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STUDIES DIRECTED TOWARDS THE ISOLATION AND CHARACTERIZATION OF THE PARAMAGNETIC CATIONS $[Re_2X_4(LL)_2]^+$ (X = Cl OR Br; LL = $Ph_2PCH_2PPh_2$, $Ph_2AsCH_2AsPh_2$ OR $Ph_2PNHPPh_2$), AND THE CRYSTAL STRUCTURE OF $Re_2Cl_4(Ph_2PNHPPh_2)_2 \cdot (CH_3)_2CO$

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Abstract—The synthesis of the triply bonded dirhenium(II) complexes $Re_2X_4(dpam)_2$ (X = Cl or Br; dpam = $Ph_2AsCH_2AsPh_2$) has been accomplished through the reactions of $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ with dpam in hot methanol. Solutions of these complexes, and of $Re_2X_4(dppm)_2$ (X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$) and $Re_2Cl_4(dppa)_2$ (dppa = $Ph_2PNHPPh_2$), in n-Bu_4NPF_6/CH_2Cl_2 have been oxidized electrochemically (at *ca* +0.5 V vs Ag/AgCl) to generate solutions of the paramagnetic, ESR-active monocations. The salts $[Re_2X_4(dppm)_2]PF_6$ have been prepared by the reaction of $Re_2X_4(dppm)_2$ with $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in acetone. Cyclic voltammetric data for solutions of all these complexes in 0.1 M n-Bu_4NPF_6/CH_2Cl_2 are reported. The crystal structure of $Re_2Cl_4(dppa)_2 \cdot (CH_3)_2CO$ has been determined and shown to resemble that of $Re_2Cl_4(dppm)_2$. The crystallographic data are as follows: monoclinic space group $P2_1/n$, $a = 11.382(2)$, $b = 23.273(5)$, $c = 19.212(3)$ Å, $\beta = 92.429(8)°$, $V = 5084(3)$ Å^3 and $Z = 4$. The structure was refined to $R = 0.031$ ($R_w = 0.036$) for 4490 data with $I > 3.0\sigma(I)$. The complex has a Re—Re bond distance of 2.2417(5) Å, and contains intramolecular dppa ligand bridges. A staggered rotational geometry is characterized by average Cl—Re—Re—Cl and P—Re—Re—P torsional angles of 51.7[2] and 41.8[5]°, respectively.

The triply bonded dirhenium(II) complexes $Re_2X_4(PR_3)_4$ (X = Cl, Br or I; PR_3 = monodentate phosphine) are readily converted to salts of their mono- and dicationic species $[Re_2X_4(PR_3)_4]PF_6$ and $[Re_2X_4(PR_3)_4](PF_6)_2$ that possess Re—Re bond orders of 3.5 and 4, respectively, with associated ground-state electronic configurations of $\sigma^2\pi^4\delta^2\delta^{*1}$ and $\sigma^2\pi^4\delta^2$.[1-4] The complexes $Re_2X_4(\mu\text{-LL})_2$, where LL represents an intramolecular bridging ligand such as $Ph_2PCH_2CH_2PPh_2$ (dppe) that has a —$(CH_2)_2$— unit linking the donor atoms of the ligands LL, have also been oxidized in this fashion and salts of the corresponding cations can be isolated in certain circumstances.[5,6]

Although $Re_2Cl_4(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$) has been oxidized to $Re_2Cl_5(dppm)_2$ and subsequently to $Re_2Cl_6(dppm)_2$, by controlled potential electrolysis in the presence of chloride ion,[7] the simple monocation $[Re_2Cl_4(dppm)_2]^+$ has never been isolated, in spite of the accessibility of two sequential one-electron oxidations as shown by electrochemical measurements on this complex.[7] The same is true for other complexes of dirhenium(II) in which there is a *single* bridgehead group linking the two phosphorus atoms of the bidentate phosphine ligand.[7]

In view of the importance of $Re_2Cl_4(dppm)_2$ and related complexes as synthetic precursors to a wide range of dirhenium complexes,[8,9] we have examined the redox chemistry of such complexes with a view

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to generating and characterizing their oxidized derivatives. In the present report we describe (1) the syntheses of the new complexes $Re_2X_4(dpam)_2$ (X = Cl or Br; dpam = $Ph_2AsCH_2AsPh_2$), (2) the electrochemical and chemical oxidations of these complexes and of $Re_2X_4(dppm)_2$ (X = Cl, Br or I) and $Re_2Cl_4(dppa)_2$ (dppa = $Ph_2PNHPPh_2$), and (3) the crystal structure of $Re_2Cl_4(dppa)_2 \cdot (CH_3)_2CO$.

EXPERIMENTAL

Starting materials

The complexes $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (X = Cl, Br or I),[10] $Re_2Cl_4(dppa)_2$,[11] $Re_2X_4(dppm)_2$[12] and ferrocenium hexafluorophosphate $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$,[13] were prepared according to the reported methods. Bis(diphenylarsino)methane (abbreviated dpam) was purchased from Pressure Chemicals and was used without further purification. Solvents used in the preparation of the complexes were of commercial grade and were thoroughly deoxygenated with dinitrogen prior to use.

Reactions procedures

All reactions were performed under an atmosphere of dry dinitrogen.

(a) *Preparation of* $Re_2X_4(dpam)_2$. (i) $Re_2Cl_4(dpam)_2$: A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.20 g, 0.24 mmol) and 4 equiv. of dpam (0.45 g, 0.96 mmol) in methanol (20 cm^3) was refluxed for 24 h. The resulting purple–brown precipitate was filtered hot and washed with 3 × 15 cm^3 portions of hot methanol. Recrystallization from dichloromethane–methanol at 0°C gave the product as a purple powder; yield, 0.045 g (10%). Found: C, 39.8; H, 2.9. Calc. for $C_{50}H_{44}Cl_4As_4Re_2$: C, 41.2; H, 3.0%. This sample probably contains some dichloromethane of crystallization, thereby accounting for the slightly low carbon and hydrogen elemental microanalyses.

(ii) $Re_2Br_4(dpam)_2$: The preparation of this complex was carried out in exactly the same manner as that described in section a(i); yield, 40%. Found: C, 35.7; H, 2.7; Br, 19.8. Calc. for $C_{50}H_{44}Br_4As_4Re_2$: C, 36.7; H, 2.7; Br, 19.5%.

(b) *Oxidation of* $Re_2X_4(dppm)_2$ *with* $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$. (i) $[Re_2Cl_4(dppm)_2]PF_6$: A quantity of $Re_2Cl_4(dppm)_2$ (0.20 g, 0.16 mmol) was allowed to react with 1 equiv. of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.052 g, 0.16 mmol) in acetone (15 cm^3) for 5 min at room temperature. The resulting green–brown solution was filtered into a large excess of diethyl ether ($\simeq$ 100 cm^3) to yield a green precipitate. This was filtered off, washed with diethyl ether and dried *in vacuo*; yield, 0.19 g (85%). Found: C, 41.9; H, 3.3. Calc. for $C_{50}H_{44}Cl_4F_6P_5Re_2$: C, 42.1; H, 3.1%.

(ii) $[Re_2Br_4(dppm)_2]PF_6$: The preparation of this complex was carried out in exactly the same manner as that described in section b(i); yield, 70%. Found: C, 37.9; H, 3.0. Calc. for $C_{50}H_{44}Br_4F_6P_5Re_2$: C, 37.4; H, 2.8%.

(c) *Bulk electrolysis of* $Re_2X_4(dppm)_2$, $Re_2Cl_4(dppa)_2$ *and* $Re_2Br_4(dpam)_2$. Approximately 0.02 g quantities of these compounds were dissolved in 0.1 M $n\text{-}Bu_4NPF_6\text{–}CH_2Cl_2$ (20 cm^3) contained in an H-cell. Exhaustive electrolysis was performed on these solutions at *ca* +0.50 V for approximately 15 min at room temperature. Cyclic voltammograms were recorded and found to be essentially the same as those for their neutral precursors except that the processes at $E_{1/2} \simeq +0.3$ V (vs Ag/AgCl) now corresponded to reductions of the bulk complexes, thereby confirming that a one-electron oxidation had taken place.

Preparation of single crystals of $Re_2Cl_4(dppa)_2 \cdot (CH_3)_2CO$

Crystals were grown by diffusion of heptane vapour into a toluene solution of the complex that also contained a small amount of acetone.

X-ray crystallographic studies

The structure of $Re_2Cl_4(dppa)_2 \cdot (CH_3)_2CO$ was determined with the use of general procedures that are described elsewhere.[14] A summary of the crystallographic data is given in Table 1. The cell constants are based on 25 reflections with $20° < \theta < 23°$. Three standard reflections were measured after every 5000 s of beam time during data collection. There was no systemmatic variations in intensity. Calculations were performed on a Micro VAX II computer using the Enraf–Nonius structure determination package.

The crystal selected for the structure determination belonged to the monoclinic space group $P2_1/n$ with $Z = 4$. As a check on crystal quality, omega scans of several intense reflections were measured; the width at half-height was 0.70° with a take-off angle of 2.4° indicating relatively poor crystal quality. The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the rhenium atoms in the asymmetric unit. The remaining atoms were located in succeeding difference Fourier syntheses. Lorentz and polarization corrections were applied to the data. An empirical absorption correction was

Table 1. Crystal data and data collection parameters for $Re_2Cl_4(dppa)_2 \cdot (CH_3)_2CO$[a]

Formula	$Re_2Cl_4P_4ON_2C_{51}H_{48}$
Formula weight	1343.07
Space group	$P2_1/n$ (No. 14)
a (Å)	11.382(2)
b (Å)	23.273(5)
c (Å)	19.212(3)
β (°)	92.479(8)
V (Å^3)	5084(3)
Z	4
d_{calc} (g cm^{-3})	1.755
Crystal dimensions (mm)	0.26 × 0.22 × 0.14
Temperature (°C)	20
Radiation (wavelength)	Mo-K_α (0.71073 Å)
Monochromator	Graphite
Linear absorption coefficient (cm^{-1})	51.97
Absorption correction applied	Empirical[b]
Transmission factors: min, max	0.69, 1.00
Diffractometer	Enraf–Nonius CAD4
Scan method	ω–2θ
h, k, l limits	−12–12, 0–25, 0–20
2θ range (°)	4.00–45.00
Scan width (°)	$0.70+0.35 \tan \theta$
Take-off angle (°)	2.40
Programs used	Enraf–Nonius SDP
$F(000)$	2616.0
p-Factor used in weighting	0.040
Data collected	6835
Unique data	6835
Data with $I > 3.0\sigma(I)$	4490
Number of variables	557
Largest shift/ESD in final cycle	0.00
R[c]	0.031
R_w[d]	0.036
Goodness-of-fit[e]	0.937

[a] Number in parentheses following certain data are ESDs occurring in the least significant digit.

[b] N. Walker and D. Stuart, *Acta Cryst.* 1983, **A39**, 158.

[c] $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$.

[d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$.

[e] Goodness-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

applied,[15] the linear absorption coefficient being 51.97 cm^{-1}. No corrections for extinction were applied. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$; w is the weighting factor defined as $w = 1/\sigma^2(F_o)$.

During the course of the refinement, it became apparent that residual electron density at a fairly close contact to the bridgehead NH group of one of the dppa ligands could be satisfactorily modelled as lattice acetone. This was located on a general position, and it refined to a site of full occupancy, the carbon and oxygen atoms having satisfactory thermal parameters. Accordingly, the unit cell contains one molecule of acetone for each dirhenium molecule. Positions for the hydrogen atoms of the dppa ligands and the lattice acetone were calculated by assuming idealized geometry and a C—H bond distance of 0.95 Å. We also assumed that the value of B(H), i.e. the isotropic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_o, they were not included in the least-squares refinement. With the exception of the lattice acetone molecules, all non-hydrogen atoms were refined anisotropically; corrections for anomalous scattering

Table 2. Selected bond distances (Å) and angles (°) for $Re_2Cl_4(dppa)_2 \cdot (CH_3)_2CO$[a]

Distances

Bond	Distance	Bond	Distance
Re(1)—Re(2)	2.2417(5)	Re(2)—P(21)	2.413(3)
Re(1)—Cl(11)	2.353(3)	Re(2)—P(22)	2.422(3)
Re(1)—Cl(12)	2.357(3)	P(11)—N(1)	1.683(8)
Re(1)—P(11)	2.450(3)	P(12)—N(2)	1.702(8)
Re(1)—P(12)	2.428(3)	P(21)—N(1)	1.679(8)
Re(2)—Cl(21)	2.352(2)	P(22)—N(2)	1.684(8)
Re(2)—Cl(22)	2.362(3)		

Angles

Angle	Value	Angle	Value
Re(2)—Re(1)—Cl(11)	117.93(7)	Re(1)—Re(2)—P(22)	93.05(6)
Re(2)—Re(1)—Cl(12)	119.26(8)	Cl(21)—Re(2)—Cl(22)	128.0(1)
Re(2)—Re(1)—P(11)	90.31(6)	Cl(21)—Re(2)—P(21)	86.68(9)
Re(2)—Re(1)—P(12)	89.55(6)	Cl(21)—Re(2)—P(22)	91.92(9)
Cl(11)—Re(1)—Cl(12)	122.8(1)	Cl(22)—Re(2)—P(21)	92.52(9)
Cl(11)—Re(1)—P(11)	95.43(9)	Cl(22)—Re(2)—P(22)	85.08(9)
Cl(11)—Re(1)—P(12)	84.46(9)	P(21)—Re(2)—P(22)	175.63(9)
Cl(12)—Re(1)—P(11)	84.46(9)	Re(1)—P(11)—N(1)	105.4(3)
Cl(12)—Re(1)—P(12)	95.77(9)	Re(1)—P(12)—N(2)	107.0(3)
P(11)—Re(1)—P(12)	179.88(9)	Re(2)—P(21)—N(1)	106.6(3)
Re(1)—Re(2)—Cl(21)	114.80(7)	Re(2)—P(22)—N(2)	105.7(3)
Re(1)—Re(2)—Cl(22)	117.23(7)	P(11)—N(1)—P(21)	119.1(5)
Re(1)—Re(2)—P(21)	91.29(6)	P(12)—N(2)—P(22)	118.6(5)

[a] Numbers in parentheses are ESDs in the least significant digits.

were applied to all atoms so refined.[16] The largest peak in the final difference Fourier map was 0.83 e $Å^{-3}$.

Further details concerning the data set and the structure solution and refinement may be obtained from Dr P. E. Fanwick. Table 2 lists important bond distances and angles.†

Physical measurements

IR spectra were recorded as Nujol mulls between KBr plates on an IBM Instruments IR/32 Fourier transform spectrometer or a Perkin–Elmer Model 1420 spectrophotometer. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (n-Bu_4NPF_6 or TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a}+E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions, $E_{1/2} = +0.47$ vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were performed with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett–Packard Model 7035 B *x-y* recorder. Conductivity measurements were performed on 1×10^{-3} M methanol solutions of the complexes on an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with the use of an internal deuterium lock and 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuterated solvent.

Analytical procedures

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

RESULTS AND DISCUSSION

(a) *Preparation and characterization of* $Re_2X_4(dpam)_2$

The bidentate arsine ligands 1,2-bis(diphenylphosphino)ethane (dpae; $Ph_2AsCH_2CH_2AsPh_2$) and 1-diphenylphosphino-2-diphenylarsinoethane

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† Atomic positional and thermal parameters and full listings of bond lengths and angles have been deposited with the Editor and with the Director, Cambridge Crystallographic Data Centre.

(arphos; $Ph_2PCH_2CH_2AsPh_2$) have been shown to react with $(n\text{-}Bu_4N)_2Re_2Cl_8$ to yield $Re_2Cl_6(dpae)_2$ and $Re_2Cl_4(arphos)_2$, respectively.[17] However, with the use of similar reaction conditions to these, we have been unable to synthesize the corresponding derivatives with 1,2-bis(diphenylarsino) methane (dpam; $Ph_2AsCH_2AsPh_2$). The synthetic approach we successfully employed followed the one we have recently developed for the preparation of $Re_2X_4(dppm)_2$,[12] i.e. the reactions of the bis (acetate) complexes $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ with an excess of dpam in hot methanol. The chloride derivative was produced in only a 10% yield. The use of different reaction solvents, and also $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ or $Re_2Cl_4(PEt_3)_4$ in place of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$, failed to generate any identifiable products. Despite this rather low preparative yield for $Re_2Cl_4(dpam)_2$, satisfactory elemental microanalyses and cyclic voltammetric (CV) data were obtained for this complex. Two reversible one-electron oxidations, at $E_{1/2} = +0.32$ V and $+0.84$ V vs Ag/AgCl, were observed; these redox potentials are very close to those obtained for $Re_2Cl_4(dppm)_2$ as shown in Table 3. The bromide derivative $Re_2Br_4(dpam)_2$ was obtained in a much higher yield (*ca* 40%) than its chloride analogue. Its CV properties and electronic absorption spectrum are very similar to those for $Re_2Br_4(dppm)_2$ (Table 3). Accordingly, it may be concluded that $Re_2X_4(dpam)_2$ and $Re_2X_4(dppm)_2$ are structurally and electronically closely related.

The NMR spectral properties for $Re_2X_4(dppm)_2$ (X = Cl, Br or I) and $Re_2Br_4(dpam)_2$ are also listed in Table 3, and show a close similarity to one another. Note that electrochemical and spectroscopic data for $Re_2Br_4(dppm)_2$ and $Re_2I_4(dppm)_2$ are reported here for the first time. A comparison is also made with the corresponding data for $Re_2Cl_4(dppa)_2$.

(b) *Preparation and characterization of* $[Re_2X_4(dppm)_2]PF_6$

Nitrosonium hexafluorophosphate ($NOPF_6$) has been successfully used to oxidize dirhenium(II) complexes that contain monodentate and bidentate phosphines. Examples include $[Re_2Cl_4(PEt_3)_4]PF_6$,[18] $[Re_2Cl_4(PMe_2Ph)_4]PF_6$,[2] $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$,[2] $[Re_2Cl_4(dppe)_2]PF_6$[5] and $[Re_2Cl_4(arphos)_2]PF_6$,[5] all of which can be prepared from their neutral precursors. However, acetone or THF solutions of $Re_2Cl_4(dppm)_2$ react readily with $NOPF_6$ to give unidentifiable products that may contain the nitrosyl ligand but which were not the desired oxi-

Table 3. Electrochemical and spectroscopic data for $Re_2X_4(LL)_2$ (X = Cl, Br or I; LL = dppm, dppa or dpam) and for $[Re_2X_4(dppm)_2]^+$ (X = Cl or Br)

	CV half-wave potentials, V[a]		Electronic absorbance spectra	^1H NMR (δ)[c]	
Complex	$E_{1/2}(2)$	$E_{1/2}(1)$	λ (nm) (ε)[b]	—CH_2—[d]	$^{31}P\{^1H\}$ NMR (δ)[e]
$Re_2Cl_4(dppm)_2$	+0.87(ox)[f]	+0.29(ox)[f]	680 sh, 510(500), 420 sh[g]	+5.21 p[g]	−3.30 s[g]
$Re_2Br_4(dppm)_2$	+0.94(ox)	+0.34(ox)	600 sh, 545(800), 450(780)	+5.39 p	−5.44 s
$Re_2I_4(dppm)_2$	+0.95(ox)	+0.34(ox)	614(950)	+5.63 p[h]	+8.54 s
$Re_2Cl_4(dppa)_2$	+0.94(ox)	+0.40(ox)[i]	635(40), 510(500), 440sh[g]		
$Re_2Cl_4(dpam)_2$	+0.84(ox)	+0.32(ox)	[j]	[j]	
$Re_2Br_4(dpam)_2$	+0.92(ox)	+0.37(ox)	680 sh, 540(830), 425 sh	+4.97 s	
$[Re_2Cl_4(dppm)_2]PF_6$	+0.88(ox)	+0.30(red)	1520(540), 670(1900), 520 sh, 445(2300)	[k]	
$[Re_2Br_4(dppm)_2]PF_6$	+0.92(ox)	+0.33(red)	1545(600), 695(860), 460(2350)	[k]	

[a] Versus Ag/AgCl. Recorded on solutions in 0.1 M TBAH/CH_2Cl_2 by the use of a Pt-bead electrode. Data obtained at a scan rate of 200 mV s^{-1}. For each couple, the value of ΔE_p (i.e. $E_{p,a} - E_{p,c}$) falls in the range 110–140 mV.

[b] Measured in dichloromethane; molar extinction coefficients (ε) are given in parentheses.

[c] Spectra recorded in CD_2Cl_2 unless otherwise stated.

[d] The —CH_2— resonance of the dppm or dpam ligands; p = pentet, s = singlet.

[e] Spectra recorded in CD_2Cl_2; s = singlet.

[f] Data similar to that reported in ref. 7.

[g] Data taken from ref. 7.

[h] Spectrum recorded in $CDCl_3$.

[i] Data similar to that reported in ref. 11.

[j] Not measured.

[k] Paramagnetic complex.

dized product. By resorting to the milder oxidant ferrocenium hexafluorophosphate, $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$, we have found that this reagent cleanly oxidizes acetone solutions of $Re_2X_4(dppm)_2$ to $[Re_2X_4(dppm)_2]PF_6$ (X = Cl or Br). A similar strategy in the case of $Re_2Cl_4(dppa)_2$ and $Re_2Br_4(dpam)_2$ (acetone or dichloromethane as solvents) failed to give pure products, even when low reaction temperatures were employed. The monocations are apparently very unstable and prone to decomposition under these reaction conditions, although they can be generated electrochemically (*vide infra*).

Conductivity measurements on methanol solutions of $[Re_2X_4(dppm)_2]PF_6$ ($c_m \simeq 1 \times 10^{-3}$ M) show them to be 1 : 1 electrolytes ($\Lambda_m \simeq 105\ \Omega^{-1}\ cm^2\ mol^{-1}$).[19] Also, the IR spectra of these complexes confirm the presence of the PF_6^- anion (ν(P—F) at $\simeq 840\ cm^{-1}$). The electrochemical properties of these salts (Table 3) resemble those of $Re_2X_4(dppm)_2$; the only difference being that the process at $E_{1/2} \simeq +0.3$ V (vs Ag/AgCl) now corresponds to a reduction of the bulk complex. Their electronic absorption spectra (Table 3) show a broad absorption at $\simeq 1500$ nm in the near-IR region. This band appears to be typical of species that contain a $\sigma^2\pi^4\delta^2\delta^{*1}$ electronic configuration[18,20] and may be assigned to a $\delta \rightarrow \delta^*$ transition. This is further evidence that the Re_2^{5+} moiety is present in these oxidized species.

Magnetic moments of dichloromethane solutions of these monocations (determined by the Evans method[21]) were found to be 1.5 (±0.1) BM at room temperature. X-band ESR spectra of frozen dichloromethane solutions (−160°C) also confirm the paramagnetism of these complexes. Complex patterns showing a considerable amount of hyperfine structure were observed. The spectra are centred at 2750 G ($g \simeq 2.35$) for the chloride and 2700 G ($g \simeq 2.40$) for the bromide derivative, and have a spectral width of approximately 3500 G.

(c) *Electrochemical generation of* $[Re_2X_4(dppm)_2]^+$ (X = Cl *or* Br), $[Re_2Cl_4(dppa)_2]^+$ *and* $[Re_2Br_4(dpam)_2]^+$

Bulk electrolyses of purple solutions of $Re_2X_4(dppm)_2$ (X = Cl or Br), $Re_2Cl_4(dppa)_2$ and $Re_2Br_4(dpam)_2$ in $n\text{-}Bu_4NPF_6\text{–}CH_2Cl_2$ generated solutions of the paramagnetic monocations that are green–brown in colour, except for $[Re_2Cl_4(dppa)_2]^+$ which is red. In all instances, CV measurements confirmed that oxidation had proceeded with little evidence for decomposition. In view of the reversibility of the couple at *ca* +0.3 V (Table 3), it is apparent that the oxidations proceed with retention of the staggered rotational geometry that is characteristic of the structurally characterized derivatives $Re_2Cl_4(dppm)_2$[22] and $Re_2Cl_4(dppa)_2$ (*vide infra*).

The X-band ESR spectra of these solutions, recorded at −160°C (Fig. 1), verified the paramagnetism of these species. The spectrum of $[Re_2Cl_4(dppa)_2]^+$ (not shown) is similar to that of the other derivatives; in all instances, the spectra are centred at *ca* 3000 G (i.e. $g \simeq 2.16$) with a spectral width of *ca* 3500 G. As can be seen in Fig. 1, the spectra are very similar and, in spite of the poorer resolution of the spectrum of $[Re_2Br_4(dppm)_2]^+$, it is apparent that the hyperfine structure must primarily be associated with the rhenium nuclei; an eleven-line pattern is expected for coupling to two rhenium nuclei with $I = 5/2$. There is little evidence for coupling to phosphorus or halogen nuclei in these spectra. Further confirmation that these signals are due to the monocations was shown by cycling between the oxidized and neutral species

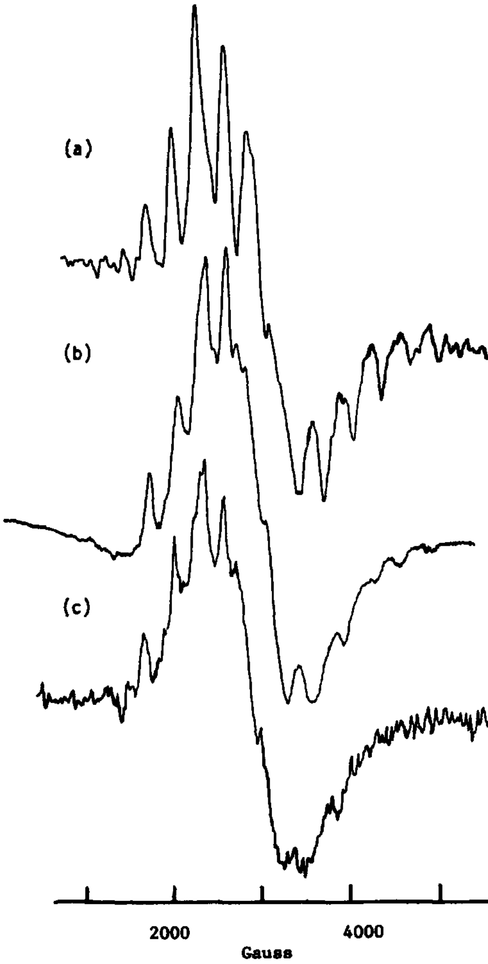

Fig. 1. The X-band ESR spectra, in frozen dichloromethane solutions at −160°C, for (a) $[Re_2Br_4(dpam)_2]^+$, (b) $[Re_2Cl_4(dppm)_2]^+$ and (c) $[Re_2Br_4(dppm)_2]^+$. All species were generated electrochemically.

and monitoring the growth and disappearance of the spectra.

(d) *Structural considerations*

At the outset, we had hoped to obtain crystals of one or more derivatives of the type $[Re_2X_4(LL)_2]PF_6$ (LL = dppm, dppa or dpam) in order to confirm that they did indeed possess a structure similar to that of $Re_2Cl_4(dppm)_2$.[22] Unfortunately, all attempts to grow such crystals led to the decomposition of the complexes. However, during the course of this aspect of our work we obtained crystals of $Re_2Cl_4(dppa)_2 \cdot (CH_3)_2CO$ and took the opportunity to determine its structure and compare it to $Re_2Cl_4(dppm)_2$.[22]

The structure of the dirhenium complex $Re_2Cl_4(dppa)_2$, as present in the crystals of $Re_2Cl_4(dppa)_2 \cdot (CH_3)_2CO$, is that of a multiply bonded M_2L_8 complex.[3] An ORTEP representation of the structure is shown in Fig. 2 and gives the full atomic numbering scheme. There is no crystallographically imposed symmetry for the asymmetric unit. The important structural parameters are listed in Table 2. While the bridging dppa ligands are in a *trans* disposition to one another, the molecule assumes an overall staggered rotational geometry. This geometry can best be defined in terms of the averages of the torsional angles Cl(11)—Re(1)—Re(2)—Cl(21) and Cl(12)—Re(1)—Re(2)—Cl(22), and P(11)—Re(1)—Re(2)—P(21) and P(12)—Re(1)—Re(2)—P(22), which are 51.7[2] and 41.8[5]°, respectively. These can be compared with average Cl—Re—Re—Cl and P—Re—Re—P angles of 56[1] and 47[1]°, respectively, in the structure of $Re_2Cl_4(dppm)_2$.[22]

The Re—Re distance of 2.2417(5) Å is similar to that of 2.234(3) Å in the structure of $Re_2Cl_4(dppm)_2$.[22] Very close similarities are also seen between the sets of Re—Cl and Re—P distances and the corresponding angles of these two structures. The compounds have essentially identical average Re—P and Re—Cl distances; these are 2.43[2] and 2.356[5] Å for the dppa derivative and 2.45[3] and 2.360[11] Å for the analogous dppm complex.

One molecule of acetone per formula unit of $Re_2Cl_4(dppa)_2$ was found in the unit cell. The oxygen atom of the acetone molecule was found to be 3.12(1) Å away from N(1) of the dirhenium complex. This represents, at best, a very weak hydrogen-bonding interaction. Typical lengths of N—H···O hydrogen bonds fall in the range 2.81–3.04 Å.[23] Recently, Usón *et al.*[24] have reported a case of a diplatinum(I)–dppa complex that

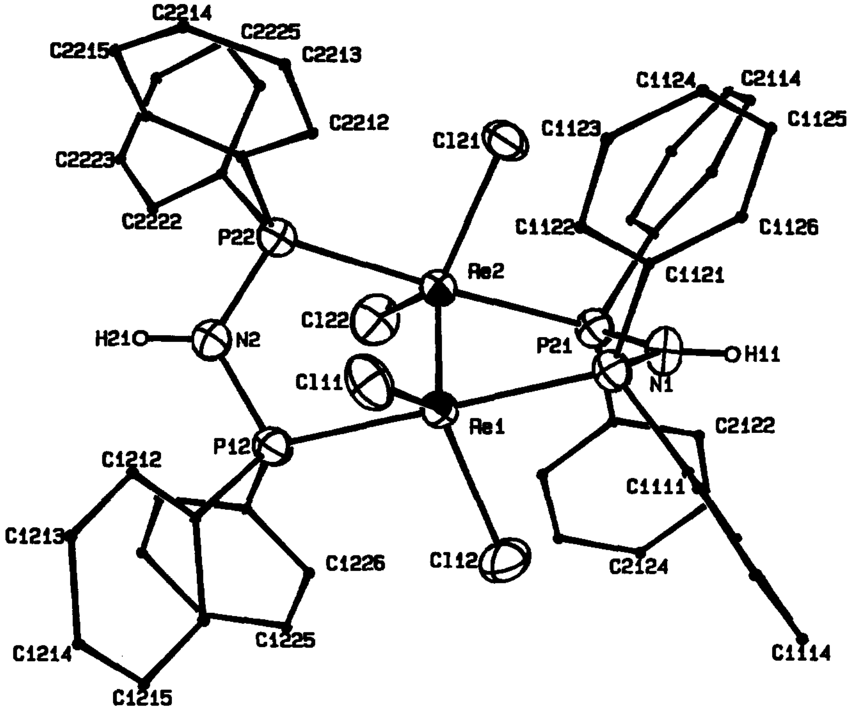

Fig. 2. ORTEP representation of the structure of the complex $Re_2Cl_4(dppa)_2$ showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. The molecule of lattice acetone is not shown.

exhibits $(CH_3)_2CO \cdots H—N$ hydrogen-bonding; the $N—H \cdots O$ distance (for $Pd_2Cl_2(\mu\text{-dppa})_2 \cdot (CH_3)_2CO$) was determined to be 2.915(7) Å. To our knowledge, there are only five other reports describing the structures of dimetal complexes that contain bridging dppa ligands. These are the aforementioned diplatinum complex,[24] the dirhenium(II) complexes *cis*-$Re_2(O_2CCH_3)_2Cl_2(\mu\text{-dppa})_2$ and *cis*-$[Re_2(O_2CCH_3)_2Cl_2(\mu\text{-dppa})_2]PF_6$,[11] $Au_2Cl_2(C_6F_5)_2(\mu\text{-dppa})$[25] and $Rh_2(\mu\text{-CO})(\mu\text{-Cl})(\mu\text{-dppa})_2(CO)_2$;[26] several of these contain solvent of crystallization hydrogen-bonded to the N—H group of dppa.

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