of $[Re_2Cl_6(PR_3)_2]^-$ to the corresponding dianion. For the $PMePh_2$ and $PEtPh_2$ compounds, this reduction approaches chemical reversibility (*n* values ~1); however, it is apparently irreversible ($i_{p,a}/i_{p,c} \neq 1$) for the complexes that contain the trialkylphosphine ligands PEt_3 and $P\text{-}n\text{-}Pr_3$. Also, for the complex $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(PEtPh_2)_2]$, the couples due to $[(\eta^5\text{-}C_5H_5)_2Co]^+/[(\eta^5\text{-}C_5H_5)_2Co]$ and to $[Re_2Cl_6(PR_3)_2]^-/[Re_2Cl_6(PR_3)_2]^{2-}$ were sufficiently close so as to overlap, thereby giving a "couple" at −0.95 V that possessed twice the expected current. Representative voltammograms are shown in Figure 1a,b.

One of our interests in isolating salts of the $[Re_2Cl_6(PR_3)_2]^-$ anions that possess the Re_2^{5+} core was to study their reactivity toward phosphine ligands. We had observed previously[6] while studying the oxidation chemistry of the $Re_2Cl_4(PR_3)_4$ systems (Re_2^{4+} core) that coupled electrochemical (E)–chemical (C) reactions (involving reaction with Cl^-) led to the formation of $Re_2Cl_5(PR_3)_3$ and $Re_2Cl_6(PR_3)_2$, the processes being designated either EECC or ECEC depending upon the selection of the potential used for oxidation of $Re_2Cl_4(PR_3)_4$, i.e. depending upon whether oxidation to $[Re_2Cl_4(PR_3)_4]^+$ or $[Re_2Cl_4(PR_3)_4]^{2+}$ had occurred. An analogous mechanism could be envisioned to exist for the reverse process, that is the stepwise reduction of dinuclear Re_2^{6+} complexes to Re_2^{5+} and then to the Re_2^{4+}, either chemically or electrochemically, followed by the reaction of the resulting anion with phosphine ligand. An example of the first step (i.e. $Re_2^{6+} \rightarrow Re_2^{5+}$) is the cobaltocene reduction of $Re_2Cl_6(PEt_3)_2$ to the monoanion $[Re_2Cl_6(PEt_3)_2]^-$ and its subsequent reaction with 1 equiv of PEt_3 (eq 1 and 2) to yield the substitution product

$$Re_2Cl_6(PEt_3)_2 + (C_5H_5)_2Co \rightarrow [(C_5H_5)_2Co][Re_2Cl_6(PEt_3)_2] \qquad (1)$$

$$[(C_5H_5)Co][Re_2Cl_6(PEt_3)_2] + PEt_3 \rightarrow Re_2Cl_5(PEt_3)_3 + [(C_5H_5)_2Co]^+ + Cl^- \qquad (2)$$

$Re_2Cl_5(PEt_3)_3$ in high yield (see Experimental Section part C(i)). The identity of this compound was confirmed by comparing its electrochemical properties and X-band ESR spectrum to those reported for an authentic sample of this complex.[6] A conversion of the type $Re_2^{5+} \rightarrow Re_2^{4+}$ is discussed in the next section.

b. Preparation and Reactivity of the Monocation and Monoanion of $Re_2Cl_5(PMePh_2)_3$. The one-electron reduction of $Re_2Cl_5(PMePh_2)_3$, which occurs at $E_{1/2}$ = −0.62 V vs. SCE as measured by cyclic voltammetry, can be accomplished chemically via a one-electron-transfer reaction with cobaltocene (eq 3). The resulting complex is quite air sensitive even in the solid state, which is not surprising in view of the fact that it possesses an oxidation at a rather negative potential; nonetheless, it can be handled in solution under stringent anaerobic conditions. This complex, which is the only one of its kind to have yet been prepared, exhibits electrochemistry that is consistent with its formulation as the one-electron-reduction product of the parent neutral compound. The diamagnetic dirhenium(II) anion possesses two reversible one-electron oxidations at $E_{1/2}(\text{ox})_1$ = −0.62 V and $E_{1/2}(\text{ox})_2$ = +0.51 V vs. SCE, each with $i_{p,a}/i_{p,c}$ = 1 and $\Delta E_p \simeq$ 95 mV. The

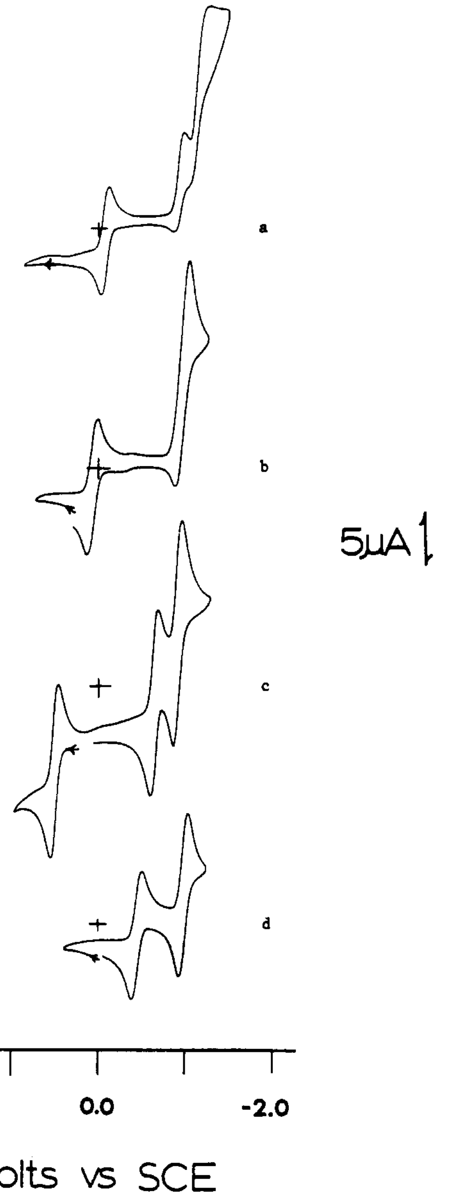
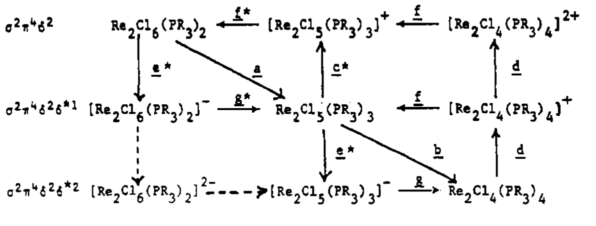


Figure 1. Cyclic voltammograms in 0.2 M TBAH–dichloromethane (at 200 mV/s with a Pt-bead electrode): (a) $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(PEt_3)_2]$; (b) $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(PMePh_2)_2]$; (c) $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3]$; (d) $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(O_2CCMe_3)_4Cl_2]$.

---

(15) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

Scheme I



Chemical reactions are as follows: (a) reaction with PR_3 at room temperature; (b) reaction with PR_3 under reflux; (c) reaction with $NO^+PF_6^-$ in CH_2Cl_2 at room temperature; (d) reaction with $NO^+PF_6^-$ in CH_3CN at room temperature; (e) reaction with Cp_2Co in acetone at room temperature; (f) reaction with one-equivalent of Cl^-; (g) reaction with one equivalent of PR_3.

usual couple due to the cation is located at $E_{1/2} = -0.89$ V (Figure 1c).

The reaction of the dirhenium(II) complex $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3]$ with 1 equiv of $PMePh_2$ yields the product $Re_2Cl_4(PMePh_2)_4$, through the loss of chloride ion and substitution by a phosphine ligand (eq 4). This new compound is one of a class of $Re_2Cl_4(PR_3)_4$ complexes that can be prepared directly by reaction of $[Re_2Cl_8]^{2-}$ with PR_3 or PR_2Ph (R = alkyl).[3] In the case of phosphines containing two phenyl groups such as $PMePh_2$ or $PEtPh_2$, the reaction stops at the stage $Re_2Cl_5(PRPh_2)_3$ due, we believe, to the poorer reducing tendencies of these particular phosphines. When the phosphine is switched to PPh_3, then the reaction does not proceed beyond the substitution product $Re_2Cl_6(PPh_3)_2$, due perhaps in part to the insolubility of the product, which leads to its immediate precipitation from the reaction solution. However, steric and/or electronic factors may also be important. That the extent of reduction is dependent on the basicity of the phosphines and less so upon steric factors, except perhaps in the case of PPh_3, is supported by the successful isolation of $Re_2Cl_4(PMePh_2)_4$ (eq 4) in this work, as well as by two previous observations. First, addition of $NaBH_4$ to a solution contaning $(n\text{-}Bu_4N)_2Re_2Cl_8$ and $PEtPh_2$ leads to reduction to $Re_2Cl_4(PEtPh_2)_4$.[16] Second, the isolation of the quadruply bonded dimolybdenum(II) complexes $Mo_2Cl_4(PRPh_2)_4$ (R = Me, Et) confirms that the steric bulk of these phosphine ligands is not sufficient to destabilize the eclipsed $M_2X_4(PRPh_2)_4$ structure.[17]

$$Re_2Cl_5(PMePh_2)_3 + (C_5H_5)_2Co \rightarrow [(C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3] \quad (3)$$

$$[(C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3] + PMePh_2 \rightarrow Re_2Cl_4(PMePh_2)_4 + [(C_5H_5)_2Co]^+ + Cl^- \quad (4)$$

In addition to the accessibility of the one-electron reduction of $Re_2Cl_5(PMePh_2)_3$ (vide supra), this type of complex possesses an equally accessible oxidation, at least as has been demonstrated by cyclic voltammetry.[6] This has been accomplished chemically in the present study through the reaction of the parent neutral compound with nitrosonium hexafluorophosphate. This yields the dirhenium(III) monocation in $[Re_2Cl_5(PMePh_2)_3]PF_6$ (eq 5), the first example of its kind to have been isolated. This diamagnetic salt is fairly stable, and it possesses two one-electron reductions with half-wave potentials of +0.50 and −0.64 V vs. SCE (Table II). As expected, the addition of Cl^- ion to an electrochemical cell that contained a solution of $[Re_2Cl_5(PMePh_2)_3]PF_6$ in 0.2 M TBAH–dichloromethane leads to the formation of $Re_2Cl_6(PMePh_2)_2$ (eq 6) in close to quantitative yield, as monitored by cyclic voltammetry.

$$Re_2Cl_5(PMePh_2)_3 + NOPF_6 \rightarrow [Re_2Cl_5(PMePh_2)_3]PF_6 + NO \quad (5)$$

$$[Re_2Cl_5(PMePh_2)_3]PF_6 + Cl^- \rightarrow Re_2Cl_6(PMePh_2)_2 + PMePh_2 + PF_6^- \quad (6)$$

c. Cobaltocene Reductions of the Neutral Carboxylates $Re_2(O_2CR)_4Cl_2$ (R = C_3H_7, CMe_3, C_6H_5). A group of three different carboxylate anions were prepared in order to demonstrate the general utility of the cobaltocene reduction procedure. These reactions proceed rapidly in acetone solution at room temperature or 0 °C, although neither the neutral complex nor cobaltocene is particularly soluble in this solvent. The salts precipitate immediately upon their formation and are difficult to purify because of their very limited solubility in polar solvents and their air sensitivity. In the case of the benzoate, an analytically pure sample could not be isolated. The paramagnetic nature of these compounds was confirmed by measuring their low-temperature X-band ESR spectra. A fairly detailed interpretation of these complex signals was published by Cotton and Pedersen,[14] who recorded the frozen-solution ESR spectrum of electrochemically generated $[Re_2(O_2CC_6H_5)_4Cl_2]^-$. A more complete spectroscopic study was later conducted by Srinivasan and Walton,[18] who investigated a much wider range of electrochemically generated $[Re_2(O_2CR)_4X_2]^-$ anions, including those where X = Cl, Br, or I. As far as we can tell, the X-band ESR spectra of $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(O_2CR)_4Cl_2]$ (R = C_3H_7, CMe_3, C_6H_5) are identical in every respect with the spectra of the electrochemically generated anions.[14,18]

These complexes form solutions in acetonitrile that have conductivities in accord with their behaving as 1:1 electrolytes (Table I). An investigation of their electronic absorption spectra (as mulls and in acetonitrile) showed that their lowest energy absorption band occurs quite close to 700 nm ($\epsilon_{max} \approx 100\text{–}150$; see Table I). Since the $\delta \rightarrow \delta^*$ transition of the neutral $Re_2(O_2CR)_4X_2$ species is apparently located in the vicinity of 500 nm,[18-20] a shift of such a transition to lower energy (in this instance to 700 nm) in the case of the analogous Re_2^{5+} derivatives $[Re_2(O_2CR)_4Cl_2]^-$ is quite reasonable and is, perhaps, to be expected.[13] A shift of this kind, although of a different magnitude, is observed upon comparing the spectra of the Re_2^{6+} complexes $Re_2Cl_6(PR_3)_2$ with their Re_2^{5+} analogues $[Re_2Cl_6(PR_3)_2]^-$ (and with $Re_2Cl_5(PR_3)_3$ and $[Re_2Cl_4(PR_3)_4]^+$).

The paramagnetic cobaltocenium salts of the $[Re_2(O_2CR)_4Cl_2]^-$ anions display the expected electrochemistry, namely a very accessible one-electron oxidation in which the corresponding neutral carboxylate species is regenerated. The voltammetric half-wave potentials for the three carboxylate anions prepared in this study are listed in Table II, and the cyclic voltammogram of the pivalate derivative is shown in Figure 1d. The potentials for this oxidation reflect the trend noted in the earlier study of the neutral compounds by Srinivasan and Walton;[18] that is, the $E_{1/2}$ values become more negative as the R group of the carboxylate becomes more electron donating. All three complexes are easily oxidized when their solutions are exposed to air, an unidentified blue-green decomposition product being formed along with some of the original neutral carboxylate $Re_2(O_2CR)_4Cl_2$.

d. Concluding Remarks. The chemical redox and substitution reactions that are described in sections a and b may be incorporated into Scheme I, which summarizes the rich chemical redox chemistry that characterizes the dirhenium unit in multiply bonded complexes containing Re–Re bond orders of 4, 3.5, and 3.[21] This scheme incorporates the results of the present study (*these steps are denoted by an asterisk*) together with those from earlier investigations.[3,6,8] It reveals that the mixed halide–phosphine complexes of Re_2^{n+} (n = 6, 5, 4) exhibit the most extensive and

---

(16) Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2674.
(17) Glicksman, H. D.; Hamer, a. D.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 2205.
(18) Srinivasan, V.; Walton, R. A. *Inorg. Chem.* **1980**, *19*, 1635.
(19) Collins, D. M.; Cotton, F. A.; Gage, L. D. *Inorg. Chem.* **1979**, *18*, 1712.
(20) Martin, D. S.; Huang, H.-W.; Newman, R. A. *Inorg. Chem.* **1984**, *23*, 699.
(21) Walton, R. A. *Isr. J. Chem.*, in press.

best defined redox chemistry of any class of multiply bonded dimetal species.[1] The only conversions that remain to be accomplished are shown by dashed lines in Scheme I. These await the one-electron chemical reduction of $[Re_2Cl_6(PR_3)_2]^-$ to $[Re_2Cl_6(PR_3)_2]^{2-}$, a transformation that has so far defied our attempts.

Acknowledgment. Support from the National Science Foundation (Grant No. CHE82-06117) is gratefully acknowledged. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered to the American Chemical Society, for partial support of this research.

Registry No. $[(C_5H_5)_2Co][Re_2Cl_6(PEt_3)_2]$, 93806-21-4; $[(C_5H_5)_2Co][Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2]$, 93806-23-6; $[(C_5H_5)_2Co][Re_2Cl_6(PMePh_2)_2]$, 93806-25-8; $[(C_5H_5)_2Co][Re_2Cl_6(PEtPh_2)_2]$, 93806-27-0; $[(C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3]$, 93841-95-3; $[Re_2Cl_5(PMePh_2)_3]PF_6$, 93806-29-2; $Re_2Cl_4(PMePh_2)_4$, 93806-30-5; $[(C_5H_5)_2Co][Re_2(O_2CC_3H_7)_4Cl_2]$, 93806-31-6; $[(C_5H_5)_2Co][Re_2(O_2CCMe_3)_4Cl_2]$, 93806-33-8; $[(C_5H_5)_2Co][Re_2(O_2CC_6H_5)_4Cl_2]$, 93806-35-0; $[Re_2Cl_6(PEt_3)_2]^{2-}$, 93806-36-1; $[Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2]^{2-}$, 93806-37-2; $[Re_2Cl_6(PMePh_2)_2]^{2-}$, 93806-38-3; $[Re_2Cl_6(PEtPh_2)_2]^{2-}$, 93806-39-4; $[Re_2Cl_5(PMePh_2)_3]^+$, 93806-28-1; $Re_2Cl_6(PEt_3)_2$, 19584-31-7; $Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2$, 41021-44-7; $Re_2Cl_6(PMePh_2)_2$, 55661-11-5; $Re_2Cl_6(PEtPh_2)_2$, 55661-10-4; $Re_2Cl_5(PMePh_2)_3$, 55450-43-6; $Re_2Cl_5(PEt_3)_3$, 61840-74-2; $Re_2(O_2CC_3H_7)_4Cl_2$, 15654-30-5; $Re_2(O_2CCMe_3)_4Cl_2$, 15654-33-8; $Re_2(O_2CC_6H_5)_4Cl_2$, 15654-34-9; $(n\text{-}Bu_4N)_2Re_2Cl_8$, 14023-10-0; $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$, 38832-70-1; $Re_2Cl_6(PMe_2Ph)_2$, 92359-79-0; $[(C_5H_5)_2Co]$, 1277-43-6.

Contribution from the Laboratory of Analytical Chemistry,
Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan

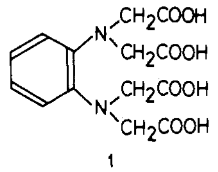
Complexation of *o*-Phenylenediaminetetraacetic Acid with Some Bivalent First-Row Transition-Metal Ions in Aqueous Solution

NORIYUKI NAKASUKA, MIHOKO KUNIMATSU, KAZUNORI MATSUMURA, and MOTOHARU TANAKA*

Received April 23, 1984

Potentiometric and spectrophotometric studies have been carried out on the complexation of *o*-phenylenediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid (PhDTA, H_4L) with some transition-metal ions in aqueous solution at 25 °C and at an ionic strength of 1 M ($NaClO_4$). The studied metal ions include manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II). The usual pH titration method gave satisfactory results for the formation constants K_{ML} for manganese(II) and iron(II), but this was not the case for the other transition metals, whose complexes do not dissociate to an appreciable extent even at pH as low as 2. Therefore copper-selective and mercury electrodes were used to monitor free metal ion concentration in a ligand buffer containing an excess of a second metal ion. Spectrophotometric measurements resulted in an equilibrium constant for a relevant exchange reaction, from which K_{ML} was also obtained. Reduced basicity of the nitrogen atom in PhDTA is reflected in the formation constants of its complexes, which are lower than those of the corresponding EDTA and CyDTA complexes. However, the conditional formation constants of PhDTA complexes become the highest when these complexes are reacted in the acid region. This is due to the lower basicity of the ligand and the formation of diprotonated PhDTA complexes. The logarithmic formation constants of PhDTA complexes are linearly related with those of CyDTA complexes.

Considerable efforts have been devoted to improve the complexing ability of amino polycarboxylates such as ethylenediaminetetraacetic acid (EDTA) by increasing the number of donor atoms or by introducing some groups into the skeleton.[1-3] Although the gauche character of the chelate ring is usually retained in a variety of EDTA derivatives, substitution of the phenylene group for the ethylenic backbone leads to the planar configuration of the N–C–C–N moiety and decreases the basicity of two nitrogen atoms.[4,5] Complexation of *o*-phenylenediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid (**1**) has been, however, little investigated, in spite of the interesting features expected from such structural and electronic modifications. This may be partly due to the considerable difficulty in synthesizing this ligand with chloroacetic acid.[6] The purpose of the present paper is to describe an experimental study on the complexation of this ligand with some divalent transition-metal ions in an aqueous solution.



1

Experimental Section

Reagents. *o*-Phenylenediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid (1,2-phenylenedinitrilotetraacetic acid, abbreviated as PhDTA or H_4L) was prepared according to the method of McCandlish et al.[5] with slight modifications.[7] The reaction mixture was monitored with a combination electrode to maintain the constant pH of the solution.

Triethylenetetramine (trien, Wako, technical grade) was distilled at 160 °C under reduced pressure. The distillate (200 g) was dissolved in 700 g of ethanol, and concentrated hydrochloric acid was added dropwise. 2,2′,2″-Triaminotriethylamine (tren) precipitated first when 100 cm³ of the acid was added. Then a mixture of tren and trien was obtained after 360 cm³ of acid was added. Further addition of hydrochloric acid (570 cm³) and ethanol (100 cm³) gave a white crystal of trien·4HCl. Identification of compounds was carried out by the carbon-13 NMR method. trien·4HCl was recrystallized by dissolving the product in a small quantity of hot water (60 °C), followed by addition of cool ethanol.[8] This procedure was repeated three times, and then the Volhard determination of chloride was applied, resulting in a value of purity of 99.43% for trien·4HCl.

Sodium and other metal perchlorates were prepared by reacting metal carbonates with or by dissolving 99.99% metals in 60% perchloric acid (Wako Pure Chemical Industries), and they were recrystallized two or three times from water.[9] All other chemicals used were of reagent grade.

---

(1) (a) Schwarzenbach, G. *Helv. Chim. Acta* **1946**, *29*, 1338. (b) Schwarzenbach, G. *Adv. Inorg. Chem. Radiochem.* **1961**, *3*, 257–285.
(2) Chaberek, S.; Martell, A. E. "Organic Sequestering Agents"; Wiley: New York, 1959.
(3) Anderegg, G. In "Coordination Chemistry"; Martell, A. E., Ed., Van Nostrand Reinhold: New York, 1971; ACS Monogr. 168, pp 427–490.
(4) Grimes, J. H.; Huggard, A. J.; Wilford, S. P. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1225.
(5) McCandlish, E. F. K.; Michael, T. K.; Neal, J. A.; Lingafelter, E. C.; Rose, N. J. *Inorg. Chem.* **1978**, *17*, 1383.
(6) Otozai, K.; Kato, I. *Jpn. Anal.* **1959**, *8*, 259.
(7) Anal. Calcd for $C_{14}H_{16}O_8N_2$: C, 49.42; N, 8.23; H, 4.74. Found: C, 49.52; N, 8.25; H, 4.74.
(8) Utsuno, S., private communication on the method for purifying trien.
(9) Nakasuka, N.; Makimura, K.; Kajiura, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3749.

0020-1669/85/1324-0010$01.50/0