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(37) If we assume that the maximum amount of a six-coordinate Mn(TPP)(O₂)(py) complex that could go undetected in our titrations is 20% of the total porphyrinatomanganese dioxygen complex present, we can place an upper limit on the equilibrium constant for the binding of a pyridine to Mn(TPP)(O₂) at −78 °C of ~2 × 10⁴. From the equilibrium constant (K^+) at 23 °C in toluene determined for the replacement reaction Crᴵᴵᴵ(TPP)(Cl)(acetone) + py ⇌ Crᴵᴵᴵ(TPP)(Cl)(py) + acetone, ref 32, and using a reasonable value for the change in enthalpy of the reaction of ΔH = −10 kcal/mol (similar to those observed for the bonding of N-donor ligands to metalloporphyrin complexes, Table II), we estimate a value for the log K' of the replacement reaction at −78 °C of ~8.1. We note that for the addition of a pyridine to the five-coordinate Crᴵᴵᴵ(TPP)(Cl), the equilibrium constant would be larger than this value.

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Electrochemical Oxidations of Complexes of Rhenium(II) Containing Metal–Metal Triple Bonds. Synthesis and Characterization of Paramagnetic Cations of the Type [Re₂X₄(PR₃)₄]⁺, Where X = Cl or Br, Possessing Metal–Metal Bonds of Order 3.5

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Abstract: The electrochemical oxidation of the rhenium(II) dimers Re₂X₄(PR₃)₄, where X = Cl, Br, or I and R = Et, *n*-Pr, or *n*-Bu, has been investigated using cyclic voltammetry and coulometry techniques. These studies, coupled with related ones on complexes of the types Re₂X₅(PR₃)₃ and Re₂X₆(PR₃)₂, show that the oxidation of Re₂X₄(PR₃)₄ to [Re₂X₄(PR₃)₄]ⁿ⁺, where *n* = 1 or 2, is followed by the conversion of these cations to Re₂X₅(PR₃)₃ and then Re₂X₆(PR₃)₂. The oxidation of Re₂X₄(PR₃)₄ to Re₂X₆(PR₃)₂ proceeds by both EECC and ECEC coupled electrochemical (E)–chemical (C) reaction series. The difference between these two pathways is the selection of the potential used for the oxidation of Re₂X₄(PR₃)₄. The occurrence of both pathways within the same system is unprecedented, and points to the existence of coupled reactions in the electrochemistry of other metal complexes containing triple and quadruple metal–metal bonds. The mechanism of the chemical reaction which follows the electrochemical oxidation of Re₂X₄(PR₃)₄ has been explored. It is believed that halide ion, generated by the complete disruption of a small proportion of the dimers, reacts with the electrochemically generated cations [Re₂X₄(PR₃)₄]⁺ and [Re₂X₄(PR₃)₄]²⁺ to produce Re₂X₅(PR₃)₃ and [Re₂X₅(PR₃)₃]⁺, respectively. [Re₂X₅(PR₃)₃]⁺ then reacts further with X⁻ to form the final product, Re₂X₆(PR₃)₂. The chemical oxidation of Re₂X₄(PEt₃)₄, where X = Cl or Br, has been achieved using NO⁺PF₆⁻ to afford the salts [Re₂X₄(PEt₃)₄]PF₆. These paramagnetic species possess a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ ground-state electronic configuration and have ESR and electronic absorption spectra which are in accord with a structure in which the cations retain the eclipsed configuration of the parent Re₂X₄(PEt₃)₄ complexes and therefore possess a metal–metal bond order of 3.5. The properties of these new complexes are discussed in detail.

Introduction

There are three main groups of transition metal dimers which are currently recognized as possessing metal–metal triple bonds.[1,2] Those of molybdenum(III) and tungsten(III) which are of the type M₂L₆, where L = CH₂SiMe₃, NMe₂, NEt₂, OCH₂CMe₃, or OSiMe₃,[3–8] or derivatives thereof, have a $(\sigma)^2(\pi)^4$ ground-state electronic configuration and have been the subject of detailed crystallographic and spectral characterizations.[2] The second group comprises the tertiary phosphine derivatives of rhenium(II), Re₂X₄(PR₃)₄, where X = Cl, Br, or I, which may be prepared[9,10] by the phosphine-induced reductions of the octahalodirhenate(III) anions. These complexes have a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ electronic configuration[11] and possess a molecular structure[12] which is similar to that of Re₂X₅(PR₃)₃ and Re₂X₆(PR₃)₂, which contain metal–metal bonds of order 3.5 and 4, respectively.[9,13] In addition, there are the carbonyl derivatives (η⁵-C₅X₅)₂M₂(CO)₄, where X = H or Me and M = Cr, Mo, or W,[14–17] for which an 18-electron configuration would require the presence of a metal–metal triple bond, an assumption which is supported by crystallographic studies.[15,17]

Of these three groups, it is the derivatives of rhenium(II) which exhibit the most interesting and extensive redox chemistry, arising as a consequence of changes within the δ and δ* sets of metal-based orbitals. Re₂Cl₄(PR₃)₄ can be oxidized to Re₂Cl₅(PR₃)₃, Re₂Cl₆(PR₃)₂, and (R₃PCl)₂Re₂Cl₈ by O₂, CH₃OH–HCl, and CCl₄, respectively,[9,18] while their preparation via the phosphine reductions of (Bu₄N)₂Re₂Cl₈ and (Bu₄N)Re₂Cl₉ show[9,19] that the Re₂ⁿ⁺ core may survive at least a four-electron oxidation or reduction without being disrupted. In order to explore the possibility that the Re₂X₄(PR₃)₄ dimers may be reduced still further and to gain further insight into the consequences of oxidizing dimers which possess the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ electronic configuration and therefore a metal–metal triple bond, we have carried out a detailed investigation of their electrochemistry. The present study has led to the discovery of a novel series of coupled electrochemical–chemical reactions, the isolation and characterization of paramagnetic cations of the type [Re₂X₄(PR₃)₄]⁺, and an understanding of the mechanism of the oxidation sequence Re₂X₄(PR₃)₄ → Re₂X₅(PR₃)₃ → Re₂X₆(PR₃)₂. We previously reported,[20] in preliminary form, the existence of these coupled electrochemical–chemical reactions and we now describe in full the results of our detailed studies on the electrochemistry of Re₂Cl₄(PR₃)₄.

Experimental Section

Starting Materials. The phosphine and arsine ligands used in this study were purchased from Strem Chemicals, Inc. The systematic names of the bidentate ligands, together with their abbreviations, are as follows: (a) 1-diphenylphosphino-2-diphenylarsinoethane, arphos; (b) bis(1,2-diphenylphosphino)ethane, dppe; (c) bis(diphenylphosphino)methane, dppm. All of the phosphine and arsine ligands employed were used as received, except for dppe, which was recrystallized from acetonitrile. Tetraethylammonium chloride (TEACl) and tetrabutylammonium bromide (TBABr) were purchased from Eastman Organic Chemicals, Inc. To purify the TEACl, it was dissolved in acetonitrile, filtered to remove impurities, precipitated with anhydrous diethyl ether, and dried in vacuo. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by reacting tetra-*n*-butylammonium iodide with KPF_6 in hot water. The product was recrystallized from aqueous ethanol and dried in vacuo. $NOPF_6$ was purchased from Alfa Products. $(Bu_4N)_2Re_2X_8$, where X = Cl or Br, were prepared according to the standard method.[21] The complexes of the types $Re_2X_6L_2$, where X = Cl or Br and L = PEt_3, P-*n*-Pr_3, P-*n*-Bu_3, PEt_2Ph, $PMePh_2$, or $PEtPh_2$; $Re_2X_5L_3$, where X = Cl or Br and L = PEt_3, P-*n*-Pr_3, $PMePh_2$, or $PEtPh_2$; and $Re_2X_4L_4$, where X = Cl or Br and L = PEt_3, P-*n*-Pr_3, P-*n*-Bu_3, PMe_2Ph, or PEt_2Ph, were prepared by established procedures.[9,22] Samples of the previously unreported iodide complexes $Re_2I_4(PR_3)_4$, where R = Et, *n*-Pr, or *n*-Bu, were provided by Mr. H. D. Glicksman; details of their synthesis and full characterization will be described in detail elsewhere.[10] Samples of the complexes *cis*-$ReCl_4B$, where B = dppe, dppm, arphos, or 2CH_3CN, and *trans*-$ReCl_4L_2$, where L = PEt_3, P-*n*-Pr_3, P-*n*-Bu_3, $PMePh_2$, or PPh_3, were kindly provided by Dr. R. E. Myers. *mer*-$ReCl_3(PMe_2Ph)_3$ was synthesized following the method of Douglas and Shaw.[23]

Solvents used for electrochemical experiments were the highest purity commercially available and were used without further purification. The acetonitrile used in the $NOPF_6$ reactions was refluxed over CaH_2 and distilled under N_2. The CH_2Cl_2 used in obtaining the ESR glass spectra was freshly distilled and stored under N_2 in the dark prior to use.

Synthetic Procedures. (1) [$Re_2Cl_4(PEt_3)_4$]PF_6. In a typical reaction 0.40 g (0.41 mmol) of *freshly prepared*, powdered $Re_2Cl_4(PEt_3)_4$ was suspended in 10 mL of dry, distilled acetonitrile. Approximately 0.15 g (~0.9 mmol) of $NOPF_6$ was added. A gas was released and the $Re_2Cl_4(PEt_3)_4$ dissolved forming a deep greenish-blue solution. Within 5-10 min the lime green product, [$Re_2Cl_4(PEt_3)_4$]PF_6, precipitated and the solution turned green or green-brown. Further precipitation of product was induced by chilling the reaction mixture to 0 °C. The product (0.32 g) was collected by filtration, washed with 5 mL of MeOH and 5 mL of Et_2O, and dried under reduced pressure. Anal. Calcd for $C_{24}H_{60}Cl_4F_6P_5Re_2$: C, 25.5; H, 5.3; Cl, 12.5; P, 13.6. Found: C, 25.7; H, 5.2; Cl, 12.5; P, 13.7; yield, 69%. The product isolated from the reaction flask is analytically pure but, if necessary, it can be recrystallized from CH_2Cl_2 by the slow addition of Et_2O.

(2) [$Re_2Br_4(PEt_3)_4$]PF_6. The reaction procedure is identical with that described in (1) and yields the pure olive-green complex. Anal. Calcd for $C_{24}H_{60}Br_4F_6P_5Re_2$: C, 22.0; H, 4.6; Br, 24.4. Found: C, 22.1; H, 4.6; Br, 24.2; yield, 55%.

Physical Measurements. Infrared spectra (4000-200 cm^{-1}) were recorded as Nujol mulls on a Beckman IR-12 spectrophotometer. Melting points were obtained with a Fisher Meltemp apparatus and are uncorrected. Diffuse reflectance spectra were measured with a Beckman DU-2 spectrophotometer and CH_2Cl_2 solution UV-visible spectra were recorded with a Cary 14 spectrophotometer. A Hewlett-Packard 5950A ESCA spectrometer equipped with a monochromated Al Kα (1486.6 eV) x-ray source was used to obtain the x-ray photoelectron spectra (XPS). Samples were crushed onto gold-coated copper plates. Binding energies were internally referenced to the C 1s peak (285.0 eV) of the phosphine ligands. Peaks were resolved and relative peak areas were measured using a Du Pont 310 curve resolver. X-Band ESR spectra of CH_2Cl_2 glasses were recorded at 150 K with a Varian E-109 spectrometer.

Electrochemical measurements were made on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte and acetonitrile solutions containing 0.1 M TBAH as supporting electrolyte. $E_{1/2}$ values are referenced to the saturated sodium chloride calomel electrode (SSCE) at 22 ± 2 °C, and are uncorrected for junction potentials. Cyclic

Table I. $E_{1/2}$ Values for the Rhenium(III) Dimers, $Re_2X_6(PR_3)_2$, in Dichloromethane[a]

compd	$E_{1/2}$(red)(1)[b]	$E_{1/2}$(red)(2)[b]
$Re_2Cl_6(PEt_3)_2$	−0.10	
$Re_2Cl_6(PPr_3)_2$	−0.11	
$Re_2Cl_6(PBu_3)_2$	−0.13	
$Re_2Cl_6(PEt_2Ph)_2$	0.00	−0.95
$Re_2Cl_6(PMePh_2)_2$	+0.02	−0.95
$Re_2Cl_6(PEtPh_2)_2$	−0.02	−0.99
$Re_2Br_6(PEt_3)_2$	+0.02	
$Re_2Br_6(PMePh_2)_2$	+0.06	−0.85
$Re_2Br_6(PEtPh_2)_2$	+0.03	

[a] With 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. [b] Volts vs. the saturated sodium chloride calomel electrode (SSCE) with a Pt-bead working electrode.

voltammetry and voltammetry experiments were performed using a BioAnalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B *x-y* recorder. Potential control for coulometric experiments was maintained with a potentiostat purchased from BioAnalytical Systems, Inc. Values of *n*, where *n* is the total number of equivalents of electrons transferred in exhaustive electrolyses at constant potentials, were calculated after measuring the total area under current vs. time curves for the complete reactions. The reactions were judged to be complete when the current had fallen below 1% of the initial value. All voltammetric measurements were made at a platinum electrode in solutions deaerated with a stream of dry nitrogen.

Analytical Procedures. Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

Electrochemical Reduction of $Re_2X_6(PR_3)_2$. Voltammetric half-wave potentials vs. the saturated sodium chloride electrode (SSCE) for a series of rhenium halogen complexes $Re_2X_6(PR_3)_2$ are presented in Table I. The compounds can be divided into two groups depending upon the number of electrochemically reversible[24] reductions that they undergo in CH_2Cl_2. One group exhibits a single reduction, $Re_2X_6(PR_3)_2$ + e → [$Re_2X_6(PR_3)_2$]$^-$, while the other set possesses two reductions, $Re_2X_6(PR_3)_2$ + e → [$Re_2X_6(PR_3)_2$]$^-$ + e → [$Re_2X_6(PR_3)_2$]$^{2-}$. Therefore, these dimers can exist in either two or three separate oxidation states, i.e., [$Re_2X_6(PR_3)_2$]$^{0,1-}$ or [$Re_2X_6(PR_3)_2$]$^{0,1-,2-}$. Clean reductions to the monoanion for the complexes $Re_2Cl_6(PPr_3)_2$ and $Re_2Cl_6(PMePh_2)_2$ and the dianion for the latter were totally reversible and the *n* values for these processes approached 1.

The ESR spectrum of the electrochemically generated anion [$Re_2Cl_6(PPr_3)_2$]$^-$ is complex (Figure 1A), as expected from the low symmetry of the complex (no better than C_i) and the hyperfine splittings arising from the rhenium ($I = \frac{5}{2}$) and phosphorus ($I = \frac{1}{2}$) nuclei. No obvious patterns are observed in the spectrum. Given the total number of lines possible (at least 99 for C_i symmetry, not counting possible intermediate orientations or the small splittings due to the combinations of the two rhenium isotopes) and the observed complexity of the spectrum, no attempt was made to interpret the spectrum of the anion in any detail.

Electrochemical Processes of $Re_2X_5(PR_3)_3$. Voltammetric half-wave potentials are given in Table II for several dimers of the type $Re_2X_5(PR_3)_3$. Figure 2A shows a cyclic voltammogram of a solution of $Re_2Cl_5(PEtPh_2)_3$ in 0.2 M TBAH/CH_2Cl_2. All $Re_2X_5(PR_3)_3$ dimers studied behave in an identical fashion; therefore, we will need to discuss only this one representative. The cyclic voltammogram shows two electrochemically reversible,[24] one-electron (by coulometry) waves. The more anodic wave ($E_{1/2}$ = +0.44 V) is formally an oxi-
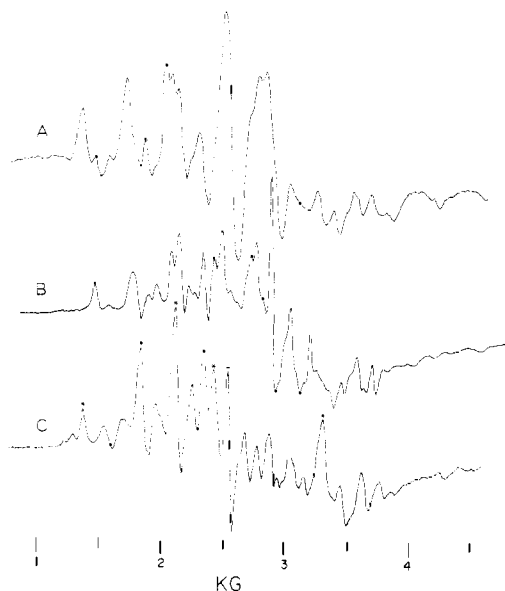
Figure 1. ESR spectra of CH_2Cl_2 glasses recorded at -150 °C: A, electrochemically generated $[Re_2Cl_6(PPr_3)_2]^-$; B, chemically generated $[Re_2Cl_4(PEt_3)_4]PF_6$; C, chemically generated $Re_2Cl_5(PPr_3)_3$.

Table II. $E_{1/2}$ Values for $Re_2X_5(PR_3)_3$ in Dichloromethane[a]

compd	$E_{1/2}(ox)$[b]	$E_{1/2}(red)$[b]
$Re_2Cl_5(PEt_3)_3$	+0.34	−0.88
$Re_2Cl_5(PPr_3)_3$	+0.31	−0.88
$Re_2Cl_5(PEtPh_2)_3$	+0.44	−0.66
$Re_2Br_5(PMePh_2)_3$	+0.48	−0.55
$Re_2Br_5(PEtPh_2)_3$	+0.45	−0.59

[a] With 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. [b] Volts vs. the saturated sodium chloride calomel electrode (SSCE) with a Pt-bead working electrode.

dation while the cathodic wave ($E_{1/2} = -0.66$ V) is a reduction. Thus, the $Re_2X_5(PR_3)_3$ dimers can exist in three distinct oxidation states, $[Re_2X_5(PR_3)_3]^{1+,0,1-}$. Figure 2B shows a cyclic voltammogram of the solution in Figure 2A after an exhaustive electrolysis at +0.6 V (i.e., past the oxidation wave of $Re_2Cl_5(PEtPh_2)_3$ ($n = 0.98$)). The cyclic voltammogram reveals that in addition to $[Re_2Cl_5(PEtPh_2)_3]^+$ ($E_{1/2} = +0.44$, -0.66 V) there is a new wave at $E_{1/2} = -0.02$ V arising from the formation of the rhenium(III) dimer, $Re_2Cl_6(PEtPh_2)_2$ (see Table I). In contrast to the oxidation, exhaustive electrolysis past the $E_{1/2}$ for reduction in these compounds produced only $[Re_2X_5(PR_3)_3]^-$ (i.e., $Re_2X_5(PR_3)_3 + e \rightarrow [Re_2X_5(PR_3)_3]^-$), the n values for this process being in the range 0.96–0.99. Thus, when $Re_2X_5(PR_3)_3$ is oxidized evidence of new product formation is found, whereas reduction only results in the production of the monoanion.

Electrochemical Oxidation of $Re_2X_4(PR_3)_4$. The only previous study on the electrochemical properties of phosphine complexes of rhenium dimers is that by Cotton and Pedersen,[25] who found that $Re_2Cl_4(PEt_3)_4$ could be oxidized to the 1+ and 2+ ions; however, electrochemical studies on this system were not pursued in further detail. Voltammetric half-wave potentials vs. the saturated sodium chloride calomel electrode for the complete series of rhenium halide dimers $Re_2X_4(PR_3)_4$, where X = Cl, Br, or I and R = Et, *n*-Pr, or *n*-Bu, are presented in Table III. Since all the complexes in this series behave in an identical fashion, for the sake of brevity, we shall discuss only one representative of this series, namely, $Re_2Cl_4(PPr_3)_4$. Figure 3A shows a cyclic voltammogram of $Re_2Cl_4(PPr_3)_4$ in 0.2 M $TBAH/CH_2Cl_2$ (dichloromethane was the only suitable
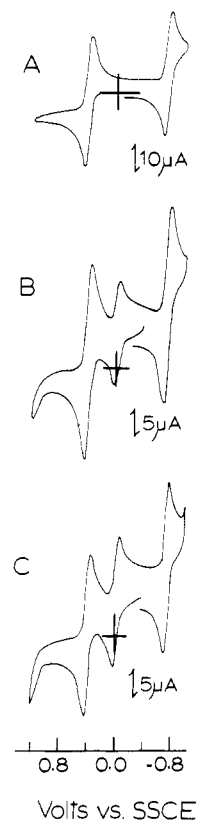

Figure 2. Cyclic voltammograms in 0.2 M TBAH–dichloromethane of A, $[Re_2Cl_5(PEtPh_2)_3]$; B, solution A 10 min after complete electrolysis at +0.6 V; C, solution A 20 min after electrolysis.

Table III. $E_{1/2}$ Values for $Re_2X_4(PR_3)_4$ in Dichloromethane[a]

compd	$E_{1/2}(ox)(1)$[b]	$E_{1/2}(ox)(2)$[b]
$Re_2Cl_4(PEt_3)_4$	−0.42	+0.80
$Re_2Cl_4(PPr_3)_4$	−0.44	+0.79
$Re_2Cl_4(PBu_3)_4$	−0.44	+0.82
$Re_2Cl_4(PMe_2Ph)_4$	−0.30	+0.83
$Re_2Cl_4(PEt_2Ph)_4$	−0.25	+0.85
$Re_2Br_4(PEt_3)_4$	−0.31	+0.825
$Re_2Br_4(PPr_3)_4$	−0.38	+0.84
$Re_2Br_4(PBu_3)_4$	−0.40	+0.82
$Re_2I_4(PEt_3)_4$	−0.27	+0.77
$Re_2I_4(PPr_3)_4$	−0.22	+0.85
$Re_2I_4(PBu_3)_4$	−0.25	+0.825

[a] With 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. [b] Volts vs. the saturated sodium chloride calomel electrode (SSCE) with a Pt-bead working electrode.

electrochemical solvent in which all of these compounds exhibited sufficient solubility for these experiments ($\sim 10^{-4}$ M)). This cyclic voltammogram demonstrates that the dimer has two electrochemically reversible,[24] on the cyclic voltammetry time scale, one-electron (by coulometry) oxidations. This shows that these dimers exist in three distinct oxidation states, $[Re_2X_4(PR_3)_4]^{0,1+,2+}$.

When an exhaustive electrolysis was performed on a solution of $Re_2Cl_4(PPr_3)_4$ at 0.0 V ($n = 0.98$), in addition to the expected $[Re_2Cl_4(PPr_3)_4]^+$ ($E_{1/2} = +0.79$, -0.44 V) two unexpected waves were discovered at $E_{1/2} = +0.31$ and -0.88 V (Figure 3B). The origin of these new waves was found to be due to $Re_2Cl_5(PPr_3)_3$, since a pure sample of $Re_2Cl_5(PPr_3)_3$ exhibits the identical electrochemical properties (i.e., $E_{1/2} = +0.31$ and -0.88 V). In the cyclic voltammogram of $Re_2Cl_4(PEt_3)_4$ which was reported by Cotton and Pedersen[25] (in

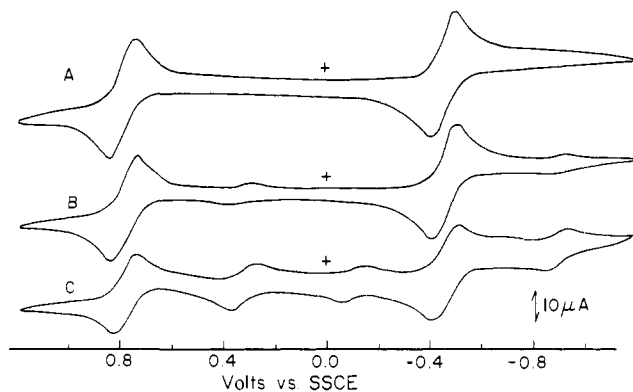**Figure 3.** Cyclic voltammograms in 0.2 M TBAH–dichloromethane of A, [Re$_2$Cl$_4$(PPr$_3$)$_4$]; B, solution A following oxidation at 0.0 V; C, solution A following oxidation at +1.0 V (scan rate 200 mV/s at a Pt-bead electrode vs. the saturated sodium chloride calomel electrode at 22 ± 2 °C).

0.1 M TBAClO$_4$/CH$_2$Cl$_2$) the presence of a small wave at ~0.4 V was attributed to an impurity (see Figure 2 in ref 25). Our work shows that this impurity is Re$_2$Cl$_5$(PEt$_3$)$_3$.
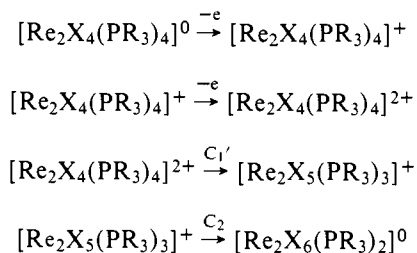
Figure 3C shows the cyclic voltammogram of the solution in Figure 3B after further electrolysis at 1.0 V, in other words, past the second oxidation wave of Re$_2$Cl$_4$(PPr$_3$)$_4$ (n = 0.95). Besides the expected products, [Re$_2$Cl$_4$(PPr$_3$)$_4$]$^{2+}$ ($E_{1/2}$ = +0.79, −0.44 V) and [Re$_2$Cl$_5$(PPr$_3$)$_3$]$^+$ ($E_{1/2}$ = +0.31, −0.88 V), a new wave was observed at $E_{1/2}$ = −0.11 V. This wave was found to result from the formation of Re$_2$Cl$_6$(PPr$_3$)$_2$; a pure sample of Re$_2$Cl$_6$(PPr$_3$)$_2$ has a wave at −0.11 V in CH$_2$Cl$_2$ (Table I).

In summary, when Re$_2$X$_4$(PR$_3$)$_4$ is oxidized, some of the oxidized dimers are converted to Re$_2$X$_5$(PR$_3$)$_3$ and finally Re$_2$X$_6$(PR$_3$)$_2$. In keeping with this result, we have seen in separate experiments that the oxidation of Re$_2$X$_5$(PR$_3$)$_3$ to [Re$_2$X$_5$(PR$_3$)$_3$]$^+$ is followed by the conversion of a proportion of these cations to Re$_2$X$_6$(PR$_3$)$_2$. Thus, chemical changes following electrolysis of dimers of the type Re$_2$X$_{6-x}$(PR$_3$)$_{2+x}$ (where x = 1 or 2) occur only for oxidations.

The Coupled Chemical–Electrochemical Reactions of Re$_2$X$_4$(PR$_3$)$_4$. As we have mentioned, a careful study of the cyclic voltammetry of Re$_2$X$_5$(PR$_3$)$_3$ and Re$_2$X$_4$(PR$_3$)$_4$ (Figures 2 and 3) shows that the electrochemical *oxidations* are accompanied by chemical transformations which result in easily identifiable products which only differ from their precursors in their relative numbers of halide and PR$_3$ ligands.

Two distinct pathways exist for this transformation and are representative of either EECC or ECEC processes.[26] The first pathway starts with the two one-electron oxidations of Re$_2$X$_4$(PR$_3$)$_4$ to [Re$_2$X$_4$(PR$_3$)$_4$]$^{2+}$ (Scheme I).

Scheme I. EECC Process

$$[Re_2X_4(PR_3)_4]^0 \xrightarrow{-e} [Re_2X_4(PR_3)_4]^+$$

$$[Re_2X_4(PR_3)_4]^+ \xrightarrow{-e} [Re_2X_4(PR_3)_4]^{2+}$$

$$[Re_2X_4(PR_3)_4]^{2+} \xrightarrow{C_1'} [Re_2X_5(PR_3)_3]^+$$

$$[Re_2X_5(PR_3)_3]^+ \xrightarrow{C_2} [Re_2X_6(PR_3)_2]^0$$

This scheme is demonstrated in Figure 4 in which the cyclic voltammograms show the changes in relative concentration with time after the completion of an electrochemical oxidation of Re$_2$Cl$_4$(PPr$_3$)$_4$ at 1.0 V in CH$_2$Cl$_2$ with 0.2 M TBAH as the
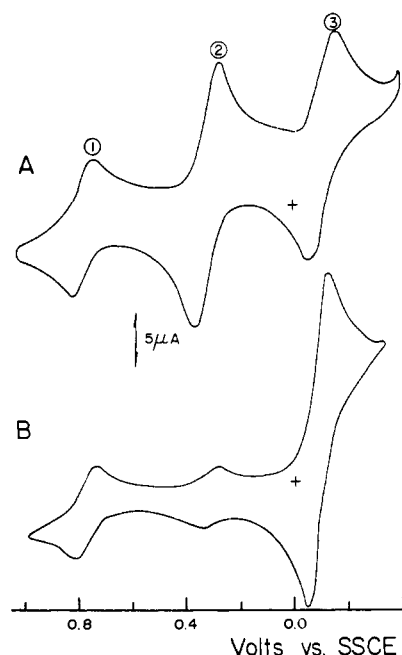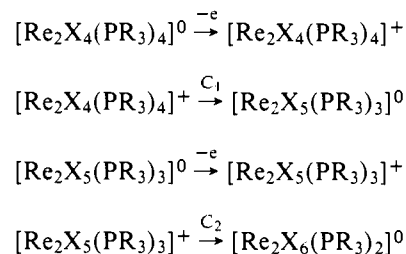

Figure 4. Cyclic voltammograms in 0.2 M TBAH–dichloromethane following exhaustive electrolysis of [Re$_2$Cl$_4$(PPr$_3$)$_4$] at +1.0 V: A, 15 min after complete electrolysis; B, 120 min (scan rate 200 mV/s at a Pt-bead electrode vs. the saturated sodium chloride calomel electrode at 22 ± 2 °C). 1, [Re$_2$Cl$_4$(PPr$_3$)$_4$]; 2, [Re$_2$Cl$_5$(PPr$_3$)$_3$]; 3, [Re$_2$Cl$_6$(PPr$_3$)$_2$].

supporting electrolyte. (Only the anodic half of the cyclic voltammogram is pictured.) Figure 4B shows the relative concentrations of [Re$_2$Cl$_4$(PPr$_3$)$_4$]$^{2+}$, [Re$_2$Cl$_5$(PPr$_3$)$_3$]$^+$, and Re$_2$Cl$_6$(PPr$_3$)$_2$ 2 h after the completion of the electrolysis. The major product is Re$_2$Cl$_6$(PPr$_3$)$_2$ and there is still some of the oxidized starting dimer, [Re$_2$Cl$_4$(PPr$_3$)$_4$]$^{2+}$, together with a small amount of the oxidized intermediate product, [Re$_2$Cl$_5$(PPr$_3$)$_3$]$^+$. These cyclic voltammograms (Figure 4) show that [Re$_2$Cl$_4$(PPr$_3$)$_4$]$^{2+}$ reacts to form [Re$_2$Cl$_5$(PPr$_3$)$_3$]$^+$ slower than [Re$_2$Cl$_5$(PPr$_3$)$_3$]$^+$ reacts to form Re$_2$Cl$_6$(PPr$_3$)$_2$, or $kC_1' < kC_2$.

If instead of oxidizing Re$_2$X$_4$(PR$_3$)$_4$ to [Re$_2$X$_4$(PR$_3$)$_4$]$^{2+}$ the oxidation is performed at a lower potential (0.5–0.6 V) in order to generate the monocation, [Re$_2$X$_4$(PR$_3$)$_4$]$^+$, then the reaction sequence is altered. The choice of 0.5–0.6 V is important in that it is also high enough to oxidize Re$_2$X$_5$(PR$_3$)$_3$ to [Re$_2$X$_5$(PR$_3$)$_3$]$^+$. This second reaction pathway is shown in Scheme II.

Scheme II. ECEC Process

$$[Re_2X_4(PR_3)_4]^0 \xrightarrow{-e} [Re_2X_4(PR_3)_4]^+$$

$$[Re_2X_4(PR_3)_4]^+ \xrightarrow{C_1} [Re_2X_5(PR_3)_3]^0$$

$$[Re_2X_5(PR_3)_3]^0 \xrightarrow{-e} [Re_2X_5(PR_3)_3]^+$$

$$[Re_2X_5(PR_3)_3]^+ \xrightarrow{C_2} [Re_2X_6(PR_3)_2]^0$$

Because reaction C$_1$ is very slow (at least 24 h), following this pathway by cyclic voltammetry is very difficult. But, since we have shown that [Re$_2$X$_4$(PR$_3$)$_4$]$^+$ converts to Re$_2$X$_5$(PR$_3$)$_3$ (Figure 3B), then the ECEC pathway is confirmed by following the conversion of [Re$_2$X$_5$(PR$_3$)$_3$]$^+$ to Re$_2$X$_6$(PR$_3$)$_2$. Figures 2B and 2C clearly show this chemical conversion with time.

The essential difference between these two pathways

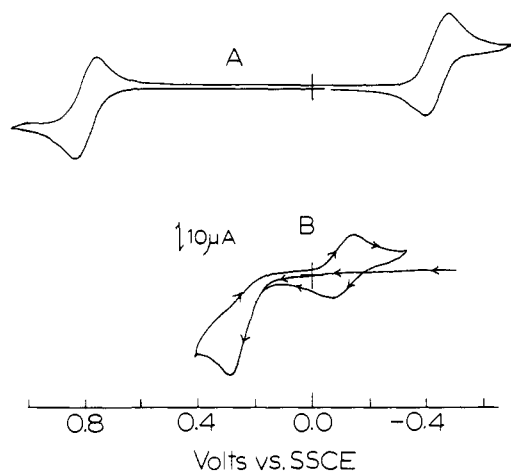**Figure 5.** Cyclic voltammograms in 0.2 M TBAH–dichloromethane of A, $[Re_2Cl_4(PEt_3)_4]PF_6$; B, solution A with 0.05 M tetraethylammonium chloride.

Table IV. $E_{1/2}$ Values for Rhenium(III) and Rhenium(IV) Monomers in Dichloromethane[a]

compd	$E_{1/2}(red)$[b]	$E_{1/2}(ox)$[b]
mer-ReCl₃(PMe₂Ph)₃	−0.95	+0.67
trans-ReCl₄(PEt₃)₂	−0.32	
trans-ReCl₄(PPr₃)₂	−0.34	
trans-ReCl₄(PBu₃)₂	−0.46	
trans-ReCl₄(PMePh₂)₂	−0.07	
trans-ReCl₄(PPh₃)₂	−0.12	
cis-ReCl₄(dppm)	+0.005	
cis-ReCl₄(dppe)	+0.085	
cis-ReCl₄(arphos)	+0.03	
cis-ReCl₄(CH₃CN)₂	−0.03	

[a] With 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. [b] Volts vs. the saturated sodium chloride calomel electrode (SSCE) with a Pt-bead working electrode.

(Schemes I and II) is the selection of potential used for the oxidation of $Re_2X_4(PR_3)_4$. If the potential is past the $E_{1/2}$ for the second oxidation of $Re_2X_4(PR_3)_4$ (producing, initially $[Re_2X_4(PR_3)_4]^{2+}$, Figure 3C) then the reaction will proceed by the EECC mechanism. If, instead, the potential chosen for the oxidation is past the $E_{1/2}$ of both the first oxidation for $Re_2X_4(PR_3)_4$ and past the oxidation for $Re_2X_5(PR_3)_3$ but below the $E_{1/2}$ for the second oxidation of $Re_2X_4(PR_3)_4$, then the reaction will proceed by the ECEC mechanism (this potential will produce, initially, $[Re_2X_4(PR_3)_4]^+$ then after the chemical reaction and subsequent oxidation, $[Re_2X_5-(PR_3)_3]^+$).

The electrochemical oxidations of $Re_2X_4(PR_3)_4$ are unique in that they lead to a series of coupled electrochemical-chemical reactions which can proceed by two separate pathways to produce the identical product $Re_2X_6(PR_3)_2$. The occurrence of both EECC and ECEC reaction series[26] within the same system is unprecedented.

Mechanism of the Chemical Reactions Which Follow the Electrochemical Oxidation of $Re_2X_4(PR_3)_4$. The overall results of the reaction sequences presented in Schemes I and II cannot be doubted. We believe that the chemical steps C_1, C_1', and C_2 involve reaction of "free" halide ion with $[Re_2X_4(PR_3)_4]^{2+}$, $[Re_2X_4(PR_3)_4]^+$, and $[Re_2X_5(PR_3)_3]^+$, respectively. There are several reasons to believe that this is the correct mechanism and that the source of halide ion must be the breakup of some of the dimers.

(1) Since we observe no difference in the electrochemical behavior of any of these dimers in dichloromethane and acetonitrile we can rule out the possibility that, in the case of $Re_2Cl_4(PR_3)_4$, the source of chloride ion is the dichloromethane solvent.

(2) It does not appear that reactions C_1, C_1', and C_2 involve a disproportionation step as we have no electrochemical evidence for the formation of any other rhenium halide–phosphine complexes (e.g., $ReX_3(PR_3)_3$ and $ReX_4(PR_3)_2$, Table IV).

(3) We have previously found[18] that when a benzene solution of $Re_2Cl_4(PEt_3)_4$ is exposed to O_2, $Re_2Cl_5(PEt_3)_3$ is produced together with small quantities of ReO_4^- and phosphine oxide. Thus the formation of halide ion from the reaction of a small proportion of dimers with adventitious O_2 (i.e., $Re_2X_4(PR_3)_4 + O_2 \rightarrow ReO_4^- + X^- + PR_3$) is a likely explanation for the source of free halide. The release of phosphine could also explain the fact that total conversion of $[Re_2X_4(PR_3)_4]^{2+}$ to $Re_2X_6(PR_3)_2$ is not achieved since the free phosphine will undergo a back reaction with $Re_2X_6(PR_3)_2$ to re-form some $Re_2X_4(PR_3)_4$.[9] Of course, some of the phos-

phine will react with O_2 to form phosphine oxide allowing the reaction to proceed, in the net sense, to the right. It would appear that the release of halide ion from the breakup of $[Re_2X_4(PR_3)_4]^{2+}$ or $[Re_2X_5(PR_3)_3]^+$ is the rate-determining step. The rate of disappearance of $[Re_2Cl_4(PPr_3)_4]^{2+}$ was found to be 9×10^{-2} M^{-1} s^{-1} by monitoring the conversion of $[Re_2Cl_4(PPr_3)_4]^{2+}$ to products using cyclic voltammetry.[27]

The overall reaction for the ECEC mechanism involves the same general features as mentioned above, i.e., breakup of some dimers ($[Re_2X_4(PR_3)_4]^+$) to release halide ions and their incorporation into the oxidized dimer to produce $Re_2X_5(PR_3)_3$.

To confirm the supposition that release of halide ions is the rate-determining step, a simple experiment was performed. This involved adding an external source of chloride ion to a solution containing $[Re_2Cl_4(PEt_3)_4]^+$. Figure 5A shows a cyclic voltammogram of $[Re_2Cl_4(PEt_3)_4]^+$ in 0.2 M TBAH/CH_2Cl_2. Figure 5B shows a cyclic voltammogram of the same solution after the addition of TEACl (approximate concentration of 0.05 M).

The direction of the scan is indicated by arrows; on the initial sweep no evidence of $Re_2Cl_4(PEt_3)_4$ is found (no wave at -0.40 V). However, a wave is seen at $E_{p,a} = +0.38$ V, indicating that the $Re_2Cl_4(PEt_3)_4$ has been converted to $Re_2Cl_5(PEt_3)_3$ (peak currents would indicate full conversion). On the reverse sweep, however, no wave for the reduction of $[Re_2Cl_5(PEt_3)_3]^+$ to $[Re_2Cl_5(PEt_3)_3]^0$ is observed; instead, a new wave is seen at $E_{p,c} = -0.14$ V. The second forward sweep shows that this new wave is reversible and that $E_{1/2} = -0.10$ V and the compound formed is $Re_2Cl_6(PEt_3)_2$ (Table I). Thus, the conversion of $[Re_2Cl_4(PEt_3)_4]^+$ to $[Re_2Cl_5(PEt_3)_3]^0$ occurs almost instantaneously and the conversion of $[Re_2Cl_5(PEt_3)_3]^+$ to $[Re_2Cl_6(PEt_3)_2]^0$ is accomplished at a rate faster than the recapture of $[Re_2Cl_5(PEt_3)_3]^+$ at the electrode. Thus, the contention that release of Cl$^-$ is the rate-determining step would appear to be confirmed.

Chemical Oxidation of $Re_2X_4(PEt_3)_4$. Isolation of the $[Re_2X_4(PEt_3)_4]^+$ Cations. From the work presented here and the results described previously by Cotton and Pedersen,[25] it has been demonstrated that the species $[Re_2X_4(PR_3)_4]^+$ can be generated electrochemically and that they are at least moderately stable in solution. The electrochemical results suggested that selection of the proper chemical oxidant would lead to isolation of the cationic complexes.

The nitrosonium cation, NO$^+$, is a useful reagent for generation of transition metal nitrosyl complexes and for clean, one-electron oxidations. In its reactions with $Re_2X_4(PEt_3)_4$, NO$^+$ behaves as a one-electron oxidizing agent, itself forming NO gas. The redox potential for NO$^+$/NO is not accurately

Table V. Physical Properties of the Complexes [$Re_2X_4(PEt_3)_4$]PF_6 (X = Cl or Br)

	[$Re_2Cl_4(PEt_3)_4$]PF_6	[$Re_2Br_4(PEt_3)_4$]PF_6
mp[a]	194–196	188–192
characteristic IR absorptions, cm^{-1} [b]	1053 (s)	1055 (s)
	856 (vs)	853 (vs)
	330(s), 305(m)	
electronic absorption spectra, nm		
diffuse reflectance	430 (s), 510 (sh)	450 (s), 525 (sh)
	600 (m), 715 (vw)	615 (m), 730 (vw)
CH_2Cl_2	413 (s), 490 (sh)	447 (s), 515 (w, sh)
	600 (m), 1410 (s, br)	1450 (s, br)
XPS binding energies, eV[c]		
Re 4f$_{7/2}$	42.3 (1.4)	42.2 (1.3)
P 2p$_{3/2}$[d]	131.3 (1.4) PEt_3	131.2 (1.4) PEt_3
	136.2 (1.4) PF_6	136.4 (1.4) PF_6
X[e]	199.2 (1.3)	69.8 (1.6)
ESR (CH_2Cl_2 glass)[f]		
$g_{\parallel}$	~2.0 (280)	~2.0
$g_{\perp}$	~2.25 (170)	~2.3
electrochemistry[g]		
$E_{1/2}$(ox)	+0.80	+0.825
$E_{1/2}$(red)	−0.42	−0.31

[a] Melting points obtained in open capillaries and are uncorrected (°C). [b] Bands at 330 and 305 cm^{-1} are assigned to ν(Re–Cl). [c] Internally referenced to a C 1s binding energy of 285.0 eV; values in parentheses are full width at half maxima of core level peaks. [d] Area ratio of P 2p PEt_3:PF_6 is 4.0:1.0. [e] X is Cl 2p$_{3/2}$ or Br 3d$_{5/2}$. [f] The values in parentheses are approximate values of $A_{\parallel}$ and $A_{\perp} \times 10^4$ cm^{-1}. [g] Volts vs. SSCE; in 0.2 M TBAH/CH_2Cl_2; potentials are identical with those for $Re_2X_4(PEt_3)_4$; see Table III.

known, but based on the chemical behavior of NO$^+$ it is probably between 0.85 and 1.00 V, vs. 0.1 M Ag$^+$/Ag electrode.[30] The oxidizing potential of NO$^+$ then is quite sufficient for the one-electron oxidation of the $Re_2X_4(PR_3)_4$ complexes (Table III). Even though the estimated oxidizing potential of NO$^+$ suggests that it may be high enough to convert $Re_2X_4(PR_3)_4$ to [$Re_2X_4(PR_3)_4$]$^{2+}$, this oxidation does not occur. Two possible explanations for this observation are (1) the estimate for the oxidizing strength of NO$^+$ is too high and actually NO$^+$ cannot oxidize $Re_2X_4(PEt_3)_4$ to the dication or, thermodynamically, (2) the oxidation can occur but no mechanistic pathway for this oxidation is available.

Treatment of the neutral dimers $Re_2X_4(PEt_3)_4$ (X = Cl or Br) with NOPF$_6$ in acetonitrile affords the green salts [$Re_2X_4(PEt_3)_4$]PF_6. Although chemical oxidation of the other dimers of general formula $Re_2X_4(PR_3)_4$ was not pursued, it is reasonable to assume, based on the electrochemical data, that the NO$^+$ oxidation is applicable to all the complexes listed in Table III.

The physical data for the oxidized dimers are summarized in Table V. The IR spectra were typical of coordinated PEt_3 and, in addition, exhibited an intense band at 855 cm^{-1} due to the ν_3 mode (P–F stretch) of PF_6^-. No evidence for coordinated NO (in the region 1500–1900 cm^{-1}) or rhenium oxide species (950–1050 cm^{-1}) was found in the IR spectra. The relative intensities of the (XPS) P 2p$_{3/2}$ binding energy peaks at 131.2 and 136.3 eV establish[32-34] the presence of PEt_3 and PF_6^- in a ratio of 4:1. In addition, the Re 4f$_{7/2}$ peaks are consistent[32] with the presence of a single rhenium species with an oxidation state between 2+ and 3+. The diffuse reflectance and acetone solution electronic absorption spectra show that the species examined are the same in solution as in the solid state. The Re_2^{4+} and Re_2^{5+} moieties can be readily distinguished in the near IR region. Re_2^{5+} species exhibit a strong, broad absorption at ~1400 nm but no such absorption is observed in complexes of Re_2^{4+}.[9,35] This band appears to be

typical of species containing a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ electronic configuration[9,35,36] and may be assigned[36] to a $\delta \rightarrow \delta^*$ transition. Thus, observation of strong, broad absorptions at ~1400 nm confirms the presence of the Re_2^{5+} moiety in the oxidized complexes. Finally, the cyclic voltammograms of [$Re_2Cl_4(PEt_3)_4$]PF_6 and the analogous bromide salt are identical with those of the parent complexes $Re_2X_4(PEt_3)_4$ and the electrochemically generated [$Re_2X_4(PEt_3)_4$]$^+$.

X-Band ESR spectra of CH_2Cl_2 glasses of [$Re_2Cl_4(PEt_3)_4$]PF_6 and [$Re_2Br_4(PEt_3)_4$]PF_6 were recorded at −150 °C. The spectrum of [$Re_2Cl_4(PEt_3)_4$]PF_6 is presented in Figure 1B. Cotton and Pedersen[25] have published the X-band ESR spectrum of a CH_2Cl_2 glass of the electrochemically generated [$Re_2Cl_4(PEt_3)_4$]$^+$ at −196 °C. We find that the spectra are very similar except for the absence or decrease in intensity of six moderately intense peaks in the spectrum of the chemically generated cation which are present in the spectrum of the electrochemically generated cation. We believe that the source of this discrepancy is the presence of a small amount of $Re_2Cl_5(PEt_3)_3$ in the solution of the electrochemically generated cation. Our evidence for this is twofold. First, Cotton and Pedersen[25] noted the presence of an "impurity" in the cyclic voltammogram of $Re_2Cl_4(PEt_3)_4$. This impurity has been demonstrated by us to be $Re_2Cl_5(PEt_3)_3$, by a comparison of the cyclic voltammogram of an authentic sample of $Re_2Cl_5(PEt_3)_3$ with that of $Re_2Cl_4(PEt_3)_4$. From the peak heights in the cyclic voltammogram recorded after exhaustive one-electron electrolysis of $Re_2Cl_4(PEt_3)_4$ to form [$Re_2Cl_4(PEt_3)_4$]$^+$, we estimate that ~15% of the starting material is converted to $Re_2Cl_5(PEt_3)_3$. Second, six of the most prominent peaks observed in the ESR spectrum of an acetone glass of $Re_2Cl_5(PPr_3)_3$ recorded at −150 °C (these peaks are denoted by asterisks in Figure 1C) coincide with the six "extra" peaks which are present in the ESR spectrum of the electrochemically generated cation.[25]

In the spectrum of [$Re_2Cl_4(PEt_3)_4$]PF_6 we find that $g_{\perp}$ is approximately 2.25 and $A_{\perp}$ is ~170 × 10^{-4} cm^{-1}. These values are in reasonable agreement with those reported previously.[25] Owing to the absence of $Re_2Cl_5(PEt_3)_3$ in the spectrum of [$Re_2Cl_4(PEt_3)_4$]PF_6, $A_{\parallel}$ can be estimated from the spacing of the two lowest field, $J = 5$, $g_{\parallel}$ lines (at 1450 and 1750 G) to be 280 × 10^{-4} cm^{-1}. Based on an approximate spacing of 300 G for the 11 components of the $g_{\parallel}$ line due to coupling with two equivalent rhenium nuclei [2(2)($^5/_2$) + 1], $g_{\parallel}$ is deduced to be ~2.0.

The X-band ESR spectra of the complexes $Re_2Br_5(PEtPh_2)_3$ and [$Re_2Br_4(PEt_3)_4$]PF_6 were also recorded. In both the solid and frozen solution spectra of these complexes, the resolution was much poorer than that observed in the chloro analogues of these types. Accordingly, all that can usefully be said concerning the ESR spectra of the bromide complexes is that the prominent features and band envelopes match those of their chloride analogues.

Although the $Re_2X_5(PR_3)_3$ and [$Re_2X_4(PEt_3)_4$]PF_6 dimers have many similar physical properties, the two groups of complexes do differ significantly in the fwhm of the (XPS) Re 4f$_{7/2}$ peaks. The fwhm is between 1.7 and 1.9 eV for the $Re_2X_5(PRPh_2)_3$ complexes[32] but between 1.3 and 1.4 eV for the [$Re_2X_4(PEt_3)_4$]PF_6 complexes. The broader Re 4f peaks in the XPS spectra of the $Re_2X_5(PRPh_2)_3$ complexes have been attributed to dissimilar rhenium environments.[32] In contrast, the rhenium environments in the cationic complexes are identical and the Re 4f peaks remain narrow.

Differences between the Reactions of $Re_2X_4(PR_3)_4$ with CO and NO$^+$. The one-electron oxidation of $Re_2X_4(PR_3)_4$ by NO$^+$ with retention of the dimer is very interesting and perhaps somewhat surprising in view of the facile cleavage of the Re–Re triple bond by CO (isoelectronic with NO$^+$) to initially form the paramagnetic monomers $Re(CO)_2Cl_2(PR_3)_2$.[22]

Based on X-α scattered wave calculations[11] and the eclipsed structure of $Re_2Cl_4(PEt_3)_4$,[12] the ground-state electronic configuration is thought to be $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$. Reduction of NO^+ to NO requires the addition of an electron to one of the empty π^*_{NO} orbitals. However, if this electron transfer were effected by direct end-on binding of NO^+ to one of the empty, axial positions of the $Re_2X_4(PR_3)_4$ dimer, then a typical HOMO–LUMO electron transfer does not appear possible because the net overlap between the δ^*_{metal} and π^*_{NO} orbitals must, by symmetry, be zero. Therefore, the mechanism of the electron transfer warrants further investigation. It may be that transfer occurs from one of the filled π_{metal} orbitals followed by "relaxation" of an electron from the filled δ^*_{metal} orbital to the π_{metal} orbital.

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Oxygen-17 Nuclear Magnetic Resonance Studies on Bound Water in Manganese(II)–Adenosine Diphosphate

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Abstract: Oxygen-17 line broadening and shift measurements have been made on aqueous solutions containing manganese-ADP complexes. Mono and bis complexes are considered. Log K_2 ($K_2 = [ML_2]/([ML][L])$) is ca. 2.6 at 25 °C and ΔH_2 is ca. -1 kcal/mol. The mono complex appears to have four bound waters which are kinetically equivalent. The bis complex appears to have three or four bound waters suggesting that it is not the usual sort of bis complex but a stacked one. The kinetics of water exchange are not greatly different for $Mn(H_2O)_6^{2+}$, $Mn(ATP)(H_2O)_3^{2-}$, $Mn(ADP)(H_2O)_4^-$, and $Mn(ADP)_2(H_2O)_3^{4-}$. Implications of the results are discussed in regard to mechanisms, NMR and EPR studies, and structures. The work supports the validity of using precise measurements of small shifts to determine numbers of bound water molecules.

Many enzymic trans-phosphorylation reactions involving ATP (adenosine triphosphate) and ADP (adenosine diphosphate) require divalent metal ions as cofactors. Consequently, the interactions of such metal ions with nucleotides, particularly ATP, have been the subject of numerous studies, most of which have been discussed in the reviews by Phillips[1] and Izatt et al.[2]

Metal-adenosine diphosphate complexes have received considerably less attention than similar ATP complexes. In this paper we report on Mn(II)–ADP, a complex which is impor-

tant as a leaving group in many in vitro enzyme studies. This complex has been studied by Cohn and Hughes,[3] who found that both the α and β phosphate groups were bound to the manganese. They reported also that manganese interacts with the adenine ring, although the authors recognized that their large $[ADP]_{total}-[Mn]_{total}$ ratio could produce complexes other than $MnADP^-$ which might be responsible for the observed interaction. (In this connection Frey and Stuehr[4] have shown that the stability constant for the $Ni(ADP)_2^{4-}$ complex is of the order of 10^2 M^{-1}.)