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MIXED CARBONYL-THIOCARBONYL DIRHENIUM(III) COMPLEXES OF THE TYPE $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(\mu\text{-dppm})_2(CO)]PF_6$ ($X = Cl$ OR Br) AND THEIR CONVERSION TO THE ANALOGOUS μ-SULPHUR DIOXIDE COMPOUNDS

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Abstract—The reactions of $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-dppm})_2$ ($X = Cl$ or Br) with $TlPF_6$ and CO mixtures in CH_2Cl_2 afford green complexes of the type $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(\mu\text{-dppm})_2(CO)]PF_6$. The treatment of these carbonyl-containing products with $NOPF_6/O_2$ mixtures leads to the formation of the corresponding sulphur dioxide complexes $[Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(\mu\text{-dppm})_2(CO)]PF_6$. The μ-S and μ-SO_2 complexes exhibit a rich redox chemistry, which in the case of $[Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(\mu\text{-dppm})_2(CO)]PF_6$ has led to the isolation of the stable one- and two-electron reduction products $Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(\mu\text{-dppm})_2(CO)$ and $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(\mu\text{-dppm})_2(CO)]$. A comparison of the cyclic voltammetric and IR spectral properties of these carbonyl complexes with those of the previously isolated species $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-dppm})_2$, $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(\mu\text{-dppm})_2(L)]PF_6$ ($L = RCN$ or RNC) and their μ-SO_2 analogues reveals a clear dependence of the potentials of the metal-based redox couples and the frequencies of the ν(CS) mode upon the electron-withdrawing ability of the ancillary ligand (CO, RCN or RNC).

The multi-electron redox chemistry of the complexes $Re_2X_4(\mu\text{-dppm})_2$ ($X = Cl$ or Br; dppm = $Ph_2PCH_2PPh_2$) which contain the triply-bonded dirhenium(II) core has been a focus of several recent studies, including the reductive coupling of nitriles[1] and the reduction of small molecules such as dihydrogen sulphide[2,3] and carbon disulphide.[4] The two-electron reduction of carbon disulphide afforded edge-sharing bioctahedral complexes of the type $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-dppm})_2$.[4] These reactions were especially noteworthy because they constituted the first examples of the two-electron reduction of CS_2 with incorporation of the CS and S^{2-} fragments into a metal–metal bonded dimetal product. In the course of exploring the redox chemistry of these complexes and the closely related nitrile derivatives, $[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCR)]PF_6$, we discovered that the μ-S unit is readily oxygenated to μ-SO_2 in the presence of $NOPF_6/O_2$ mixtures with no change in the remainder of the coordination geometry.[5] In this report we describe the synthesis and properties of the related carbonyl-containing complexes $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]PF_6$ as well as their conversion to the analogous μ-SO_2 compounds. These species represent the first examples of mixed CO/CS complexes of the metal–metal bonded dirhenium(III) unit.

EXPERIMENTAL

Starting materials

The compounds $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-dppm})_2$ ($X = Cl$ or Br) were prepared according to the literature procedures.[4] All solvents were obtained from commercial sources and were used as received. Except where otherwise noted, syntheses were performed with the use of an atmosphere of dry nitrogen and solvents were deoxygenated prior to use.

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Reaction procedures

(A) *Synthesis of* $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]PF_6 \cdot CH_2Cl_2$. (i) X = Cl. A mixture of $Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2$ (0.200 g, 0.147 mmol), $TlPF_6$ (0.051 g, 0.147 mmol) and CH_2Cl_2 (20 cm^3) was stirred in a round bottomed flask. The flask was then flushed with carbon monoxide, the gas ports closed and the mixture stirred for 24 h at room temperature. The resulting green mixture was filtered to remove insoluble TlCl and the components of the filtrate were separated using column chromatography. A silica gel (230–400 mesh) column (length 10 cm and diameter 1.5 cm) was used with CH_2Cl_2 and acetone as eluants. A small blue band of unknown composition was first eluted with CH_2Cl_2, followed by a green band of $[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(CO)]PF_6$ with acetone. This green fraction was concentrated to *ca* 15 cm^3 and n-pentane was added to precipitate a green solid, which was filtered off and dried; yield 0.127 g (58%). Found: C, 40.5; H, 2.9. Calc. for $C_{53}H_{46}Cl_5F_6OP_5Re_2S_2$ (i.e. $[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(CO)]PF_6 \cdot CH_2Cl_2$): C, 40.3; H, 2.9%. The presence of lattice CH_2Cl_2 was confirmed by ^1H NMR spectroscopy using $CDCl_3$ as the solvent.

(ii) X = Br. A procedure similar to A(i) was used to prepare $[Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_2(CS)(dppm)_2(CO)]PF_6$ in 55% yield. Found: C, 38.9; H, 2.8. Calc. for $C_{52}H_{44}Br_4F_6OP_5Re_2S_2$: C, 39.2; H, 2.7.%

(B) *Synthesis of* $[Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]PF_6$. (i) X = Cl. This complex was prepared upon combining $[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(CO)]PF_6$ (0.100 g, 0.067 mmol) and $NOPF_6$ (0.011 g, 0.067 mmol) in CH_2Cl_2 (10 cm^3), which had *not* been deoxygenated. The mixture was stirred for 1 h, during which time the colour of the reaction mixture changed from green to red. The reaction mixture was filtered, the filtrate reduced in volume to *ca* 5 cm^3 and an excess diethyl ether added to initiate the precipitation of a red solid. The product was filtered off, washed with diethyl ether and vacuum dried; yield 0.075 g (78%). Found: C, 40.6; H, 2.9. Calc. for $C_{52}H_{44}Cl_3F_6O_3P_5Re_2S_2$: C, 40.8; H, 2.9%.

(ii) X = Br. Through the use of a procedure similar to that described in B(i), this complex was isolated in 77% yield. Found: C, 37.8; H, 2.9. Calc. for $C_{52}H_{44}Br_3F_6O_3P_5Re_2S_2$: C, 37.6; H, 2.7%.

(C) *Synthesis of* $Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)$. (i) X = Cl. The one-electron reduction of $[Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(CO)]PF_6$ was achieved upon stirring an equimolar mixture of this complex (0.100 g, 0.065 mmol) and $(\eta^5\text{-}C_5H_5)_2Co$ (0.012 g, 0.065 mmol) in acetone (10 cm^3) for 1 h at room temperature. The insoluble green product was filtered off and washed with acetone (15 cm^3) to remove trace amounts of unreacted cobaltocene, as well as the $[(\eta^5\text{-}C_5H_5)_2Co]PF_6$ reaction by-product. The remaining solid was finally washed with diethyl ether (15 cm^3) and vacuum dried; yield 0.072 g (80%). Found: C, 44.7; H, 3.2. Calc. for $C_{52}H_{44}Cl_3O_3P_4Re_2S_2$: C, 45.1; H, 3.2%.

(ii) X = Br. With the use of a procedure similar to that described in C(i), a green solid was isolated in 74% yield. Found: C, 42.4; H, 3.3. Calc. for $C_{55}H_{50}Br_3O_4P_4Re_2S_2$ [i.e. $Re_2(\mu\text{-}SO_2)(\mu\text{-}Br)Br_2(CS)(dppm)_2(CO) \cdot (CH_3)_2CO)$]: C, 41.9; H, 3.2%. The presence of lattice acetone was confirmed by ^1H NMR spectroscopy.

(D) *Synthesis of* $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]$. (i) X = Cl. A mixture of $[Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(CO)]PF_6$ (0.100 g, 0.065 mmol) and 2 equivalents of $(\eta^5\text{-}C_5H_5)_2Co$ (0.025 g, 0.013 mmol) in acetone (15 cm^3) was stirred for 3 h. During this time, a lime green solid formed initially and reacted further to give an olive green solid. This product was filtered off, washed with acetone (2 × 15 cm^3) and diethyl ether and vacuum dried; yield 0.082 g (80%). The identity of this product was based upon its IR spectrum and cyclic voltammetric properties.

(ii) X = Br. By using a procedure similar to that described in D(i), a brown–green solid was isolated in 75% yield. The identity of this complex was based upon its IR spectrum and cyclic voltammetric properties.

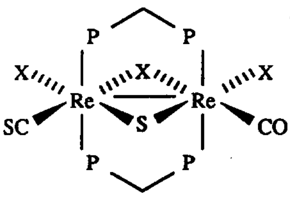
Physical measurements

A Perkin–Elmer 1800 FTIR spectrometer was used to record the IR spectra of the compounds as mineral oil (Nujol) mulls. Electrochemical measurements were performed on dichloromethane or acetonitrile solutions that contained 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a}+E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/Ag/Cl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions, $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were performed with a Bioanalytical Systems Inc. Model CV-27 instrument in conjunction with a Bioanalytical Systems Inc. *X–Y* recorder. All NMR spectra were recorded on CD_2Cl_2 solutions of the complexes. The $^{31}P\{^1H\}$ NMR spectra were obtained with the use of a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock and 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on a Varian Gemini-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent ($\delta + 5.35$). X-Band ESR spectra were recorded at *ca* $-160°C$ with the use of a Varian E-109 spectrometer. Conductivity measurements were performed on *ca* 10^{-3} M acetonitrile solutions by using an Industrial Instruments Inc. Model RC-16B2 conductivity bridge.

Elemental microanalyses were performed by Dr H. D. Lee of the Purdue University Microanalytical Laboratory.

RESULTS AND DISCUSSION

The reactions of $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-dppm})_2$ ($X = Cl$ or Br) with $TlPF_6$ and CO in CH_2Cl_2 result in the labilization of one of the terminal Re—X bonds and afford green complexes of the type $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]PF_6$ in moderate yield (55–60%). This behaviour resembles that seen in the case of the reactions of $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(dppm)_2$ with nitriles and isocyanides in the presence of $TlPF_6$.[4] The IR spectra (Nujol mulls) of the products reveal the presence of a terminal CO group, characterized by a single intense $\nu(CO)$ mode at 2038 cm^{-1}, and a terminal CS ligand, with an intense $\nu(CS)$ mode at *ca* 1330 cm^{-1} (Table 1). Conductivity measurements on acetone solutions of these complexes (*ca* 1×10^{-3} M) are in accord with their formulation as 1 : 1 electrolytes ($\Lambda_M = 122\text{–}127\ \Omega^{-1}\,cm^2\,mol^{-1}$).[6] The ^1H NMR spectral properties of $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]PF_6$ are similar and reveal the methylene protons of the dppm ligands as AB patterns with superimposed P—H coupling (Table 1). Like the corresponding spectra of the analogous nitrile-containing derivatives,[4] this ABX_4 pattern (Table 1) is shifted appreciably upfield of the comparable pattern in the spectra of the $\mu\text{-}SO_2$ complexes (*vide infra*). The $^{31}P\{^1H\}$ spectrum of $[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(CO)]PF_6$ (recorded in CD_2Cl_2) reveals the expected AA′BB′ pattern with multiplets centred at δ -47.1 and δ -52.4. This characteristic, along with the other aforementioned properties of this complex, suggests that like the analogous structurally characterized nitrile and isocyanide complexes, $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(\mu\text{-dppm})_2(L)]PF_6$ ($L = RCN$ or RNC), these carbonyl-containing compounds have the unsymmetrical edge-sharing bioctahedral structure **I**, with different ligand environments about each rhenium nucleus.



I

The reactions of $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]PF_6$ and $NOPF_6$ in dichloromethane lead to the formation of the analogous $\mu_2\text{-}SO_2$ compounds $[Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]PF_6$. These reactions occur only when O_2 is present and almost certainly involve NO_2 as the actual oxygen transfer reagent, as we have found in the case of the conversions of $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-dppm})_2$ and $[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-dppm})_2(NCR)]PF_6$ to their $\mu\text{-}SO_2$ analogues.[5] These complexes comprise an interesting and unique series of edge-sharing bioctahedral metal–metal bonded dirhenium compounds that contain a combination of CO, CS and SO_2 ligands.

The IR spectra of the $\mu\text{-}SO_2$ complexes display $\nu(CO)$ and $\nu(CS)$ modes at frequencies similar to those of their μ-S analogues and a characteristic $\nu(SO_2)$ mode at 1070 cm^{-1} (Table 1). While two $\nu(SO)$ modes should characterize a bridging $\mu\text{-}SO_2$ ligand,[5,7–10] the higher frequency mode in the present cases appears to be overlapped by other ligand modes and is not clearly discernible. The methylene protons of the dppm ligands appear in the ^1H NMR spectra as AB patterns with superimposed P—H coupling (Table 1). These resonances are characteristically[4] downfield of the corresponding multiplets in the spectra of their μ-S analogues. The $^{31}P\{^1H\}$ NMR spectrum of $[Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-dppm})_2(CO)]PF_6$ (recorded in CD_2Cl_2) is similar to that of its μ-S precursor complex in exhibiting the expected AA′BB′ splitting pattern; the multiplets are centred at δ -9.7 and δ -13.6. Conductivity measurements on an acetone solution of this chloro complex showed behaviour in accord with it being a 1 : 1 electrolyte ($\Lambda_m = 110\ \Omega^{-1}\,cm^2\,mol^{-1}$ for $c_m = 1.0 \times 10^{-3}$ M).[6]

The electrochemical properties of the μ-S and $\mu\text{-}SO_2$ complexes were measured by use of the cyclic voltammetric (CV) technique. These data are presented in Table 1 for solutions of these complexes in 0.1 M $TBAH/CH_2Cl_2$. The complexes $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(\mu\text{-dppm})_2(CO)]PF_6$ exhibit one oxidation and two reductions, but attempts to access chemically the first reduction $[E_{1/2}(red)(1)]$ led to decomposition of the solutions. The electrochemical data for the chloro complex are compared in Table 2 with literature data[4,5] for the complexes $Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(CS)(\mu\text{-dppm})_2$ and $[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-dppm})_2(CNR)]PF_6$, where $R = Bu^t$ or xylyl. As might be expected, the relatively strong electron-withdrawing effect of the CO ligand results in the values of $E_{1/2}(ox)(1)$ and

Table 1. Important spectroscopic and electrochemical properties of mixed carbonyl-thiocarbonyl complexes of dirhenium

Complexes	IR (cm^{-1})^a ν(CO)	 ν(CS)	 ν(SO$_2$)^d	^{1}H NMR (δ)^b —CH$_2$—	CV half-wave potentials (V)^c $E_{1/2}$(ox)(1)	 $E_{1/2}$(red)(1)	 $E_{1/2}$(red)(2)	 $E_{1/2}$(red)(3)
[Re$_2$(μ-S)(μ-Cl)Cl$_2$(CS)(μ-dppm)$_2$(CO)]PF$_6$	2038 s	1334 s		+2.62 m, +0.40 m	+1.17(70)	+0.04(60)	−1.56(80)	
[Re$_2$(μ-S)(μ-Br)Br$_2$(CS)(μ-dppm)$_2$(CO)]PF$_6$	2038 s	1330 s		+3.41 m, +1.25 m	+1.16(80)	+0.03(80)	−1.61^e	
[Re$_2$(μ-SO$_2$)(μ-Cl)Cl$_2$(CS)(μ-dppm)$_2$(CO)]PF$_6$	2036 s	1338 s	1070 m	+5.94 m, +4.50 m		+0.53(70)	−0.36(70)	−1.65^e
[Re$_2$(μ-SO$_2$)(μ-Br)Br$_2$(CS)(μ-dppm)$_2$(CO)]PF$_6$	2034 s	1336 s	1070 m	+5.98 m, +4.68 m		+0.59(70)	−0.29(70)	−1.64^e
Re$_2$(μ-SO$_2$)(μ-Cl)Cl$_2$(CS)(μ-dppm)$_2$(CO)	2004, 1980 s	1314 s	1038 m	^{f}		+0.56^g	−0.37	−1.67^e
Re$_2$(μ-SO$_2$)(μ-Br)Br$_2$(CS)(μ-dppm)$_2$(CO)	2002, 1982 s	1310 s	1038 m	^{f}		+0.56^g	−0.33	−1.68^e
[(η^5-C$_5$H$_5$)$_2$Co][Re$_2$(μ-SO$_2$)(μ-Cl)Cl$_2$(CS)(μ-dppm)$_2$(CO)]	1936 s	1264 s	1002 m	^{h}		+0.56^g	−0.36^g	−1.65^e
[(η^5-C$_5$H$_5$)$_2$Co][Re$_2$(μ-SO$_2$)(μ-Br)Br$_2$(CS)(μ-dppm)$_2$(CO)]	1936 s	1264 s	1000 m-w	^{h}		+0.56^g	−0.32^g	−1.65^e

[a] Recorded as Nujol mulls. The hexafluorophosphate salts show a characteristic intense ν(P—F) mode at *ca* 840 cm^{-1}.

[b] Measured in CD$_2$Cl$_2$. Resonances are of the two principal components of an ABX$_4$ splitting pattern.

[c] Measured on 0.1 M TBAH/CH$_2$Cl$_2$ solutions of the complexes and referenced to the Ag/AgCl electrode, with a scan rate (ν) of 200 mV s^{-1} at a platinum-bead electrode. Numbers in parentheses are $E_{p,a}$-$E_{p,c}$ values.

[d] A second, higher frequency ν(SO$_2$) mode is partially obscured by other ligand modes and, therefore, is not quoted.

[e] $E_{p,c}$ value.

[f] Paramagnetic complex.

[g] $E_{1/2}$(ox) value.

[h] Too insoluble to give a satisfactory spectrum.

Table 2. Comparison of the electrochemical and IR spectral properties of μ-sulphido and μ-sulphur dioxide complexes of dirhenium^a

Complexes	CV half-wave potentials (V) $E_{1/2}$(ox)(2)	 $E_{1/2}$(ox)(1)	 $E_{1/2}$(red)(1)	 $E_{1/2}$(red)(2)	 $E_{1/2}$(red)(3)	IR (cm^{-1}) ν(CS)	Ref.
Re$_2$(μ-S)(μ-Cl)Cl$_3$(CS)(μ-dppm)$_2$	+1.40	+0.40	−0.45	−1.50^b		1291	4
[Re$_2$(μ-S)(μ-Cl)Cl$_2$(CS)(μ-dppm)$_2$(CNBu^t)]PF$_6$		+0.91	−0.28	−0.84	−1.23	1310	4
[Re$_2$(μ-S)(μ-Cl)Cl$_2$(CS)(μ-dppm)$_2$(CNxyl)]PF$_6$		+0.88	−0.19	−0.73	−1.29	1308	4
[Re$_2$(μ-S)(μ-Cl)Cl$_2$(CS)(μ-dppm)$_2$(CO)]PF$_6$		+1.17	+0.04	−1.56		1334	This work
Re(μ-SO$_2$)(μ-Cl)Cl$_3$(CS)(μ-dppm)$_2$		+1.12	−0.20	−1.08		1308	5
[Re$_2$(μ-SO$_2$)(μ-Cl)Cl$_2$(CS)(μ-dppm)$_2$(NCMe)]PF$_6$		+1.75	+0.23	−0.68		1328	5
[Re$_2$(μ-SO$_2$)(μ-Cl)Cl$_2$(CS)(μ-dppm)$_2$(NCEt)]PF$_6$		+1.72	+0.22	−0.72		1328	5
[Re$_2$(μ-SO$_2$)(μ-Cl)Cl$_2$(CS)(μ-dppm)$_2$(CO)]PF$_6$			+0.53	−0.36	−1.65^b	1338	This work

[a] Data for chloro complexes only are given. In those instances where the corresponding bromo complexes have been characterized the same trends are observed.

[b] $E_{p,c}$ value.

$E_{1/2}$(red)(1) being the most positive for this set of complexes, while the unsubstituted complex $Re_2(\mu$-$S)(\mu$-$Cl)Cl_3(CS)(\mu$-dppm$)_2$ has the most negative values. A consequence of this shift in the potentials is that a second oxidation [$E_{1/2}$(ox)(2)] becomes accessible for $Re_2(\mu$-$S)(\mu$-$Cl)Cl_3(CS)(\mu$-dppm$)_2$ within the potential range studied (+1.5 to −1.5 V). Note that the values for $E_{1/2}$(red)(2) in Table 2 do not show this same smooth trend, an indication that this particular reduction process may involve an orbital in which there is a significant and variable ligand contribution. Paralleling these electrochemical results is a shift in the value of the ν(CS) mode for this set of complexes (see Table 2). Its frequency increases as the electron-withdrawing effect of the ancillary ligand increases (CNR < CO). An increase in ν(CS) reflects an increasing build-up of positive charge at the dimetal core and a decrease in Re(d)→ CS(π^*) back-bonding. This in turn should also lead (as it does) to a shift in the metal-based redox couples to more positive potentials. The net result is that an increase in ν(CS) is accompanied by an increase in $E_{1/2}$(ox)(1) and $E_{1/2}$(red)(1) (Table 2).

In the case of $[Re_2(\mu$-$SO_2)(\mu$-$X)X_2(CS)(\mu$-dppm$)_2(CO)]PF_6$ (X = Cl or Br), the CVs of solutions of these complexes in 0.1 M TBAH/CH_2Cl_2 (Table 1) are related to those of the previously reported $Re_2(\mu$-$SO_2)(\mu$-$X)X_3(CS)(\mu$-dppm$)_2$ (X = Cl or Br) and the nitrile-containing derivatives $[Re_2(\mu$-$SO_2)(\mu$-$Cl)Cl_2(CS)(\mu$-dppm$)_2(NCR)]PF_6$ (R = Me or Et).[5] Three reduction processes are observed for the carbonyls (Fig. 1), the first two being shifted by ca +0.3 V relative to the corresponding processes in CVs of the other μ-SO_2 complexes listed in Table 2. A third reduction is not detected in the CVs of $Re_2(\mu$-$SO_2)(\mu$-$X)X_3(CS)(\mu$-dppm$)_2$ and $[Re_2(\mu$-$SO_2)(\mu$-$Cl)Cl_2(CS)(\mu$-dppm$)_2$ $(NCR)]PF_6$, but an oxidation is now accessible for these complexes. The shifts in the values of $E_{1/2}$(red)(1) and $E_{1/2}$(red)(2) reflect an increase in the π-accepting ability of CO compared with RCN. An increase in $E_{1/2}$(red)(1) and $E_{1/2}$(red)(2) is paralleled by an increase in the frequency of the ν(CS) mode (Table 2). This is similar to the relationship between ν(CS) and the values of the metal-based potentials in the CVs of the μ-S complexes.

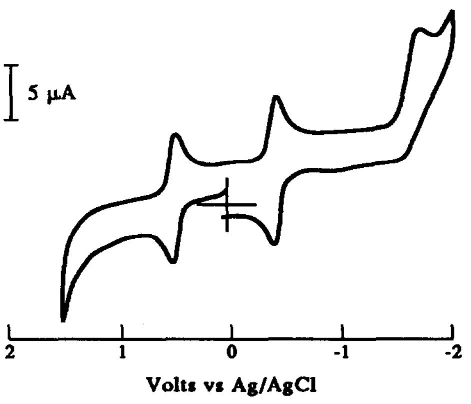


Fig. 1. The single sweep cyclic voltammogram of a solution of $[Re_2(\mu$-$SO_2)(\mu$-$Cl)Cl_2(CS)(\mu$-dppm$)_2(CO)]PF_6$ in 0.1 M TBAH/CH_2Cl_2 recorded at a sweep rate of 200 mV s^{-1}. Both reversible processes correspond to reductions for the bulk complex and can be accessed through the use of cobaltocene.

The accessibility and reversibility of the process at ca +0.5 V in the CVs of $[Re_2(\mu$-$SO_2)(\mu$-$X)X_2(CS)(\mu$-dppm$)_2(CO)]PF_6$ (Fig. 1) was demonstrated by their reductions to the green, paramagnetic compounds $Re_2(\mu$-$SO_2)(\mu$-$X)X_2(CS)(\mu$-dppm$)_2(CO)$ with the use of $(\eta^5$-$C_5H_5)_2Co$ as a reductant. Upon reduction of the dimetal core, an increase in metal-to-CO and metal-to-CS back-bonding should take place and this is indeed found to be the case as the ν(CO) modes are shifted by ca -35 cm^{-1} and the ν(CS) modes by ca -25 cm^{-1}. The CVs of $Re_2(\mu$-$SO_2)(\mu$-$X)X_2(CS)(\mu$-dppm$)_2(CO)$ are similar to those of their cationic precursors, except that the process at ca +0.5 V now corresponds to an oxidation for the bulk complex. Solutions of $Re_2(\mu$-$SO_2)(\mu$-$X)X_2(CS)(\mu$-dppm$)(CO)$ in acetone are essentially non-conducting, while their solutions in CH_2Cl_2 at −160°C possess X-band ESR spectra which exhibit fairly isotropic signals at $g \approx 2.2$, showing a well-resolved but complicated hyperfine structure. A solution of $Re_2(\mu$-$SO_2)(\mu$-$Cl)Cl_2(CS)(\mu$-dppm$)_2(CO)$ in CH_2Cl_2 was found to have a magnetic moment of 1.7 (±0.1) B.M., as determined by the Evans method.

The reversible reduction at ca −0.33 V [$E_{1/2}$(red)(2)] in the CVs of the neutral complexes $Re_2(\mu$-$SO_2)(\mu$-$X)X_2(CS)(\mu$-dppm$)_2(CO)$ can also be accessed through the use of $(\eta^5$-$C_5H_5)_2Co$, to yield the diamagnetic salts $[(\eta^5$-$C_5H_5)_2Co][Re_2(\mu$-$SO_2)(\mu$-$X)X_2(CS)(\mu$-dppm$)_2(CO)]$. The same complexes can be obtained by reacting 2 equivalents of $(\eta^5$-$C_5H_5)_2Co$ with $[Re_2(\mu$-$SO_2)(\mu$-$X)X_2(CS)(\mu$-dppm$)_2$ $(CO)]PF_6$. The shift of the ν(CO) and ν(CS) modes to lower frequencies relative to their neutral precursors is to be expected (Table 1), the shifts being ca −50 and −40 cm^{-1}, respectively. The IR spectra showed no evidence for contamination by their higher valent congeners from which they are formed. While the poor solubility properties of these complexes precluded us from obtaining satisfactory NMR spectral data, they were sufficiently soluble in 0.1 M TBAH/CH_2Cl_2 for their CVs to be recorded (Table 1). These measurements established that the structural integrity of these species had been maintained through the reduction process. Furthermore, the presence of an additional reversible process at $E_{1/2} = -0.89$ V, due to the $[(\eta^5\text{-}C_5H_5)_2Co]^+/(\eta^5\text{-}C_5H_5)_2Co$ couple, confirmed the presence of the cobaltocenium cation.

CONCLUSIONS

The formation of the complexes $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(dppm)_2(CO)]PF_6$ and their closely related $\mu\text{-}SO_2$ analogues constitutes the first examples of mixed CO/CS and CO/CS/SO_2 complexes of the metal–metal bonded dirhenium unit. The accessibility of two one-electron reductions in the case of $[Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(\mu\text{-}dppm)_2(CO)]PF_6$ has permitted the generation and isolation of the reduction products $Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(\mu\text{-}dppm)_2(CO)$ and $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(\mu\text{-}dppm)_2(CO)]$ when cobaltocene is used as the reducing agent.

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REFERENCES

1. D. Esjornson, D. R. Derringer, P. E. Fanwick and R. A. Walton, *Inorg. Chem.* 1989, **28**, 2821.
2. K.-Y. Shih, P. E. Fanwick and R. A. Walton, *J. Chem. Soc., Chem. Commun.* 1992, 375.
3. K.-Y. Shih, P. E. Fanwick and R. A. Walton, *J. Cluster Sci.* 1992, **2**, 259.
4. J.-S. Qi, P. W. Schrier, P. E. Fanwick and R. A. Walton, *Inorg. Chem.* 1992, **31**, 258.
5. P. W. Schrier, P. E. Fanwick and R. A. Walton, *Inorg. Chem.* 1992, **31**, 3929.
6. W. J. Geary, *Coord. Chem. Rev.* 1971, **7**, 81.
7. A. L. Balch, L. S. Benner and M. M. Olmstead, *Inorg. Chem.* 1979, **18**, 2996.
8. M. Cowie and S. K. Dwight, *Inorg. Chem.* 1980, **19**, 209.
9. M. Cowie and S. K. Dwight, *Inorg. Chem.* 1980, **19**, 2500.
10. A. L. Balch, B. J. Davis and M. M. Olmstead, *Inorg. Chem.* 1989, **29**, 3148.