Organometallics **1998,** *17,* 2977−2985

Systematic Studies of 17-Electron Rhenium(II) Carbonyl Phosphine Complexes

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Received October 15, 1997

Oxidative electrochemical properties in dichloromethane have been examined for compounds of the types *cis*- or *trans*-$[Re(CO)_2(P-P)_2]^+$ and *trans*-$Re(CO)(P-P)_2X$ (P−P = diphosphine ligand, X = Cl, Br) which exhibit a range of charge and ligand types. In all cases 17e Re(II) species are formed, although the oxidation potentials vary over a reasonably wide range. The Re(II) compounds have been characterized by spectroelectrochemical (IR) and electrospray mass spectrometry (ESMS) studies. The stabilities of the Re(II) species are dependent upon charge and ligand types. The trans configuration is strongly preferred in the Re(II) state, so when the starting material is cis, there is rapid isomerization following electron transfer. The major form of reactivity detected is facile reduction of the *trans*-$[Re(CO)_2(P-P)_2]^{2+}$ species. The particularly high stability of *trans*-$[Re(CO)(dpe)_2X]^+$ (dpe = $Ph_2P(CH_2)_2PPh_2$) allows solid-state studies to be undertaken for the *trans*-$[Re(CO)(dpe)_2X]^{+/0}$ couple when the compounds are mechanically attached to a graphite electrode immersed in water (electrolyte).

Introduction

Studies on the oxidation of 18e manganese carbonyl halide complexes with phosphine ligand derivatives are extensive.[3a] Although isomerization may follow the initial electron transfer step, the final product is usually a stable 17e Mn(II) derivative.[4] While there is a large number of Re(I) carbonyl halide derivatives known,[3b] there has been much less study of the oxidation of these compounds than for those of manganese. The major differences are that the rhenium compounds are more difficult to oxidize than their manganese analogues,[5] and consequently, the Re(II) products of electron transfer are likely to be more reactive in a thermodynamic sense. Furthermore, there may be the possibility of overall disproportionation reactions giving stable seven coordinate Re(III) derivatives,[3c] a reaction which is not generally available in manganese chemistry. In the photooxidation of Re(I) carbonyl compounds containing 2,2′-bipyridine and related ligands, it appears that Re(II) is short-lived and reverts to Re(I) by a variety of mechanisms.[6]

In this paper we describe the electrochemical oxidation of a series of Re(I) carbonyl complexes having systematic variation of ligands and charge. These compounds exhibit a wide range of potential for oxidation, and the stabilities of the Re(II) oxidation products are examined as a function of charge, ligand type, and oxidation potential.

Experimental Section

Materials. $Re(CO)_5X$ complexes were prepared by interaction of $Re_2(CO)_{10}$ and halogen.[7] The diphosphines (dpbz = *o*-$(Ph_2P)_2(C_6H_4)$; dpm = $Ph_2PCH_2PPh_2$; dpe = $Ph_2P(CH_2)_2PPh_2$), $NOBF_4$, and “magic blue”, (*p*-$BrC_6H_4)_3NSbCl_6$, were used as purchased (Strem). All solvents were analytical reagent, electrochemical, or HPLC grade.

Syntheses and Characterization of Products. All of the compounds are either known compounds or simply new examples of established types. The compounds were characterized by IR and ^{31}P NMR spectra, and their molecular weights of the cationic species were determined by electrospray mass spectrometry (ESMS). In all cases the diphosphines, when present, are chelated. Absence of impurities such as free halide and phosphine ligand was confirmed by voltammetry. All reflux reactions were conducted under a nitrogen atmosphere, although all the 18e products are air stable.

***cis*- and *trans*-$[Re(CO)_2(dpbz)_2]Br$ and *cis*- and *trans*-$[Re(CO)_2(dpbz)_2]BF_4$.** A 0.125 g (0.31 mmol) amount of $Re(CO)_5Br$ was treated with 0.303 g (0.66 mmol) of dpbz in refluxing mesitylene (60 mL) for 168 h. Upon cooling, the resulting white solid was washed with hexane (yield 0.30 g, 88%). Anal. Calcd for $[Re(CO)_2(dpbz)_2]Br$: C, 61.29; H, 3.98. Found: C, 61.15; H, 3.92. The IR spectrum showed two bands in the carbonyl region, and the ^{31}P NMR spectrum (Table 1) showed a singlet and two close triplets of equal intensities. The ES mass spectrum for a solution of the compound in dichloromethane showed only a single peak at *m*/*z* 1136, which corresponds to the intact ion $[Re(CO)_2$-

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[5] (a) Bond, A. M.; Colton, R.; Panagiotidou, P. *Organometallics* **1988**, *7*, 1767. (b) Bond, A. M.; Colton, R.; Gable, R. W.; Mackay, M. F.; Walter, J. N. *Inorg, Chem.* **1997**, *36*, 1181.

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S0276-7333(97)00897-2 CCC: $15.00

Table 1. Infrared and ^{31}P NMR Spectroscopic Data

compd	ν(CO), cm^{-1}	δ(^{31}P), ppm[a]	J_{P-P}, Hz
cis-$[Re(CO)_2(dpbz)_2]^+$	1980, 1923	35.1 t, 29.0 t	<5
trans-$[Re(CO)_2(dpbz)_2]^+$	1924	31.8	
trans-$[Re(CO)_2(dpbz)_2]^{2+}$	1980		
cis-$[Re(CO)_2(dpm)_2]^+$	1970, 1912	−33.3 t, −45.7 t	16
trans-$[Re(CO)_2(dpm)_2]^+$	1928	−34.1	
trans-$[Re(CO)_2(dpm)_2]^{2+}$	1989		
trans-$Re(CO)(dpe)_2Br$	1818	25.0	
trans-$[Re(CO)(dpe)_2Br]^+$	1892		
trans-$Re(CO)(dpe)_2Cl$	1818	29.3	
trans-$Re(CO)(dpm)_2Br$	1818	−30.6	
trans-Re(CO)(dpm)(dpe)Br	1837	35.4 dd, −35.3 dd	185, 24
trans-Re(CO)(dpm)(dpbz)Br	1830	41.9 dd, −33.4 dd	184, 24
trans-Re(CO)(dpm)(dpbz)Cl	1829	43.8d, −31.2 d	185[b]

[a] d = doublet, dd = doublet of doublets, and t = triplet. [b] Not further resolved.

Table 2. ESMS Data

compd	additive[a]	ions (m/z)
cis- and *trans*-$[Re(CO)_2(dpbz)_2]PF_6$		$[Re(CO)_2(dpbz)_2]^+$ (1136)
cis-$[Re(CO)_2(dpm)_2]BF_4$		$[Re(CO)_2(dpm)_2]^+$ (1011)
trans-$Re(CO)(dpe)_2Cl$	magic blue	$[Re(CO)(dpe)_2Cl]^+$ (1046)
trans-$Re(CO)(dpe)_2Br$	magic blue	$[Re(CO)(dpe)_2Br]^+$ (1090)
trans-Re(CO)(dpm)(dpbz)Cl	magic blue	$[Re(CO)(dpm)(dpbz)Cl]^+$ (1080)
trans-Re(CO)(dpm)(dpbz)Br	magic blue	$[Re(CO)(dpm)(dpbz)Br]^+$ (1124)

[a] Magic blue = $(p\text{-}BrC_6H_4)_3NSbCl_6$.

$(dpbz)_2]^+$. All these data are consistent with the product being a mixture of *cis*- and *trans*-$[Re(CO)_2(dpbz)_2]Br$. The proportions of isomers were the same for a reflux time of 68 h. Since the bromide ion is electrochemically active within the potential range of interest for these compounds, the material was dissolved in dichloromethane, and 20 mM $AgBF_4$ in toluene solution was added until bromide ion was no longer detectable by voltammetry. The solid AgBr was filtered off and voltammetry carried out on the filtered solution. The spectroscopic and mass spectral properties of the $[Re(CO)_2(dpbz)_2]BF_4$ salt were identical to those of the bromide analog.

***cis*-$[Re(CO)_2(dpm)_2]BF_4$.** The known[8] compound *cis,mer*-$Re(CO)_2(\eta^1\text{-dpm})(\eta^2\text{-dpm})Br$ was prepared by reacting $Re(CO)_5Br$ (0.5 g, 1.23 mmol) and dpm (0.96 g, 2.5 mmol) in refluxing mesitylene (60 mL) for 9 h and isolated as an insoluble product upon cooling (yield 0.95 g, 73%). A 0.5 g (0.46 mmol) amount of this product was dissolved in acetone (50 mL), 0.089 g (0.46 mmol) of $AgBF_4$ in water/acetone was added slowly, and the solution was stirred for about 1 h. The solvent was removed under vacuum and the resultant solid extracted with dichloromethane. White *cis*-$[Re(CO)_2(dpm)_2]BF_4$ was obtained after removal of the solvent (yield 0.26 g, 52%). The complete removal of bromide ion was confirmed by voltammetry in CH_2Cl_2, the ^{31}P NMR and IR spectra showed clean spectra with only the bands reported in Table 1, and the ES mass spectrum showed only a single peak due to the intact ion $[Re(CO)_2(dpm)_2]^+$ (Table 2).

***trans*-$Re(CO)(dpe)_2X$ (X = Cl, Br).** These compounds were prepared by the method previously described[8] for the chloride compound by reacting $Re(CO)_5X$ (0.5 g, 1.23 mmol (Br)) with dpe (1.0 g, 2.5 mmol) in refluxing mesitylene (60 mL) for about 100 h. The products were washed with hexane and dried (yield >95%). IR and ^{31}P NMR spectra are consistent with the trans geometry (Table 1). Anal. Calcd for $Re(CO)(dpe)_2Br$: C, 58.31; H, 4.44; P, 11.37. Found: C, 58.39; H, 4.40; P, 11.38.

***trans*-Re(CO)(dpe)(dpm)Br.** $Re(CO)_5Br$ (0.169 g, 0.39 mmol) was reacted with dpe (0.157 g, 0.39 mmol) in refluxing mesitylene (60 mL) for 1.2 h to yield the known compound *fac*-$Re(CO)_3(dpe)Br$ in solution (IR: 2031, 1955, 1909 cm^{-1}). dpm (0.158 g, 0.40 mmol) was added and the mixture refluxed for a further 160 h. The solution was cooled, and addition of hexane yielded a white precipitate (yield 0.31 g, 72%). The IR and ^{31}P NMR data (Table 1) are consistent only with the formulation *trans*-Re(CO)(dpe)(dpm)Br.

***trans*-$Re(CO)(dpm)_2Br$.** $Re(CO)_5Br$ (0.13 g, 0.32 mmol) and dpm (0.28 g, 0.73 mmol) were reacted in refluxing mesitylene (60 mL) for 184 h. The solution was filtered hot, and upon cooling, a pale yellow solid precipitated which was washed with hexane and dried (yield 0.05 g, 15%). IR and NMR data (Table 1) are consistent only with the formulation *trans*-$Re(CO)(dpm)_2Br$.

***trans*-Re(CO)(dpm)(dpbz)Br.** $Re(CO)_5Br$ (0.115 g, 0.28 mmol) and dpbz (0.126 g, 0.28 mmol) were reacted in refluxing mesitylene (60 mL) for 1.3 h to yield *fac*-$Re(CO)_3(dpbz)Br$ in solution (IR: 2034, 1962, 1914 cm^{-1}). dpm (0.122 g, 0.29 mmol) was added and the mixture refluxed for a further 110 h. Upon cooling, hexane, was added to yield a solid which was filtered off, washed with hexane and dried (yield 0.25 g, 78%). The analogous chloride compound was prepared by a similar procedure from $[Re(CO)_5Cl]$.

***trans*-$[Re(CO)(dpe)_2Br]BF_4$.** This cation was first identified electrochemically, as described in the text, but it was also prepared in solution by bulk electrolysis of *trans*-$Re(CO)(dpe)_2Br$ and isolated by $NOBF_4$ oxidation as follows. *trans*-$Re(CO)(dpe)_2Br$ (0.050 g) was dissolved in dichloromethane (10 mL) and placed in an electrochemical cell. Solid $NOBF_4$ was added and the reaction followed by microelectrode voltammetry in the absence of electrolyte. As $NOBF_4$ is insoluble, the reaction is slow and the solution was degassed to remove NO. When the reaction was complete, after about 1 h, the solution was filtered to remove excess $NOBF_4$ and evaporated to yield a sticky solid. Hexane was added to the solid and allowed to evaporate to yield a green solid which voltammetry showed to be *trans*-$[Re(CO)(dpe)_2Br]BF_4$. As the compound is paramagnetic, NMR spectroscopy cannot be used, but ESMS confirmed the molecular formulas of the cation (Table 2). Other cations of the type *trans*-$[Re(CO)(P{-}P)_2X]^+$ were prepared in solution by oxidation of *trans*-$Re(CO)(P{-}P)_2X$ with “magic blue” and characterized by ESMS.

Electrochemical Methods. Voltammetric measurements were typically obtained with 1.0 mM solutions of compound in dichloromethane, acetone, or acetonitrile with 0.1 M Bu_4NBF_4, Bu_4NPF_6, or Bu_4NClO_4 as the electrolyte using a Cypress Systems (Lawrence, KA) model CYSY-1 computer-controlled electrochemical system or a BAS 100A electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN). For conventional cyclic voltammetric experiments the working electrode was either a glassy carbon disk (0.5 mm radius) or a platinum disk (0.8 mm radius), the auxiliary electrode was a platinum wire, and the reference electrode was Ag/AgCl (saturated LiCl in dichloromethane (0.1 M Bu_4NPF_6)) separated from the test solution by a salt bridge. Near steady-state voltammograms (scan rate 10 mV s^{-1}) were recorded using 5 or 12.5 μm radius platinum microdisk electrodes. The reversible voltammetry for oxidation of an approximately 0.5 mM ferrocene (Fc) solution in the same solvent was used as a reference redox couple, and all potentials are quoted relative to Fc$^+$/Fc. Solutions were purged with solvent-saturated nitrogen before voltammetric measurements and then maintained under an atmosphere of nitrogen during measurements.

AC cyclic voltammograms were obtained using the fast Fourier transform instrumentation described elsewhere.[10] The admittance form of readout was used.

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[8] Carr, S. W.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1763.

Bulk electrolysis experiments were undertaken with either a PAR model 273 potentiostat or the BAS 100 A electrochemical analyzer using a large glassy carbon working electrode, a platinum gauze auxiliary electrode separated from the test solution by a salt bridge, and the same reference electrode as used in the voltammetric studies.

Solid-state voltammetric studies were made using carbon disk electrodes (radius 2.5 mm) made from basal plane pyrolytic graphite. Solids (1−3 mg) were placed on a coarse grade filter paper and the solid was rubbed onto the electrode using a cotton bud, so some adhered to the electrode surface as an array of microcrystalline particles.[11] For electrochemical measurements, the electrode was transferred into the electrochemical cell containing aqueous electrolyte solution. The electrode surface could be cleaned after measurements by dissolving the solid in acetone.

Spectroscopic Methods. NMR spectra were recorded on Bruker AM 300 spectrometers, ^{31}P at 121.496 MHz in dichloromethane or acetone and ^{13}C at 75.469 MHz in $CDCl_3$ solution. The high-frequency positive convention is used for chemical shifts with external 85% H_3PO_4 and internal TMS references, respectively. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1720X or a Perkin-Elmer 1430 IR spectrometer. ESR spectra were recorded on a Bruker ESP 300 spectrometer.

Infrared spectroelectrochemical experiments were carried out using a modified IR reflection−absorption (IRRAS) cell,[12,13] mounted on a specular reflectance accessory located in the sample compartment of a Bruker IFS 55 FTIR spectrometer. The electrode arrangement consisted of a polished platinum disk working electrode (radius 2.5 mm), a platinum gauze auxiliary electrode, and a silver wire pseudo-reference electrode. Electrolyses were carried out by stepping the potential of the working electrode from a rest potential to a potential sufficient to cause electrolysis (E_{appl}), typically 200 mV past the peak potential, and single scan IR spectra (resolution = 1.0 cm^{-1}) were collected as a function of time. Electrolyses were performed with a Princeton Applied Research Corp. (PAR) (Princeton, NJ) model 174A polarographic analyzer. The Bu_4NPF_6 electrolyte solution was prepared as for the voltammetric experiments, and solutions were deoxygenated before syringing into the IRRAS cell. The cell itself was thoroughly flushed with nitrogen prior to addition of the sample and maintained under a nitrogen atmosphere throughout the experiments.

Electrospray Mass Spectrometry. Electrospray mass spectra of cationic complexes were obtained with a VG Bio-Q triple quadrupole mass spectrometer using a water/methanol/acetic acid (50:50:1) mobile phase. Solutions of the compounds (2.0 mM in dichloromethane) were mixed, if necessary, with oxidant as described in the text. The mixed solution was then diluted 1:10 with methanol and immediately injected directly into the spectrometer via a Rheodyne injector fitted with a 10 μL loop. A Pheonix 20 micro LC syringe pump delivered the solution to the vaporization nozzle of the electrospray source at a flow rate of 5 μL min^{-1}. Nitrogen was used as the drying gas and for nebulization with flow rates of approximately 3 L min^{-1} and 100 mL min^{-1}, respectively. The voltage on the first skimmer (B1) was usually 40 V. Peaks are identified by the most abundant mass in the isotopic mass distribution. In all cases the agreement between experimental and theoretical isotopic mass patterns was excellent.

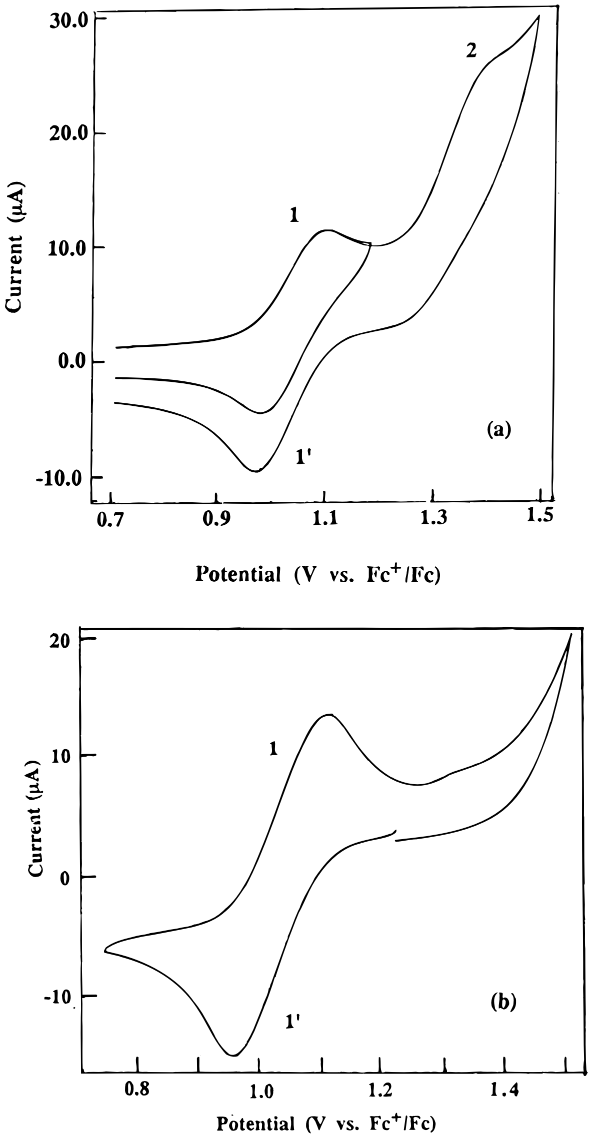

Figure 1. (a) Cyclic voltammograms at 20 °C for the oxidation of 1 mM *cis,trans*-$[Re(CO)_2(dpbz)_2]BF_4$ in dichloromethane (0.1 M Bu_4NPF_6) at a Pt disk electrode (radius 0.8 mm) at a scan rate of 500 mV s^{-1}. (b) Cyclic voltammogram at 20 °C for a solution of *trans*-$[Re(CO)_2(dpbz)_2]BF_4$ in dichloromethane (0.1 M Bu_4NPF_6), produced by electrolysis, at a Pt disk electrode (radius 0.8 mm) at a scan rate of 100 mV s^{-1}.

Results and Discussion

(a) Electrochemical and Spectroscopic Studies on the Oxidation of *cis*- and *trans*-$[Re(CO)_2(dpbz)_2]BF_4$ in Solution. Figure 1a shows oxidative cyclic voltammograms at 20 °C at a platinum macrodisk electrode for the synthesized mixture of *cis*- and *trans*-$[Re(CO)_2(dpbz)_2]BF_4$ in dichloromethane (0.1 M Bu_4NPF_6) at a scan rate of 100 mV s^{-1}. On the first forward scan two oxidation responses are observed, processes 1 and 2, with the latter being very close to the solvent limit. Examination of the reverse scan shows that process 2 is seen to be chemically irreversible. In contrast, the appearance of process 1′ (all reduction processes are signified by a prime) shows that redox couple 1 (comprising processes 1 and 1′) has considerable chemical reversibility. A cyclic voltammogram in which the potential is switched just after process 1 shows that process 1′ is enhanced if the potential is switched after process 2. On the basis of comparison with comparable metal carbonyl systems,[4,5b,14] and

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(9) Carr, S. W.; Fontaine, X. L. R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1987**, 3067.

(10) Hazi, J.; Elton, D. M.; Czerwinski, W. A.; Schiewe, J.; Vicente-Beckett, V. A.; Bond, A. M. *J. Electroanal. Chem.* **1997**, *437*, 1.

Table 3. Voltammetric Data (Scan Rate 100 mV s^{-1}) in Dichloromethane (0.1 M Bu_4NPF_6) at a Platinum Electrode at 20 °C

starting compd	process or couple	$E_p^{ox\ a}$	$E_p^{red\ a}$	$E^r_{1/2}{}^a$	ΔE_p (mV)
cis- and *trans*-$[Re(CO)_2(dpbz)_2]BF_4$	1	1.085	1.005	1.045	80
	2	1.350			
cis-$[Re(CO)_2(dpm)_2]BF_4$	1	0.810	0.730	0.770	80
	2	1.340			
trans-$Re(CO)(dpe)_2Br$	1	0.115	0.045	0.080	70
	3	0.860			
trans-Re(CO)(dpe)(dpm)Br	1	0.055	−0.015	0.020	70
	3	0.725			
trans-$Re(CO)(dpm)_2Br$	1	−0.005	−0.100	−0.050	95
	3	0.590			
trans-Re(CO)(dpbz)(dpm)Br	1	0.080	0.005	0.040	75
	3	0.720			

[a] V vs Fc^+/Fc.

theoretical considerations,[15] it seemed probable that redox couple 1 is due to the reaction

$$trans\text{-}[\mathrm{Re(CO)_2(dpbz)_2}]^+ \rightleftharpoons trans\text{-}[\mathrm{Re(CO)_2(dpbz)_2}]^{2+} + e^- \quad (1)$$

and process 2 is due to the reaction sequence

$$\begin{array}{ccl} cis\text{-}[\mathrm{Re(CO)_2(dpbz)_2}]^+ & \rightleftharpoons & cis\text{-}[\mathrm{Re(CO)_2(dpbz)_2}]^{2+} + e^- \\ & & \quad\downarrow \text{fast} \\ & & trans\text{-}[\mathrm{Re(CO)_2(dpbz)_2}]^{2+} \qquad (2) \end{array}$$

where the isomerization is believed to proceed via an internal twist mechanism.[4] Throughout this paper the identifiers 1 and 2 are associated with Re(I)/Re(II) couples relating to trans isomers (1) and cis isomers (2).

Cyclic voltammograms for couple 1 were studied as a function of scan rate over the range 20−500 mV s^{-1}. At low scan rates the peak to peak separation, ΔE_p, is 65 mV and close to the value expected for a fully reversible redox couple. At a scan rate of 500 mV s^{-1}, the value of ΔE_p is 120 mV. Since the known reversible one-electron oxidation of Fc under equivalent conditions gives the same variation of ΔE_p with scan rate, it is concluded that process 1 is fully reversible. The difference from the theoretical value is thought to be due to uncompensated resistance effects. This was confirmed by showing that ΔE_p increased with concentration for a given scan rate. Table 3 lists cyclic voltammetric data for this and other compounds at representative scan rates.

IR spectroelectrochemical studies, using an IRRAS cell,[12,13] have been undertaken to examine the products formed upon oxidation of the Re(I) complexes. The IR spectrum of the cis/trans mixture contains only two ν(CO) bands, at 1924 and 1980 cm^{-1}. Upon oxidation at $E_{appl} = +1.2$ V (i.e. at a potential sufficient to oxidize only *trans*-$[Re(CO)_2(dpbz)_2]^+$) the band at 1924 cm^{-1} decreases in absorbance by half, leaving a less intense band at 1923 cm^{-1}, while the band at 1980 cm^{-1} increases in absorbance. These changes indicate that ν(CO) for *trans*-$[Re(CO)_2(dpbz)_2]^+$ and *trans*-$[Re(CO)_2(dpbz)_2]^{2+}$ occur at 1924 and 1980 cm^{-1}, respectively, coincidently overlapping with the bands from *cis*-$[Re(CO)_2(dpbz)_2]^+$ ($\nu_{CO} \sim 1923$ and 1980 cm^{-1}). Following oxidation at $E_{appl} = +1.2$ V, if the potential of the working electrode is stepped to +1.5 V then complete disappearance of the band at 1923 cm^{-1} occurs and is accompanied by a slight increase in absorbance at 1980 cm^{-1}. This second oxidative step, i.e. oxidation of *cis*-$[Re(CO)_2(dpbz)_2]^+$, is accompanied by the rapid isomerization of *cis*-$[Re(CO)_2(dpbz)_2]^{2+}$ to *trans*-$[Re(CO)_2(dpbz)_2]^{2+}$ (eq 2). The small absorbance change at 1980 cm^{-1} is due to the coincidence of the *trans*-$[Re(CO)_2(dpbz)_2]^{2+}$ and one of the *cis*-$[Re(CO)_2(dpbz)_2]^+$ carbonyl bands, the former growing upon oxidation while the latter collapses. No bands are observed that can be attributed to transient *cis*-$[Re(CO)_2(dpbz)_2]^{2+}$, even at low temperature, implying that the isomerization (eq 2) is still fast at temperatures down to −60 °C.

Controlled potential bulk oxidative electrolysis with coulometric monitoring of a solution of *cis*- and *trans*-$[Re(CO)_2(dpbz)_2]^+$ in dichloromethane (0.1 M Bu_4NClO_4 or Bu_4NBF_4) at the potential of process 2 leads to the passage of considerably more than one electron per molecule, and the current never decays to zero. Microelectrode voltammetry under near steady-state conditions was used for in-situ monitoring of the bulk electrolysis experiment with Bu_4NBF_4 as the electrolyte. As the electrolysis proceeds, the response due to process 2 gradually decreases and finally disappears. The microelectrode voltammetry also shows that the sign of the current due to process 1, initially fully oxidative, changes to show approximately equal reductive and oxidative components which indicates that a mixture of *trans*-$[Re(CO)_2(dpbz)_2]^{2+}$ and *trans*-$[Re(CO)_2(dpbz)_2]^+$ exists in solution. The proportions of the complexes in solution does not change upon further prolonged electrolysis. However, when the oxidizing potential is removed, ^{31}P NMR and IR spectra of a sample of the solution show only the presence of the 18-electron *trans*-$[Re(CO)_2(dpbz)_2]^+$. These results suggest that *trans*-$[Re(CO)_2(dpbz)_2]^{2+}$ is unstable at room temperature on time scales significantly longer than that of the voltammetric and IR spectroelectrochemical experiments.

A reductive bulk electrolysis of the previously oxidized solution was carried out at 0.500 V vs Fc^+/Fc (less positive than redox couple 1). A near steady-state voltammogram at a microdisk electrode of the reduced solution shows only process 1 with the same limiting current as the combined processes 1 and 2 for the original solution. The sign of the current confirms that the species is the reduced form, *trans*-$[Re(CO)_2(dpbz)_2]^+$, rather than *trans*-$[Re(CO)_2(dpbz)_2]^{2+}$. Figure 1b shows a cyclic voltammogram at a Pt macrodisk electrode for the solution containing only *trans*-$[Re(CO)_2(dpbz)_2]^+$ in dichloromethane (0.1 M Bu_4NBF_4). Couple 1 is now fully reversible with $i_p^{ox} = i_p^{red}$. Under these conditions, in the absence of any cis isomer, it is possible to fully the characterize process 1, and it can readily be shown that it is both chemically and electrochemically reversible.

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The IR spectrum of the solution shows a single carbonyl absorption at 1924 cm^{-1}, and its ^{31}P NMR spectrum shows a single resonance at δ 31.8 ppm, which are the same values as those assigned to *trans*-[Re(CO)$_2$(dpbz)$_2$]$^+$ in the mixture of cis and trans isomers prepared synthetically (Table 1). The ES mass spectrum of the solution showed a single peak at *m*/*z* 1136, which corresponds to the molecular weight of [Re(CO)$_2$(dpbz)$_2$]$^+$.

The only mechanism which accords with all these data is that both *trans*- and *cis*-[Re(CO)$_2$(dpbz)$_2$]$^+$ are oxidized (processes 1 and 2, respectively) and that although *cis*-[Re(CO)$_2$(dpbz)$_2$]$^{2+}$ isomerizes to *trans*-[Re(CO)$_2$(dpbz)$_2$]$^{2+}$ on the voltammetric time scale, this species is partially reduced by the solvent or adventious water back to *trans*-[Re(CO)$_2$(dpbz)$_2$]$^+$ on the time scale of bulk electrolysis, which explains the passage of more than one electron per molecule in the oxidative electrolysis. Since *trans*-[Re(CO)$_2$(dpbz)$_2$]$^{2+}$ and *cis*-[Re(CO)$_2$(dpbz)$_2$]$^{2+}$ are generated at such positive potentials ($E^{r}_{1/2}(1) = 1.045$ V; $E_p^{ox}(2) = 1.350$ V vs Fc$^+$/Fc), it is not surprising that they are so easily reduced back to the stable *trans*-[Re(CO)$_2$(dpbz)$_2$]$^+$ form. The fact that the product after reductive electrolysis is entirely *trans*-[Re(CO)$_2$(dpbz)$_2$]$^+$ shows that isomerization in the 18e state to *cis*-[Re(CO)$_2$(dpbz)$_2$]$^+$ is extremely slow. Since, after the electrolytic oxidation and reduction cycles, the conversion of the original mixture of *cis*- and *trans*-[Re(CO)$_2$(dpbz)$_2$]$^+$ to *trans*-[Re(CO)$_2$(dpbz)$_2$]$^+$ is quantitative, there are no detectable side reactions, such as disproportionation.

(b) Electrochemical and Spectroscopic Studies on the Oxidation of *cis*-[Re(CO)$_2$(dpm)$_2$]BF$_4$ in Solution. A fundamental difference between this system and the [Re(CO)$_2$(dpbz)$_2$]$^+$ system is that only the cis isomer of [Re(CO)$_2$(dpm)$_2$]$^+$ is present in the sample. Oxidative cyclic voltammograms at 20 °C (scan rate range 20−500 mV s^{-1}) of *cis*-[Re(CO)$_2$(dpm)$_2$]BF$_4$ in dichloromethane (0.1 M Bu$_4$NPF$_6$) at a platinum disk electrode (radius 0.8 mm) give rise to an irreversible oxidation response (process 2) near the solvent limit on the initial oxidation scan, and on the reverse scan a reduction response (process 1′) is apparent. On the second scan and subsequent cycles the corresponding oxidation, process 1, is now apparent together with process 2. The overall electrochemical reactions are similar to those of the analogous [Re(CO)$_2$(dpbz)$_2$]$^{2+/+}$ system and consistent with the scheme shown in eq 3. Proof of the validity of this scheme is given in the following sections.

$$\begin{array}{ccc} \textit{cis}\text{-[Re(CO)}_2\text{(dpm)}_2]^+ & \rightleftharpoons & \textit{cis}\text{-[Re(CO)}_2\text{(dpm)}_2]^{2+} + e^- \\ & & \downarrow \text{very fast} \\ \textit{trans}\text{-[Re(CO)}_2\text{(dpm)}_2]^+ & \rightleftharpoons & \textit{trans}\text{-[Re(CO)}_2\text{(dpm)}_2]^{2+} + e^- \end{array} \qquad (3)$$

$E_p^{ox}(2)$ values (process 2) for *cis*-[Re(CO)$_2$(dpbz)$_2$]$^{2+/+}$ and *cis*-[Re(CO)$_2$(dpm)$_2$]$^{2+/+}$ are very similar. However, the $E^{r}_{1/2}$ values (couple 1) for the corresponding trans isomers differ by over 250 mV (Table 3).

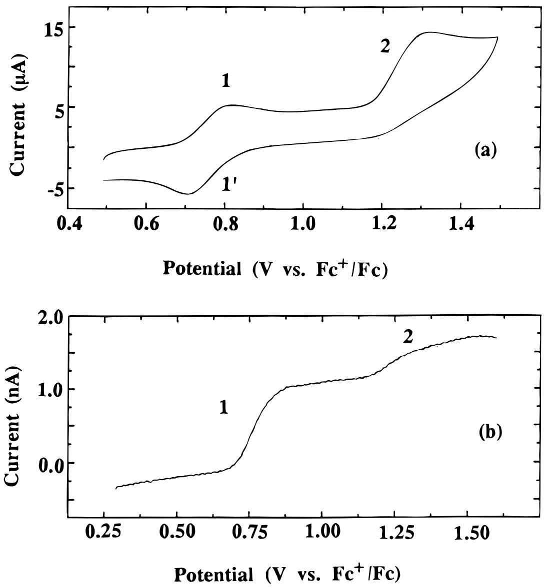

Figure 2. (a) Cyclic voltammograms at 20 °C for a 4 mM solution of *cis*-[Re(CO)$_2$(dpm)$_2$]BF$_4$ in dichloromethane (0.1 M Bu$_4$NPF$_6$) which has been subjected to partial oxidative bulk electrolysis. (b) Near steady-state voltammogram at a Pt microdisk electrode (radius 5 μm) for the same solution, scan rate 100 mV s^{-1}.

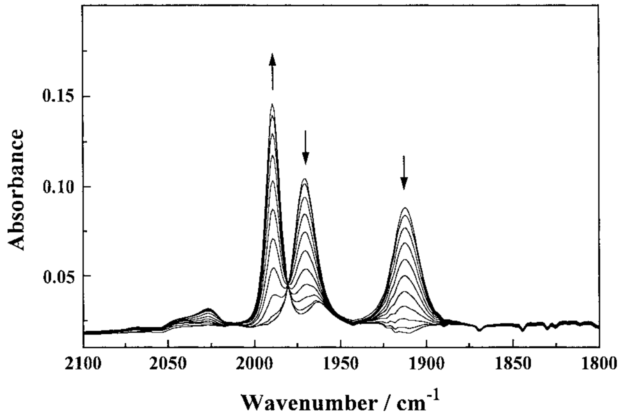

Figure 3. Changes in carbonyl region of the IR spectrum upon oxidation of *cis*-[Re(CO)$_2$(dpm)$_2$]BF$_4$ in an IRRAS cell in dichloromethane (0.1 M Bu$_4$NPF$_6$) at −60 °C.

The oxidation of *cis*-[Re(CO)$_2$(dpm)$_2$]BF$_4$ was carried out in dichloromethane (0.1 M Bu$_4$NPF$_6$) in the IRRAS cell at low temperature. As the electrolysis proceeds, the ν(CO) bands for the parent cis complex (at 1970 and 1912 cm^{-1}) decrease in intensity, and a new strong band grows at 1989 cm^{-1} (Figure 3). These changes in the IR spectrum are consistent with the rapid isomerization of *cis*-[Re(CO)$_2$(dpm)$_2$]$^{2+}$ to *trans*-[Re(CO)$_2$(dpm)$_2$]$^{2+}$, as postulated from voltammetric experiments. No bands are observed which can be assigned to *cis*-[Re(CO)$_2$(dpm)$_2$]$^{2+}$, so the isomerization (eq 3) is still fast at low temperature. Attempted rereduction at $E_{appl} = +1.0$ V does not cause any change in the IR spectrum, nor does any current flow through the cell, thus confirming that oxidation of *cis*-[Re(CO)$_2$(dpm)$_2$]$^+$ results in the formation of a species with different redox characteristics, *i.e.* *trans*-[Re(CO)$_2$(dpm)$_2$]$^{2+}$. At $E_{appl} = +0.5$ V, reduction is achieved and the ν(CO) band at 1989 cm^{-1} gives way a band of similar intensity at 1928 cm^{-1} which can be attributed to the *trans*-[Re(CO)$_2$(dpm)$_2$]$^+$ cation. While there is no evidence of isomerization of *trans*-[Re(CO)$_2$(dpm)$_2$]$^+$ to *cis*-[Re(CO)$_2$(dpm)$_2$]$^+$ at −50 °C, at room temperature some of the latter does re-form. Accompanying the formation of *trans*-[Re(CO)$_2$(dpm)$_2$]$^{2+}$ are two unidentified carbonyl containing complexes with ν(CO) bands at 2027 and 1965 cm^{-1}, respectively. While these bands are quite prominent at 20 °C, their intensity is greatly diminished when the oxidation is carried out at low temperature. These bands do not arise from the same species since that at 2027 cm^{-1} is observed to collapse upon reduction while that 1965 cm^{-1} remains.

Bulk electrolysis of a 4 mM solution of *cis*-$[Re(CO)_2(dpm)_2]BF_4$ in dichloromethane (0.1 M Bu_4NPF_6) at 1.39 V caused little color change in the solution. The close proximity of process 2 to the solvent limit means that exhaustive oxidative electrolysis is difficult to achieve. A cyclic voltammogram of the resulting solution after partial electrolysis is shown in Figure 2a, which shows the reversible couple 1 and the irreversible process 2. The sign of the current in a near steady-state voltammogram at a Pt microelectrode (Figure 2b) shows that the majority of the species responsible for couple 1 is in the reduced form. After exhaustive electrolysis of *cis*-$[Re(CO)_2(dpm)_2]^+$ only *trans*-$[Re(CO)_2(dpm)_2]^+$ was observed in solution. The infrared spectrum of the solution shows a new strong absorption at 1928 cm^{-1}, and the combination of electrochemical and IR evidence suggests that *trans*-$[Re(CO)_2(dpm)_2]^+$ is the major species produced in solution after bulk oxidative electrolysis of *cis*-$[Re(CO)_2(dpm)_2]^+$. However, a small concentration of *trans*-$[Re(CO)_2(dpm)_2]^{2+}$ which rapidly converts to *trans*-$[Re(CO)_2(dpm)_2]^+$ is detected as an intermediate, as shown by voltammetry at a microelectrode.

The bulk electrolysis was repeated using Bu_4NBF_4 as the supporting electrolyte so that ^{31}P NMR spectra could be acquired without spectral interference from the concentrated supporting electrolyte. The NMR spectrum showed two weak triplets ($J(P-P) = 16$ Hz), due to unoxidized *cis*-$[Re(CO)_2(dpm)_2]^+$, and a strong singlet at δ −34.1 ppm, assigned to *trans*-$[Re(CO)_2(dpm)_2]^+$.

All of these data confirm that *trans*-$[Re(CO)_2(dpm)_2]^{2+}$ is unstable on the longer time scale of bulk electrolysis. Thus, despite the lower $E^r_{1/2}$ value for process 1 relative to the dpbz compound, the cation *trans*-$[Re(CO)_2(dpm)_2]^{2+}$ is still reduced by adventious water, or light, to its 18e analogue.

trans-$[Re(CO)_2(dpe)_2]BF_4$ has been prepared before by the interaction of *trans*-$Re(N_2)(dpe)_2Cl$ and $TlBF_4$ in refluxing tetrahydrofuran for 12 days, with CO being passed through the solution continuously.[16] The compound exhibited a reversible one-electron oxidation process on the voltammetric time scale in acetonitrile at a potential of 1.42 V vs SCE which, after correction for the different reference electrodes, is qualitatively in the same potential range as couple 1 for other *trans*-$[Re(CO)_2(P-P)_2]^+$ compounds described in this work.

(c) Electrochemical and Spectroscopic Studies on the Oxidation of *trans*-Re(CO)(dpe)$_2$Br in Solution. Figure 4a shows a cyclic voltammogram for oxidation of a 1 mM solution of *trans*-$Re(CO)(dpe)_2Br$ in dichloromethane (0.1 M Bu_4NPF_6) at 20 °C using a scan rate of 100 mV s^{-1} at a platinum disk electrode (radius 0.8 mm). The voltammogram shows an oxidation response (process 1) and an irreversible response (process 3) with $E_p^{ox} = 0.860$ V vs Fc^+/Fc. On the reverse scan a reduction response (process 1′) is observed. For cyclic voltammograms in which the potential is switched between processes 1 and 3, redox couple 1 is completely chemically reversible over a wide range of scan rates (10−500 mV s^{-1}) and the peak to peak separation at a scan rate of 10 mV s^{-1} is 68 mV, which is typical for a reversible one-electron process in a solvent like dichloromethane when noncompensated resistance is present. Voltammetric data at a glassy carbon macrodisk electrode are very similar to that obtained at the platinum macrodisk electrode. Fourier transform AC (admittance) cyclic voltammograms (Figure 5) of the first process almost overlap in the positive and negative potential sweep directions, confirming the

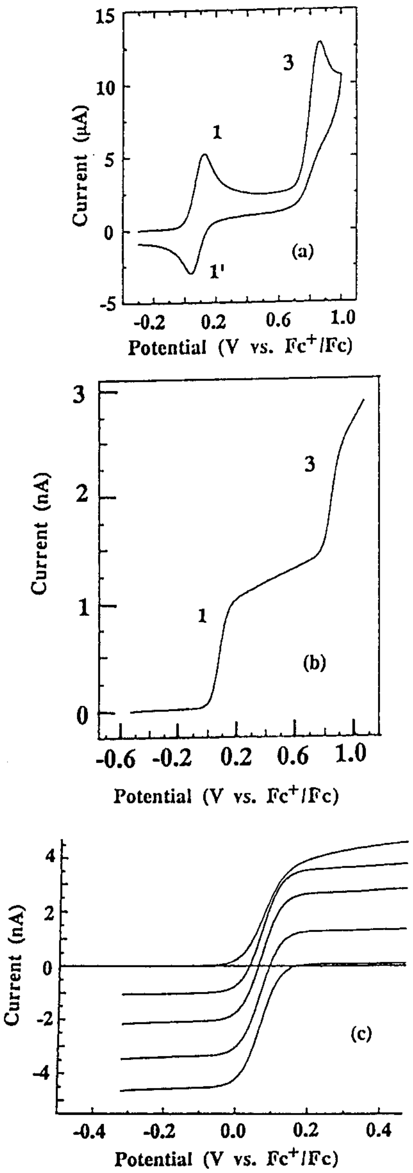

Figure 4. (a) Cyclic voltammogram at 20 °C for the oxidation of 1 mM *trans*-$Re(CO)(dpe)_2Br$ in dichloromethane (0.1 M Bu_4NPF_6) at a Pt disk electrode (radius 0.8 mm) at a scan rate of 100 mV s^{-1}. (b) Near steady-state voltammogram (scan rate 100 mV s^{-1}) recorded at a Pt microdisk electrode (radius 5 μm) for a 1 mM solution of *trans*-$Re(CO)(dpe)_2Br$ in dichloromethane (0.1 M Bu_4NPF_6). (c) Near steady-state voltammograms (scan rate 100 mV s^{-1}) recorded at a Pt microdisk electrode (radius 5 μm) during the oxidative bulk electrolysis of *trans*-$Re(CO)(dpe)_2Br$ in dichloromethane (0.1 M Bu_4NPF_6).

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[16] Pombeiro, A. J. L. *Inorg. Chim. Acta* **1985**, *103*, 95.

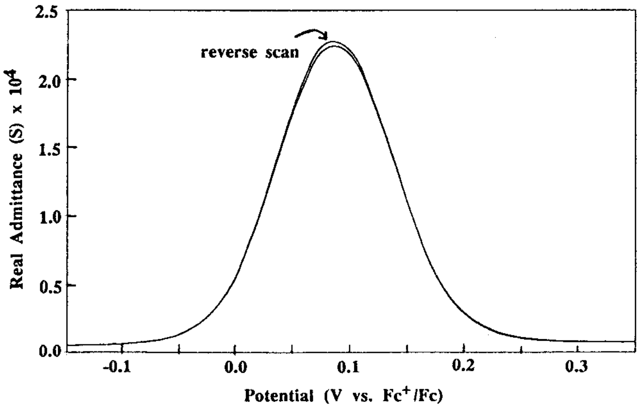

Figure 5. Fourier transform AC (admittance) cyclic voltammogram for oxidation of a 1 mM solution of *trans*-Re(CO)(dpe)$_2$Br in dichloromethane (0.1 M Bu_4NPF_6) at a Pt disk electrode (radius 0.8 mm). Frequency = 20 Hz, and total AC amplitude = 5 mV.

chemical reversibility and also confirming that the rate of electron transfer is very fast. Thus, the data suggest that redox couple 1 in dichloromethane is due to the process

$$\textit{trans}\text{-Re(CO)(dpe)}_2\text{Br} \xrightleftharpoons{\text{very fast}} \textit{trans}\text{-[Re(CO)(dpe)}_2\text{Br]}^+ + e^- \quad (4)$$

Evidence presented below confirms the assignment of *trans*-[Re(CO)(dpe)$_2$Br]$^+$ as the product.

Process 3 remains irreversible at high scan rates (up to 10 V s^{-1}) and low temperatures (−50 °C). A near steady-state voltammogram at a platinum microdisk electrode (radius 5 μm) shows the background limiting currents for oxidation processes 1 and 3 to be equal (Figure 3b), although the plateau region between the two processes has a definite slope for reasons which are unknown. Since the first process is shown to be a reversible one-electron process under these near steady-state conditions ($E^{r}_{1/2} = 0.080$ V vs Fc$^+$/Fc and E versus ln $(i_d - i)/i$ is linear with slope RT/F), process 3 can be assigned to the reaction

$$\begin{array}{ccl} \textit{trans}\text{-[Re(CO)(dpe)}_2\text{Br]}^+ & \rightleftharpoons & \textit{trans}\text{-[Re(CO)(dpe)}_2\text{Br]}^{2+} + e^- \\ & & \quad\downarrow \text{fast} \\ & & \quad\text{products} \qquad (5) \end{array}$$

Since the emphasis of this paper is on the generation of 17-electron Re(II) species, no further studies on the Re(III) products were undertaken.

The oxidation of *trans*-[Re(CO)(dpe)$_2$Br] was carried out in dichloromethane (0.1 M Bu_4NPF_6) in an IRRAS cell at 20 °C. The changes in the carbonyl region of the IR spectrum upon oxidation are shown in Figure 6. The ν(CO) band for *trans*-[Re(CO)(dpe)$_2$Br] at 1818 cm^{-1} gives way to a single band at 1892 cm^{-1}, which is assigned to the Re(II) cation, *trans*-[Re(CO)(dpe)$_2$Br]$^+$. These spectral changes are fully reversible in that rereduction regenerates, in its entirety, the original spectrum of *trans*-[Re(CO)(dpe)$_2$Br].

Bulk oxidative electrolysis of a 4 mM solution of *trans*-Re(CO)(dpe)$_2$Br in dichloromethane (0.1 M Bu_4NPF_6) at a potential slightly more positive than process 1 was monitored at a platinum microdisk electrode. Figure 3c shows the near steady-state voltammograms recorded during the electrolysis. The half-wave potential of the response ($E^{r}_{1/2}$) remained constant, but the sign of the current reversed from oxidation to reduction as the electrolysis proceeded, and the solution changed from colorless to dark green. Furthermore, during the course of the electrolysis the limiting current region assumes the ideal potential independent shape. Controlled-potential reductive electrolysis enables quantitative regeneration of *trans*-Re(CO)(dpe)$_2$Br to be achieved. Coulometric measurement showed that 0.95 ± 0.05 electrons per molecule was passed through the solution during both exhaustive oxidation and reduction electrolysis experiments. A cyclic voltammogram at a conventional macroelectrode electrode after oxidative electrolysis was qualitatively similar to that of the starting material, but the IR spectrum of the oxidized solution gave a single carbonyl stretch at 1892 cm^{-1}, compared with 1818 cm^{-1} for *trans*-Re(CO)(dpe)$_2$Br.

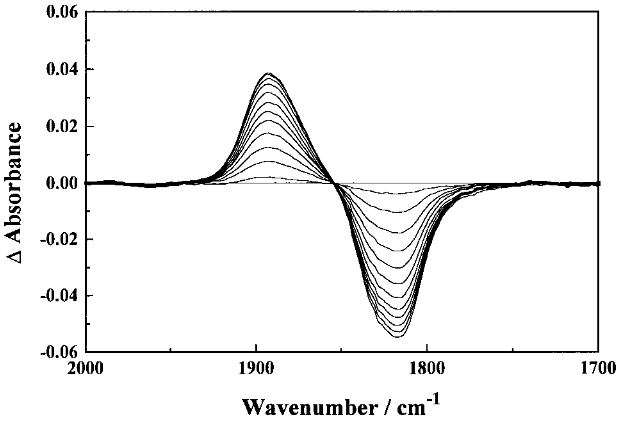

Figure 6. Changes in the carbonyl region of the IR difference spectrum upon oxidation of *trans*-[Re(CO)(dpe)$_2$Br] in an IRRAS cell in dichloromethane (0.1 M Bu_4NPF_6) at 20 °C.

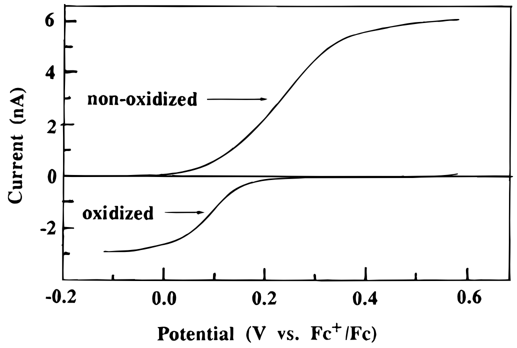

Figure 7. Near steady-state voltammograms at 20 °C at a Pt microdisk electrode (radius 5 μm) before and after oxidation of *trans*-Re(CO)(dpe)$_2$Br with $NOBF_4$ in dichloromethane (no electrolyte).

trans-[Re(CO)(dpe)$_2$Br]BF_4 was prepared in dichloromethane by oxidizing *trans*-Re(CO)(dpe)$_2$Br with $NOBF_4$, and the oxidation was monitored by microelectrode voltammetry in the absence of electrolyte. Figure 7 shows the voltammograms before and after chemical oxidation. Not only does the sign of the current change, as expected, but after oxidation the magnitude of the current is only 48% the initial value. This decrease in current after oxidation is due to the migration of the charged product to the auxiliary electrode. Theoretically, under steady-state conditions at a microdisk electrode in the absence of electrolyte, one-electron reduction of a monovalent cation should exhibit half the current observed for a one-electron oxidation of a neutral species.[17] Thus, the microelectrode voltammetry is in complete agreement with theory and the data confirm the chemical reversibilty, as well as the charge on the species associated with the *trans*-$[Re(CO)(dpe)_2Br]^{+/0}$ couple.

In principle, the product of oxidation could have been either the cis or trans isomer, since no direct spectroscopic evidence to identify the isomeric form could be obtained. However, the voltammetry (single processes for both oxidized and reduced forms with very fast electron transfer) and IR evidence (single ν_{CO} band shifted by $\approx$74 cm^{-1}) are in complete accord with retention of the trans configuration. Additionally, even though *trans*-$[Re(CO)(dpe)_2Br]BF_4$ is paramagnetic and has no observable ^{31}P NMR spectrum, its effect upon the ^{31}P NMR spectrum of *trans*-$Re(CO)(dpe)_2Br$ can be observed upon its addition to solutions of the diamagnetic 18e compound. Addition of about 0.2−0.4% of the paramagnetic species causes the single ^{31}P resonance of *trans*-$Re(CO)(dpe)_2Br$ at δ 25.0 ppm to broaden considerably and move to lower frequency, and addition of about 1% of the paramagnetic caused loss of the signal. However, addition of the strong reductant cobaltocene regenerated the sharp signal of *trans*-$Re(CO)(dpe)_2Br$ at δ 25.0 ppm. These observations are consistent with a fast self-exchange (electron exchange) reaction between isostructural 18e and 17e species.[14]

$$trans\text{-}Re^{*}(CO)(dpe)_2Br + trans\text{-}[Re(CO)(dpe)_2Br]^{+} \rightleftharpoons trans\text{-}[Re^{*}(CO)(dpe)_2Br]^{+} + trans\text{-}Re(CO)(dpe)_2Br \qquad (6)$$

In contrast, electron transfer reactions involving a structural change are likely to be slow on the NMR time scale.

The ESR spectrum (77 K) of a frozen dichloromethane solution of isolated *trans*-$[Re(CO)(dpe)_2Br]BF_4$ gives a broad signal at $g = 2.3$.

Voltammetry in acetone and acetonitrile using saturated solutions of sparingly soluble *trans*-$Re(CO)(dpe)_2Br$ also gave two well-defined oxidation responses. The reversible potentials for process 1 are 0.15 and 0.12 V, and the peak potentials for process 3 are 0.85 and 0.78 V vs Fc^+/Fc in acetone and acetonitrile, respectively. No evidence of solvent substitution reactions was found on the voltammetric time scale in either acetone or acetonitrile.

Voltammetry in dichloromethane solution of other complexes *trans*-$Re(CO)(P{-}P)_2Br$ (including those with different diphosphines) is generally similar, and data are summarized in Table 3. The corresponding cations *trans*-$[Re(CO)(P{-}P)_2Br]^+$ were produced in solution by oxidation of *trans*-$Re(CO)(P{-}P)_2Br$ with magic blue and identified by ESMS (Table 2). Monitoring by both voltammetry and ESMS showed the cations to be long-lived in solution.

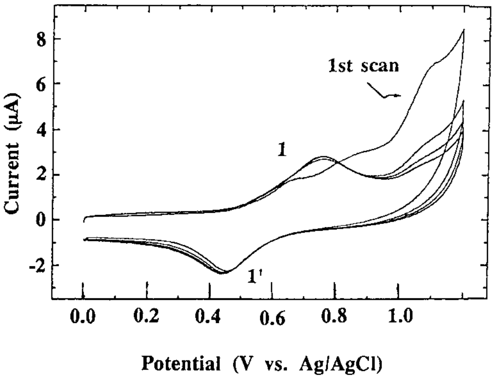

Figure 8. Cyclic voltammogram (scan rate 10 mV s^{-1}) at 20 °C for solid *trans*-$Re(CO)(dpe)_2Br$ attached to a graphite electrode immersed in water (0.1 M $NaClO_4$).

Table 4. Solid-State Voltammetric Data for *trans*-$Re(CO)(dpe)_2Br$

electrolyte	concn (M)	scan rate (mV s^{-1})	E_p^{ox} [a]	E_p^{red} [a]	ΔE (mV)	$E_{1/2}$ (V)
$NaClO_4$	0.01	10	0.80	0.52	280	0.66
	0.1	10	0.77	0.46	340	0.61
	1.0	10	0.73	0.46	270	0.59
	0.01	100	0.83	0.50	330	0.66
	0.1	100	0.80	0.44	360	0.62
	1.0	100	0.75	0.42	330	0.59
$NaClO_4$	0.05	10	0.74	0.47	270	0.60
	0.05	100	0.79	0.43	360	0.61
$CsClO_4$	0.05	10	0.77	0.50	270	0.63
	0.05	100	0.78	0.43	350	0.61
Et_4NClO_4	0.05	10	0.75	0.46	290	0.61
	0.05	100	0.79	0.43	360	0.61
KCl[b]	0.1	10	1.08	0.66	420	0.82
KPF_6	0.1	10	0.59	0.49	100	0.54
KBF_4	0.1	10	0.82	0.59	230	0.70
KNO_3	0.1	10	0.84	0.67	170	0.76
KCl[b]	0.1	100	1.03	0.61	420	0.82
KPF_6	0.1	100	0.60	0.42	180	0.51
KBF_4	0.1	100	0.86	0.54	320	0.70
KNO_3	0.1	100	0.87	0.66	210	0.77

[a] V vs Ag/AgCl. All potentials quoted vs Ag/AgCl (3 M KCl); $E_{1/2}$ of $[Fe(CN)_6]^{3-/4-}$ in 1 M KCl = 0.27 V. [b] Poorly defined oxidation peak.

(d) Solid-State Voltammetry of *trans*-$Re(CO)(dpe)_2Br$ and *trans*-$[Re(CO)(dpe)_2Br]BF_4$. Solid-state voltammograms (scan rate 10 mV s^{-1}) for *trans*-$Re(CO)(dpe)_2Br$ mechanically attached to a graphite electrode which is then placed in water (0.1 M $NaClO_4$), in which both the oxidized and reduced forms of the compound are insoluble, are shown in Figure 8. The response observed on the first cycle is complex, whereas on second and subsequent cycles a well-defined chemically reversible redox response, couple 1, is observed. The dissimilarity of the initial and subsequent scans, where a constant response is seen, has been observed previously in solid-state voltammetry.[18] Solid-state voltammetry of *trans*-$[Re(CO)(dpe)_2Br]BF_4$ is essentially indistinguishable from that of *trans*-$Re(CO)(dpe)_2Br$ except that even on the first cycle the only response is a well-defined process 1.

The potentials of the solid-state voltammograms were found to be dependent upon both electrolyte concentration and scan rate, as shown in Table 4. A higher concentration of electrolyte tended to shift both the oxidation and reduction peak potentials to less positive values. The potentials are essentially independent of

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(17) Cooper, J. B.; Bond, A. M.; Oldham, K. B. *J. Electroanal. Chem.* **1992**, *331*, 877.

(18) (a) Bond, A. M.; Colton, R.; Marken, F.; Walter, J. N. *Organometallics* **1994**, *13*, 5122.

the identity of the electrolyte cation but are dependent on the anion (Table 4). This shows that the mechanism of oxidation in the solid state involves the incorporation of the anion into the crystal structure and its expulsion upon subsequent reduction. The reaction associated with couple 1 is

$$\textit{trans}\text{-Re(CO)(dpe)}_2\text{Br} + \text{X}^- \rightleftharpoons \textit{trans}\text{-[Re(CO)(dpe)}_2\text{Br]X} + \text{e}^- \quad (7)$$

After attachment to the electrode of *trans*-[Re(CO)(dpe)$_2$Br]BF$_4$, ion exchange with the electrolyte anion occurs so consequently the voltammetry is that of *trans*-[Re(CO)(dpe)$_2$Br]X without complications on the first scan.

Conclusions and General Discussion

The 18e Re(I) carbonyl starting materials considered in this paper are either neutral or monocationic, and the other ligands vary from just diphosphines to a mixture of diphosphines and halides. This variation in charge and ligand types is reflected in a substantial potential range ($E°$ or E_p^{ox}) for oxidation (Table 3). However, despite this wide potential range, Re(II) is always thermodynamically stable in solution with these ligand combinations, although the strongest oxidants among the Re(II) species are reactive to adventious impurities, or light, and revert back to their 18e analogues. The trans form is dominant in Re(II), as predicted theoretically[15] and generally observed in earlier work, so that cis Re(II) species generated by oxidation isomerize rapidly to the trans isomers.

There is no evidence for rapid disproportionation or equivalent reactions which are a feature of the chemistry of some isoelectronic carbonyl compounds.[19] Similarly, no disproportionation reactions were observed in photochemical studies on Re(I) carbonyl compounds containing 2,2′-bipyridine and related ligands, where the photochemically generated Re(II) species are short-lived and quickly revert to Re(I) by a variety of mechanisms.[6]

Thus, the conclusion is that Re(II) carbonyl compounds described in this study are surprisingly stable in solution, although it should be noted that the related compounds [Re(CO)$_2$(P$_2$P′)X]$^+$ (P$_2$P′ = (Ph$_2$PCH$_2$CH$_2$)$_2$PPh) do show some tendency to undergo a slow overall disproportionation reaction to form the Re(III) cation [Re(CO)$_2$(P$_2$P′)X$_2$]$^+$.[5b] The same Re(III) cation, rather than the Re(II) species, is also produced by oxidation of [Re(CO)$_2$(P$_2$P′)X]$^+$ by bromine.[5b]

Acknowledgment. The authors acknowledge the financial support of the Australian Research Council and thank Dr. Georgii Lazarev and Dr. Richard Webster for recording the ESR spectrum. D.G.H. thanks the Australian Research Council for the provision of an Endeavour Fellowship, and J.N.W. thanks the Commonwealth of Australia for a Post Graduate Research Award.

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[19] Bond, A. M.; Colton, R. *Coord. Chem. Rev.* **1997**, *166*, 161.