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Electrochemical Studies of Complexes of Rhenium(II) Containing a Rhenium–Rhenium Triple Bond in a Staggered Conformation. The Oxidation of $Re_2X_4(LL)_2$, Where X = Cl, Br, or I and LL = 1,2-Bis(diphenylphosphino)ethane or 1-(Diphenylphosphino)-2-(diphenylarsino)ethane

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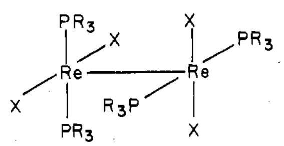
The electrochemical oxidation of the rhenium(II) dimers $Re_2X_4(LL)_2$, where X = Cl, Br, or I and LL = 1,2-bis(diphenylphosphino)ethane (dppe) or 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos), has been investigated using cyclic voltammetry and coulometry techniques. These dimers, which contain a rhenium–rhenium triple bond and a staggered rotational conformation in which the bidentate ligands are bridging, are oxidized to the cations $Re_2X_4(LL)_2^{n+}$, where n = 1 or 2. Unlike the related oxidations of the rhenium(II) dimers $Re_2X_4(PR_3)_4$ which contain monodentate tertiary phosphines, the electrochemical oxidations to $Re_2X_4(LL)_2^{n+}$ are not followed by chemical reactions. The chemical oxidation of $Re_2Cl_4(LL)_2$, where LL = dppe or arphos, can be accomplished using acetonitrile solutions of the salt $NO^+PF_6^-$. This procedure affords the paramagnetic complexes $[Re_2Cl_4(LL)_2]PF_6$ which are believed to retain the staggered structure of the parent neutral dimers and therefore still possess a metal–metal bond order close to 3.0. The spectroscopic and electrochemical properties of the dimers $Re_2X_4(LL)_2^{0,1+,2+}$ are contrasted with those of $Re_2X_4(PR_3)_4^{0,1+,2+}$ in which the rotational conformation is eclipsed.

Introduction

The tertiary phosphine complexes of rhenium(II), $Re_2X_4(PR_3)_4$, where X = Cl, Br, or I, are one of three main groups of compounds which contain metal–metal triple bonds.[1-3] These complexes possess a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ ground-state electronic configuration[4] and an eclipsed configuration (D_{2d}) in which the ReP_2 sets are staggered with respect to one another,[3] as shown in **1**. A recent study of the



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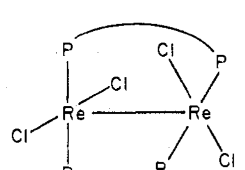
electrochemical properties of this class of dimers[5,6] showed that the oxidation of $Re_2X_4(PR_3)_4$ to $Re_2X_4(PR_3)_4^{n+}$, where n = 1 or 2, is followed by the conversion of these cations to $Re_2X_5(PR_3)_3$ and then $Re_2X_6(PR_3)_2$. These oxidations proceed by coupled electrochemical (E)–chemical (C) reaction series, either EECC or ECEC,[7] the mechanisms of which have been elucidated.[5,6] Oxidation occurs with stepwise loss of the (δ^*) electrons creating species which possess the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ and $(\sigma)^2(\pi)^4(\delta)^2$ ground-state configurations. In addition, the chemical oxidation of $Re_2X_4(PEt_3)_4$, where X = Cl or Br, has been achieved[6] using $NOPF_6$ to afford the salts $[Re_2X_4(PEt_3)_4]PF_6$.

Substitution of the PEt_3 groups of $Re_2Cl_4(PEt_3)_4$ by the bidentate donors 1,2-bis(diphenylphosphino)ethane, dppe, and 1-(diphenylphosphino)-2-(diphenylarsino)ethane, arphos, affords the complexes $Re_2Cl_4(LL)_2$ in which the *trans*-$ReCl_2L_2$ geometry about each rhenium atom is preserved. However, a novel feature of these complexes is that the bidentate ligands are bridging and the rotational conformation is staggered (**2**).[8]



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This structure provides the first example of a symmetrical Re–Re triple bond with a staggered conformation.

The interesting question which now arises concerns the consequences of oxidizing these dimers in a fashion analogous to that previously done for $Re_2X_4(PR_3)_4$.[5,6] If the staggered conformation **2** is retained in the oxidized species, this will ensure that the δ bond remains very weak or absent (depending upon the staggering angle) even though the electrons being lost are those which would have populated the δ^* orbital in an eclipsed structure of the type **1**. The results of our studies on the electrochemical and chemical oxidations of $Re_2X_4(LL)_2$ are now reported.

Experimental Section

Starting Materials. 1-(Diphenylphosphino)-2-(diphenylarsino)ethane, arphos, and bis(1,2-diphenylphosphino)ethane, dppe, were purchased from Strem Chemicals, Inc. arphos was used as received while dppe was recrystallized from acetonitrile. Tetraethylammonium chloride (TEACl) and tetra-*n*-butylammonium 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 ethanol/water and dried in vacuo. The salts $(Bu_4N)_2Re_2X_8$, where X = Cl or Br, were prepared according to the standard method.[9] Detailed methods for preparation of $Re_2X_4(LL)_2$, where X = Cl or Br and LL = dppe (bis(1,2-diphenylphosphino)ethane) or arphos (1-(diphenylphosphino)-2-(diphenylarsino)ethane) are given elsewhere.[10] The recent isolation[2] of the octaiododirhenate(III) salt $(Bu_4N)_2Re_2I_8$ has permitted us a direct route to $Re_2I_4(LL)_2$. 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 nitrogen prior to use.

Preparation of Monocations. $[Re_2Cl_4(dppe)_2]PF_6$. $Re_2Cl_4(dppe)_2$, 0.5 g (0.38 mmol), was suspended in 5 mL of dry CH_3CN at 0 °C, and ~0.1 g (0.6 mmol) of $NOPF_6$ was added. The $Re_2Cl_4(dppe)_2$ immediately dissolved forming a purple solution, and a gas evolved. The solution was stirred an additional 5 min and then 10 mL of Et_2O was added. A purple precipitate formed and an additional 5 mL of Et_2O was added. The solution was filtered. The purple solid was washed with Et_2O and dried in vacuo. Anal. Calcd for $C_{52}H_{48}Cl_4F_6P_5Re_2$: C, 42.9; H, 3.3; Cl, 9.75. Found: C, 43.0; H, 3.5; Cl, 9.6; yield 0.50 g (90%).

$[Re_2Cl_4(arphos)_2]PF_6$. The arphos monocation was prepared in an analogous manner to that described above for the dppe compound. Anal. Calcd for $C_{52}H_{48}As_2Cl_4F_6Re_2$: C, 40.5; H, 3.1. Found: C, 40.3; H, 3.3.

Physical Measurements. Infrared spectra (4000–200 cm^{-1}) were recorded as Nujol mulls on a Beckman IR-12 spectrophotometer. Diffuse reflectance spectra were measured with a Beckman DU-2

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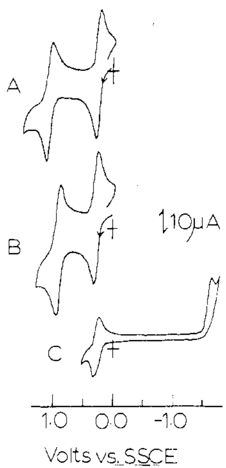

Figure 1. Cyclic voltammograms (scan rate 200 mV/s at a Pt-bead electrode unless stated otherwise) of (A) $Re_2Cl_4(dppe)_2$ in 0.2 M TBAH–CH_2Cl_2, (B) $Re_2I_4(arphos)_2$ in 0.2 M TBAH–CH_2Cl_2, and (C) $[Re_2Cl_4(dppe)_2]PF_6$ in 0.1 M TBAH–CH_3CN using a HMDE.

spectrophotometer and UV–visible spectra of acetone solutions 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. Magnetic susceptibility measurements were made by the Gouy method. Diamagnetic corrections were estimated using Pascal's constants. Conductivity measurements were made in dry acetonitrile using an Industrial Instruments Bridge, Model RC16B2.

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 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 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

(a) Electrochemical Oxidation of $Re_2X_4(LL)_2$. Voltammetric half-wave potentials vs. SSCE for $Re_2X_4(LL)_2$ (where X = Cl, Br, or I and LL = dppe or arphos) are given in Table I. Parts A and B of Figure 1, which show the 200 mV/s cyclic voltammograms of $Re_2Cl_4(dppe)_2$ and Re_2I_4 $(arphos)_2$ in 0.2 M TBAH/CH_2Cl_2, are representative of all complexes of the type $Re_2X_4(LL)_2$ listed in Table I. The complex $Re_2Cl_4(dppe)_2$ exhibits two reversible[11] one-electron (by coulometry) oxidations at $E_{1/2}$ = +0.23 and +1.04 V. Exhaustive electrolysis at +0.4 V (i.e., past the first oxidation wave) (n = 0.98) produces the monocation which is stable and, unlike the case of the $Re_2X_4(PR_3)_4$ compounds,[5,6] no other products are formed. Dichloromethane solutions of $Re_2X_4(LL)_2^+$ were quite stable when kept for several hours at room temperature.

Attempts to generate the dication in dichloromethane were complicated by its apparent reaction with the solvent. This reaction results in a wave of considerable magnitude in the

Table I. $E_{1/2}$ Values for the Rhenium(II) Dimers $Re_2X_4(LL)_2$, in Dichloromethane[a]

compound	$E_{1/2}(Ox)(1)^b$	$E_{1/2}(Ox)(2)^b$
$Re_2Cl_4(dppe)_2$	0.23	1.04
$Re_2Br_4(dppe)_2$	0.22	0.97
$Re_2I_4(dppe)_2$	0.29	0.92
$Re_2Cl_4(arphos)_2$	0.23	1.07
$Re_2Br_4(arphos)_2$	0.24	1.01
$Re_2I_4(arphos)_2$	0.28	0.91

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

Table II. Physical Properties of the Complexes $[Re_2Cl_4(dppe)_2]PF_6$ and $[Re_2Cl_4(arphos)_2]PF_6$

	$[Re_2Cl_4(dppe)_2]PF_6$	$[Re_2Cl_4(arphos)_2]PF_6$
characteristic IR absorptions, cm^{-1}	848 (vs)[a]	850 (vs)[a]
electronic absorption spectra (nm)		
diffuse reflectance	540 (s), 640 (sh)	540 (s), 650 (sh)
acetone	547 (s), 655 (sh)	545 (s)
XPS binding energies,[b] eV		
Re $4f_{7/2}$	42.5 (1.5)	~42.8 (1.7)[c]
P $2p_{3/2}$[d]	131.6 (1.2) dppe	131.7 (1.2) arphos
	136.1 (1.2) PF_6	136.2 (1.2) PF_6
Cl $2p_{3/2}$	199.2 (1.2)	199.2 (1.3)
electrochemistry,[e] V		
$E_{1/2}$(Ox)	+1.08	+1.07
$E_{1/2}$(Red)	+0.24	+0.23
magnetic moment, μ_B	2.2	
molar conductivity,[f] Λ_m, Ω^{-1} cm^2 mol^{-1}	105	

[a] ν_3 mode of the PF_6^- anion. [b] Binding energies internally referenced to a C 1s binding energy of 285.0 eV for the dppe and arphos ligands; values in parentheses are full width at half-maxima of core-level peaks. [c] Accurate measurement of this Re $4f_{7/2}$ binding energy is complicated by the presence of the As 3d peak at ~43.5 eV. The As $3p_{3/2}$ binding energy is located at 142.7 eV. [d] Area ratios of the P 2p dppe:PF_6 and arphos:PF_6 peaks are 4.0:1.0 and 2.0:1.0, respectively. [e] Volts vs. SSCE; in 0.2 M TBAH/CH_2Cl_2; potentials are vitually identical with those for $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$ (see Table I). [f] 10^{-3} M solution in acetonitrile.

resultant cyclic voltammogram at $E_{p,c}$ = −0.2 V, possibly arising from the formation of hydrogen. However, a solution of the dication can be produced by the oxidation of a suspension of $Re_2Cl_4(dppe)_2$ in 0.1 M TBAH/CH_3CN. The n value was 1.91 and the cyclic voltammogram of the resultant solution showed only the two waves for $Re_2Cl_4(dppe)_2$. Thus, these compounds exist in three distinct oxidation states (i.e., $Re_2X_4(LL)_2^{0,1+,2+}$) and the redox reactions are totally reversible in acetonitrile.

(b) Chemical Oxidation of $Re_2Cl_4(LL)_2$. Isolation of the $Re_2Cl_4(dppe)_2^+$ and $Re_2Cl_4(arphos)_2^+$ Cations. The one-electron oxidations of $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(arphos)_2$ were accomplished using $NOPF_6$, and in this regard these reactions are analogous to those of the monodentate phosphine complexes, $Re_2X_4(PR_3)_4$. Presumably, $[Re_2Cl_4(dppe)_2]PF_6$ and $[Re_2Cl_4(arphos)_2]PF_6$ are readily generated because the estimated oxidizing potential for NO^+ (+0.84 V)[12] is between the first and second oxidation potentials of the neutral complexes (i.e., approximately +0.22 and +1.00 V, respectively).

The identities of the cationic complexes have been established by a number of physical methods and most of the pertinent data are summarized in Table II. The diffuse reflectance and acetone solution electronic absorption spectra

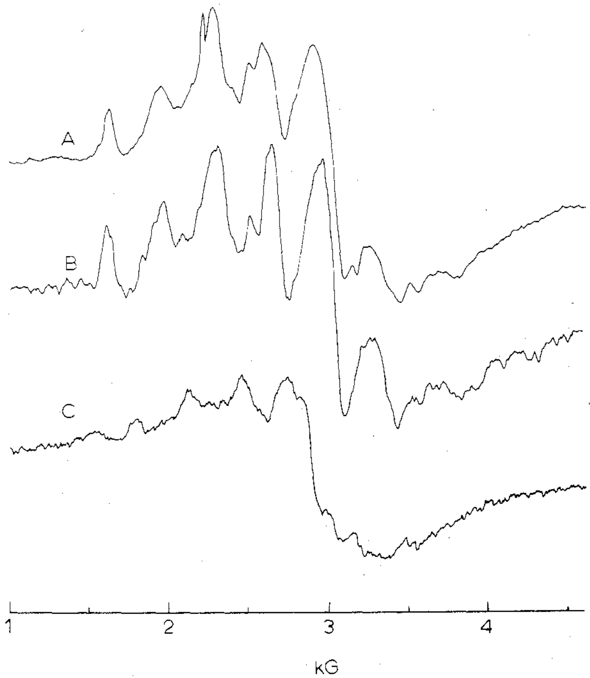

Figure 2. X-Band ESR spectra of dichloromethane glasses at −150 °C: (A) $[Re_2Cl_4(dppe)_2]PF_6$; (B) $[Re_2Cl_4(arphos)_2]PF_6$; (C) $[Re_2Br_4(PEt_3)_4]PF_6$.

of these complexes are very similar which suggests that the species in solution and the solid state are the same. Unlike the cations which are derived from the analogous dimers containing monodentate phosphines, $Re_2X_4(PR_3)_4^+$,[6] the complexes $[Re_2Cl_4(LL)_2]PF_6$, where LL = dppe or arphos, do not display a low-energy electronic absorption band between 1200 and 1800 nm. Although the dimeric cations $Re_2X_4(PR_3)_4^+$ and $Re_2X_4(LL)_2^+$ are both formally derivatives of the Re_2^{5+} core, there are clearly some differences in their electronic structures, the signicance of which will be discussed later.

In the X-ray photoelectron spectra (XPS) of $[Re_2Cl_4(LL)_2]PF_6$ (Table II), the area ratios of the P 2p peaks associated with the bidentate ligands (LL) and the PF_6^- anions are 4:1 and 2:1 for LL = dppe and arphos, respectively. This information coupled with conductance data for $[Re_2Cl_4(dppe)_2]PF_6$ in acetonitrile establishes that the complexes are 1:1 electrolytes. In addition, the cyclic voltammograms of both complexes exhibit two reversible one-electron (by coulometry) waves which are identical with those recorded for the parent neutral complexes and the electrochemically generated cations.

Upon referencing the XPS data for the monocations (Table II) and their analogous neutral derivatives[10] to the same binding energy standard (i.e., a C 1s energy of 285.0 eV for the phosphine/arsine ligands), it is apparent that the dppe and arphos P 2p binding energies are virtually unchanged by oxidation whereas the Re $4f_{7/2}$ energies of the monocations are between 0.7 and 1.0 eV greater than their neutral precursors. These increases in the Re 4f binding energies are consistent with the removal of one metal-localized electron from each of the dimers.

The magnetic moment of 2.2 μ_B determined for $[Re_2Cl_4(dppe)_2]PF_6$ is in accord with the expected paramagnetism of these cations. In addition, both the dppe and arphos salts exhibit complex ESR spectra. The X-band spectra of dichloromethane glasses were recorded at −150 °C (Figure 2A and 2B). These spectra are nearly identical. In each, six well-resolved intense peaks are observed between ~1600 and 3300 G; the peaks are regularly spaced at roughly 320–330-G intervals. Although the first-derivative profile indicates absorptions at fields as high as 4500–5000 G, no prominent features are observed in this region.

Two extreme possibilities can be envisioned in interpreting the principal features of the ESR spectra obtained for these cations. First, if the unpaired electron were localized on a single rhenium atom ($I = {}^5/_2$) in an approximately axially symmetric environment, one would expect the spectrum to be dominated by a six-line $g_\perp$ pattern with all six lines of roughly *equal* intensities. If this were the case and the six peaks observed are attributed to $g_\perp$, then $g_\perp \approx 2.70$ and the spacings of 320–330 G are assigned to the $A_\perp^{Re}$ hyperfine splitting. In the alternate possibility, the unpaired electron density might be distributed equally over both rhenium atoms in the dimer. In this event, one would expect $g_\perp$ to be composed of an 11-line spectrum due to coupling of the unpaired electron with two Re ($I = {}^5/_2$) nuclei. If this were the case, and the lowest field line at ~1600 G is the $J = 5$, $M_J = -5$ line, then $g_\perp \approx 2.00$. Our failure to resolve the five highest field $g_\perp$ components might be due to their overlap with the $g_\parallel$ components. Computer simulations were utilized to aid in distinguishing between these two extreme possibilities.[13] Although good fits of the experimental spectra were not obtained, the simulations involving coupling of the unpaired electron with two equivalent Re ($I = {}^5/_2$) nuclei gave the better agreement with the recorded spectra.

(c) Comparisons between Monocations Containing Monodentate and Bidentate Ligands. Although the syntheses of salts of the cations $Re_2X_4(PEt_3)_4^+$, where X = Cl or Br,[6] and $Re_2Cl_4(LL)_2^+$, where LL = dppe or arphos, involve the same procedure, namely the oxidation of their neutral precursors by NO^+, there are several differences in the physical properties and chemical reactivity of these two groups of complexes.

First, in the case of the monodentate tertiary phosphine complexes, oxidation of $Re_2Cl_4(PR_3)_4$ to $Re_2Cl_5(PR_3)_3$ or $Re_2Cl_4(PR_3)_4^+$ is accompanied by the appearance of an intense, broad absorption band in the near-IR region at ~1400 nm.[6,15] This feature is characteristic of species containing a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ electronic configuration[6,15,16] and may be assigned[16] to a $\delta \rightarrow \delta^*$ transition. The absence of a comparable electronic absorption band in the spectra of the salts $[Re_2Cl_4(LL)_2]PF_6$ in the region between 1000 and 2000 nm (Table II) can be due to one of two reasons. Either no δ contribution to the metal–metal bonding exists or the δ interaction is so weak that the $\delta \rightarrow \delta^*$ transition is at a very low energy, being located in the IR region where we are unable to identify it because of masking by the vibrational frequencies of the complex cations and anions. The latter interpretation seems the most likely since although the rotational conformation about the Re–Re bond in the parent complex $Re_2Cl_4(dppe)_2$ is best described as staggered,[8] the staggering angle is not 45°. This arises because of the conformational demands of the six-membered rings, Re–Re–P–C–C–P, formed by the bridging of the dppe (and arphos) ligands to the two Re atoms within the dimer.[17] Since these deviations from 45° are very likely maintained in the cations $Re_2Cl_4(LL)_2^+$, then loss of an electron from an orbital which is weakly δ antibonding in character would restore a small δ contribution to the metal–metal bonding. However, this would clearly be much less than in the eclipsed cations of the type $Re_2Cl_4(PR_3)_4^+$.

A second way in which these two systems differ concerns details of their ESR spectra. The X-band ESR spectra of CH_2Cl_2 glasses of $[Re_2X_4(PEt_3)_4]PF_6$ (at −150 °C) display[6] a complex pattern which has been interpretated in terms of the coupling of an unpaired electron with two equivalent Re nuclei. As discussed in the previous section, the ESR spectra of $[Re_2Cl_4(LL)_2]PF_6$ (Figure 2A and 2B) are much more poorly resolved than is the related spectrum of $[Re_2Cl_4(PEt_3)_4]PF_6$ and, accordingly, present more of an interpretative problem. Our conclusion that the spectra of $[Re_2Cl_4(LL)_2]PF_6$

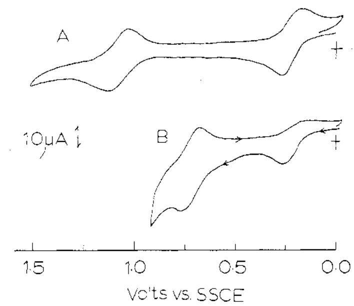

Figure 3. Cyclic voltammograms (scan rate 200 mV/s at a Pt-bead electrode) in 0.2 M TBAH–CH_2Cl_2: (A) $[Re_2Cl_4(arphos)_2]PF_6$; (B) solution A with 0.05 M tetraethylammonium chloride added.

more closely resemble those expected for systems in which coupling of the unpaired electron to two equivalent Re ($I = {}^5/_2$) nuclei is in accord with our belief that a *very weak* δ interaction persists and the unpaired electron resides in a δ^* orbital. Further support for this interpretation comes from our previous measurements[6] of the ESR spectra of frozen solutions of $[Re_2Br_4(PEt_3)_4]PF_6$. As was the case with $[Re_2Cl_4(LL)_2]PF_6$, the resolution of the ESR spectra of this bromide complex was much poorer than that observed for $[Re_2Cl_4(PEt_3)_4]PF_6$. However, the spectra of $[Re_2Br_4(PEt_3)_4]PF_6$ and $[Re_2Cl_4(LL)_2]PF_6$ are remarkably similar in the positions of their most prominent features and overall band envelopes (Figure 2). Since there is no doubt that the ground-state electronic configuration of $Re_2Br_4(PEt_3)_4^+$, like its chloride analogue, is $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$,[6] this argues for a similar configuration existing for $Re_2Cl_4(LL)_2^+$.

Third, marked electrochemical differences are observed between $Re_2X_4(PR_3)_4^+$ and $Re_2X_4(LL)_2^+$, differences which of course also exist between the parent neutral dimers. In particular, the more negative values of $E_{1/2}(Ox)$ for $Re_2X_4(PR_3)_4$[5,6] compared to those for $Re_2X_4(LL)_2$ (Table I) reflect an increase in energy of the δ^* orbital in the former species and the corresponding lowering in the voltammetric half-wave potentials associated with oxidations to species containing the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ and $(\sigma)^2(\pi)^4(\delta)^2$ configurations.

One consequence of the higher values of $E_{1/2}(Ox)$ for $Re_2X_4(LL)_2$ is that reduction to the monoanions $Re_2X_4(LL)_2^-$ would appear to be more likely than the corresponding reductions of $Re_2X_4(PR_3)_4$ to $Re_2X_4(PR_3)_4^-$. Voltammetric measurements in dichloromethane with platinum working electrodes showed no evidence of reductions for either group of compounds. However, by changing the solvent to acetonitrile (the monocation $Re_2Cl_4(dppe)_2^+$ is soluble in CH_3CN) and using a hanging mercury drop working electrode (HMDE), an irreversible reduction in the range −1.6 to −1.7 V was observed for $[Re_2Cl_4(dppe)_2]PF_6$ (Figure 1C) using scan rates of 50–500 mV/s.

A further reactivity difference concerns the greater stability of $Re_2Cl_4(LL)_2^+$ toward reaction with chloride ion. It has been shown[5,6] that the series of oxidized dimers $Re_2Cl_4(PR_3)_4^+$ react with Cl^- to produce $Re_2Cl_5(PR_3)_3$. Despite the fact that the cyclic voltammograms of $Re_2X_4(LL)_2^+$ gave no evidence for the formation of chemical products, the possibility still remained that the monocations could react with chloride ion. Therefore, 0.05 M TEACl was added to solutions of the appropriate monocation in 0.2 M TBAH/CH_2Cl_2. In the case of $Re_2Cl_4(dppe)_2^+$, no change was found in the cyclic voltammograms taken before and after addition of Cl^-. However, the analogous arphos monocation $Re_2Cl_4(arphos)_2^+$ (Figure 3A) reacted with Cl^- (Figure 3B). This new product which is formed upon reacting $Re_2Cl_4(arphos)_2^+$ with Cl^- has a reversible oxidation at +0.72 V (Figure 3B). We observed no other product waves at higher potentials, although above ~1.0 V, the cyclic voltammogram becomes complicated by the appearance of a strong oxidation wave arising from the excess Cl^- which is present. Our first thought was that the product wave at +0.72 V might be due to the formation of the rhenium(III) dimer $Re_2Cl_6(arphos)_2$. Although this complex has not been prepared previously, both $Re_2Cl_6(dppe)_2$ and $Re_2Br_6(arphos)_2$ are known.[10] Since these latter complexes would most likely display electrochemical behavior which closely resembles that of $Re_2Cl_6(arphos)_2$, we recorded the cyclic voltammograms of their solutions in dichloromethane containing 0.2 M TBAH as supporting electrolyte. Both complexes displayed two reversible oxidations ($E_{1/2} = +0.71$ and +0.87 V for $Re_2Cl_6(dppe)_2$ and $E_{1/2} = +0.59$ and +0.83 V for $Re_2Br_6(arphos)_2$). In spite of the close similarity of $E_{1/2}(Ox)(1)$ of $Re_2Cl_6(dppe)_2$ to the $E_{1/2}(Ox)$ wave of the product obtained by reacting $Re_2Cl_4(arphos)_2^+$ with Cl^-, the failure of the latter species to display a second oxidation between +0.8 and +1.0 V (Figure 3B) indicates that it is not $Re_2Cl_6(arphos)_2$. Similarly, its electrochemical properties are quite different from those of *cis*-$ReCl_4(arphos)$,[6] thereby ruling out this rhenium(IV) complex as the reaction product. It seems likely that the product from the reaction of $Re_2Cl_4(arphos)_2^+$ with Cl^- is a new arphos complex of rhenium.

The failure of $Re_2Cl_4(dppe)_2^+$ to react with Cl^- is most likely a consequence of the greater stability of the Re–Re–P–C–C–P ring system. With the analogous arphos complex, the Re–As bonds are presumably weaker and the six-membered rings more susceptible to opening upon nucleophilic attack by Cl^-.

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Registry No. $Re_2Cl_4(dppe)_2$, 58298-35-4; $Re_2Br_4(dppe)_2$, 67662-27-5; $Re_2I_4(dppe)_2$, 67662-28-6; $Re_2Cl_4(arphos)_2$, 58396-16-0; $Re_2Br_4(arphos)_2$, 58396-15-9; $Re_2I_4(arphos)_2$, 67711-42-6; $Re_2Br_4(dppe)_2^+$, 67711-44-8; $Re_2I_4(dppe)_2^+$, 67711-45-9; $Re_2Br_4(arphos)_2^+$, 67711-38-0; $Re_2I_4(arphos)_2^+$, 67711-39-1; $Re_2Cl_4(dppe)_2^{2+}$, 67662-29-7; $Re_2Br_4(dppe)_2^{2+}$, 67662-30-0; $Re_2I_4(dppe)_2^{2+}$, 67662-31-1; $Re_2Cl_4(arphos)_2^{2+}$, 67711-41-5; $Re_2Br_4(arphos)_2^{2+}$, 67711-40-4; $Re_2I_4(arphos)_2^{2+}$, 67711-43-7; $[Re_2Cl_4(dppe)_2]PF_6$, 67761-30-2; $[Re_2Cl_4(arphos)_2]PF_6$, 67761-29-9.

References and Notes

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