Reactions of the Dirhenium(II) Complexes $Re_2X_4(dppm)_2$ (X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$) with Tertiary Phosphine and Phosphite Ligands. The Isolation and Characterization of the 1:1 Adducts $Re_2X_4(dppm)_2(PR_3)$ and $Re_2Cl_4(dppm)_2[P(OR)_3]$ and the Crystal Structure of $[Re_2Cl_3(dppm)_2(NCEt)_2]PF_6$

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Abstract

The triply bonded complexes $Re_2X_4(dppm)_2$ (X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$) react with PMe_3 to afford the 1:1 adducts $Re_2X_4(dppm)_2(PMe_3)$ which may have the A-frame-like structure $X_2Re(\mu\text{-}X)(\mu\text{-}dppm)_2ReX(PMe_3)$. Similar complexes have been isolated from the reaction of $Re_2Cl_4(dppm)_2$ with $P(OR)_3$ (R = Me, Et or Ph). The PMe_3 ligand of $Re_2Cl_4(dppm)_2(PMe_3)$ is quite labile, reaction with nitrile ligands affording the complexes $[Re_2Cl_3(dppm)_2(NCR)_2]PF_6$. The structure of a crystal of the propionitrile derivative $[Re_2Cl_3(dppm)_2(NCEt)_2]PF_6\cdot2CH_2Cl_2$ has been determined by X-ray crystallography. This complex crystallizes in the tetragonal space group $P\bar{4}2_1c$ with $a = b = 16.432(2)$, $c = 24.450(4)$ Å, $V = 6601(3)$ Å^3 and $Z = 4$. The structure was refined to $R = 0.039$ ($R_w = 0.052$) for 1435 data with $I > 3.0\sigma(I)$. The structure of the dirhenium cation can be represented as $[(EtCN)_2ClRe(\mu\text{-}dppm)_2ReCl_2]^+$, with a Re–Re distance of 2.2661(9) Å.

Introduction

The triply bonded complexes $Re_2X_4(dppm)_2$ (X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$) [1–3] react with CO and organic isocyanide and nitrile ligands in a stepwise fashion with the uptake of between one and three of these ligand molecules [4–8]. In all instances, the reactions seem to proceed via the A-frame-like 1:1 adducts $X_2Re(\mu\text{-}X)(\mu\text{-}dppm)_2ReX(L)$ [7, 9–11]. In order to probe how the chemistry of the resulting complexes is influenced by the coordination of additional phosphine ligands, we have recently examined the reactions of the 1:1 and 1:2 carbonyl adducts $Re_2X_4(dppm)_2(CO)_n$ (n = 1 or 2) with the ligands PMe_3, $P(OMe)_3$ and $P(OEt)_3$ [12, 13]. This work led to the isolation and structural characterization of salts of the 'phosphine-rich' $[Re_2X_3(dppm)_2(CO)(PR_3)_2]^+$ and $[Re_2X_3(dppm)_2(CO)_2(PR_3)]^+$ cations (R = Me, OMe or OEt). Consequently, it seemed important to establish the stability of $Re_2X_4(dppm)_2$ to phosphine ligands alone. Accordingly, we have now examined their reactions with PMe_3 and $P(OR)_3$ (R = Me, Et or Ph) and isolated the 1:1 adducts $Re_2X_4(dppm)_2(PMe_3)$ (X = Cl or Br) and $Re_2Cl_4(dppm)_2[P(OR)_3]$. Details of this work are reported herein. We note that there is only one previous report of a dirhenium(II) halide complex that contains more than four phosphorus donors atoms, viz., $Re_2Cl_4(dmpm)_3$ (dmpm = $Me_2PCH_2PMe_2$) [14]. During the course of the present study we also studied the derivatization of these complexes with nitrile ligands by which means we isolated several species of the type $[Re_2Cl_3(dppm)_2(NCR')_2]PF_6$. The crystal structure of the propionitrile derivative $[Re_2Cl_3(dppm)_2(NCEt)_2]PF_6$ was determined.

Experimental

Starting Materials

The dirhenium(II) complexes $Re_2X_4(dppm)_2$ (X = Cl or Br) were prepared according to the reported method [3]. The phosphine, phosphite and nitrile ligands were obtained from Strem Chemicals and the Aldrich Chemical Co. Solvents used in the preparation of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures

All reactions were performed under an atmosphere of dry dinitrogen.

A. Reactions of $Re_2X_4(dppm)_2$ (X = Cl or Br) with PMe_3

(i) $Re_2Cl_4(dppm)_2(PMe_3)$. A quantity of $Re_2Cl_4(dppm)_2$ (0.073 g, 0.057 mmol) was dissolved in dichloromethane (10 ml). Upon the additions of one equivalent of PMe_3 (0.0058 ml, 0.057 mmol) the purple solution immediately turned dark brown. The reaction mixture was stirred at room temperature for 24 h, then evaporated to dryness and the residue

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washed with a 5 ml portion of methanol. The solid product was finally dried under vacuum; yield 0.062 g (80%). *Anal.* Calc. for $C_{53}H_{53}Cl_4P_5Re_2$: C, 46.84; H, 3.93; Cl, 10.43. Found: C, 46.06; H, 3.99; Cl, 10.02%.

A similar procedure with acetone in place of dichloromethane and a reaction time of 48 h afforded this same complex as an insoluble yellow solid. The product was filtered off, washed with a 10 ml portion of methanol and dried under vacuum; yield 85%.

(ii) $Re_2Br_4(dppm)_2(PMe_3)$. A small quantity of $Re_2Br_4(dppm)_2$ (0.080 g, 0.055 mmol) was dissolved in 10 ml of dichloromethane. The purple solution immediately turned dark brown upon the addition of one equivalent of PMe_3 (0.0056 ml, 0.055 mmol). The reaction mixture was then stirred at room temperature for 48 h. Brown crystals of the title complex were grown by the slow diffusion of hexane vapor into the resulting dichloromethane reaction solution contained within a closed system. After two weeks the crystals were filtered off, washed with a 10 ml portion of methanol and then dried in vacuum; yield 0.074 g (88%). *Anal.* Calc. for $C_{53}H_{53}Br_4P_5Re_2$: C, 41.42; H, 3.48. Found: C, 41.52, H, 4.07%.

B. Reactions of $Re_2Cl_4(dppm)_2$ with $P(OR)_3$ (R = Me, Et or Ph)

(i) $Re_2Cl_4(dppm)_2[P(OMe)_3]$. The procedure for the preparation of this complex from $Re_2Cl_4(dppm)_2$ was analogous to that described in A(i) with acetone as the reaction solvent. The product was obtained as a yellow powder; yield 61%. *Anal.* Calc. for $C_{53}H_{53}Cl_4O_3P_5Re_2$: C, 45.24; H, 3.80; Cl, 10.08. Found: C, 45.51; H, 4.16; Cl, 9.58%.

(ii) $Re_2Cl_4(dppm)_2[P(OEt)_3)]\cdot 1/2CH_2Cl_2$. This complex was prepared from $Re_2Cl_4(dppm)_2$ with the use of a procedure similar to that described in A(ii). The product was obtained as brown crystals; yield 80%. *Anal.* Calc. for $C_{56.5}H_{60}Cl_5O_3P_5Re_2$: C, 45.50; H, 4.05. Found: C, 45.45; H, 4.09%. The ^1H NMR spectrum of this sample (recorded in $CDCl_3$) showed the presence of dichloromethane of crystallization (δ +5.29).

(iii) $Re_2Cl_4(dppm)_2[P(OPh)_3]$. This complex was obtained as a brown powder with the use of a procedure similar to that given in A(i) with dichloromethane as the reaction solvent; yield 80%. *Anal.* Calc. for $C_{68}H_{59}Cl_4O_3P_5Re_2$: C, 51.26; H, 3.73. Found: C, 51.18; H, 4.11%.

C. Reactions of $Re_2Cl_4(dppm)_2(PMe_3)$ with R'CN (R' = Me, Et, Ph or CH_2Ph)

(i) $[Re_2Cl_3(dppm)_2(NCMe)_2]PF_6$. A mixture of $Re_2Cl_4(dppm)_2(PMe_3)$ (0.0525 g, 0.039 mmol), $TlPF_6$ (0.0135 g, 0.039 mmol) and 3 ml of acetonitrile in dichloromethane (10 ml) was stirred at room temperature for 24 h. The color of the reaction solution changed to brown and a white precipitate of TlCl formed. The mixture was filtered and the filtrate added directly to a large volume of diethyl ether with stirring. A gray–brown solid precipitated, and this was filtered off and dried; yield 0.040 g (69%). *Anal.* Calc. for $C_{54}H_{50}Cl_3F_6N_2P_5Re_2$: C, 43.98; H, 3.42. Found: C, 44.76; H, 4.11%.

The following complexes were prepared by the use of a procedure similar to that described in C(i).

(ii) $[Re_2Cl_3(dppm)_2(NCEt)_2]PF_6$. Yield 93%. *Anal.* Calc. for $C_{56}H_{54}Cl_3F_6N_2P_5Re_2$: C, 44.76; H, 3.62; Cl, 7.08. Found: C, 44.31; H, 4.18; Cl, 6.46%.

(iii) $[Re_2Cl_3(dppm)_2(NCPh)_2]PF_6$. Yield 93%. *Anal.* Calc. for $C_{64}H_{54}Cl_3F_6N_2P_5Re_2$: C, 48.08; H, 3.40; Cl, 6.65. Found: C, 46.22; H, 3.77; Cl, 7.04%. This complex probably contains a small amount of lattice dichloromethane.

(iv) $[Re_2Cl_3(dppm)_2(NCCH_2Ph)_2]PF_6$. Yield 68%.

Preparation of single crystals of $[Re_2Cl_3(dppm)_2(NCEt)_2]PF_6\cdot 2CH_2Cl_2$

Crystals of the title complex were grown by diffusion of diethyl ether vapor into a dichloromethane solution of the product from reaction C(ii). The exact same product was obtained serendipitously during attempts to recrystallize *cis*-$[Re_2Cl_2(dppm)_2(NCEt)_4](PF_6)_2$ [15] from dichloromethane/diethyl ether. Crystals of the latter sample were the ones chosen for the subsequent structure analysis.

X-ray Crystallography

The structure of $[Re_2Cl_3(dppm)_2(NCEt)_2]PF_6\cdot 2CH_2Cl_2$ was determined with the use of standard procedures. A summary of the crystallogaphic data is given in Table 1. The cell constants are based on 25 reflections with $20° < \theta < 22°$. Three standard reflections were measured after every 5000s of beam time during data collection. There were no systematic variations in intensity. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package.

The crystal selected for the structure determination belonged to the unusual tetragonal space group $P\bar{4}2_1c$ with $Z = 4$. As a check on crystal quality, omega scans of several intense reflections were measured; the width at half-height was 0.73° with a take-off angle of 3.2° indicating moderate 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. The dirhenium unit is on a special position exhibiting two-fold symmetry. Of the four PF_6^- anions per unit cell, two are on symmetry related special positions with $\bar{4}$ symmetry. These refined with satisfactory P–F distances and F–P–F angles although the associated thermal parameters were rather large. The remaining PF_6^- anions were found on special positions exhibiting two-fold sym-

TABLE 1. Crystallographic data and data collection parameters for $[Re_2Cl_3(dppm)_2(NCEt)_2]PF_6{\cdot}2CH_2Cl_2$

Formula	$Re_2Cl_7P_5F_6N_2C_{58}H_{58}$
Formula weight	1672.55
Space group	$P\bar{4}2_1c$ (No. 114)
a (Å)	16.432(2)
c (Å)	24.450(4)
V (Å^3)	6601(3)
Z	4
D_c (g cm^{-3})	1.683
Crystal dimensions (mm)	0.40 × 0.36 × 0.29
Temperature (°C)	20
Radiation (wavelength)	Mo Kα (0.71073 Å)
Monochromator	graphite
Linear absorption coefficient (cm^{-1})	41.73
Absorption correction applied	empirical[a]
Transmission factors: min, max	0.80, 1.00
Diffractometer	Enraf-Nonius CAD4
Scan method	ω–2θ
h, k, l limits	0 to 17, 0 to 12, 0 to 26
2θ Range (°)	4.00–45.00
Scan width (°)	0.73 + 0.35 tan(θ)
Take-off angle (°)	3.15
Programs used	Enraf-Nonius SDP
F(000)	3272.0
p-Factor used in weighting	0.040
Data collected	2540
Unique data	2540
Data with $I > 3.0\sigma(I)$	1435
Number of variables	246
Largest shift/e.s.d. in final cycle	0.56
R[b]	0.039
R_w[c]	0.052
Goodness of fit[d]	1.697

[a] See ref. 16. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. [d] Goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

metry in which each of the four symmetry related sites were refined with half occupancy. The refinement of this PF_6^- anion was not very satisfactory; the thermal parameters were large and the P–F distances and F–P–F angles covered large ranges [1.55(6)–1.19(8) Å and 75(3)–106(3)°, respectively]. Nonetheless, our modeling of the PF_6^- anions in this manner makes chemical sense based upon our knowledge of the stoichiometry of the complex. Furthermore, the difficulties we experienced in modeling one of the PF_6^- anions in no way detracts from our conclusions concerning the structure of the more chemically meaningful $[Re_2Cl_3(dppm)_2(NCEt)_2]^+$ cation. Finally, during the later stages of the structure refinement, it became apparent that residual electron density at non-bonding distances to the dirhenium cation and PF_6^- anions could be modeled as lattice dichloromethane. This was located about a general position (eight symmetry related sites per unit cell). The chlorine atoms refined satisfactorily, albeit with rather large thermal parameters, but the carbon atom was not well behaved and it may well be disordered. Accordingly, the unit cell contains eight molecules of CH_2Cl_2 for the four molecules of $[Re_2Cl_3(dppm)_2(NCEt)_2]PF_6$ that are present.

Lorentz and polarization corrections were applied to the data. An empirical absorption correction was applied [16], the linear absorption coefficient being 41.73 cm^{-1}. No corrections for extinction were applied. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. Hydrogens were not included in the refinement. With the exception of the phenyl ring carbon atoms of the dppm ligands and atoms of the lattice CH_2Cl_2 molecules, all non-hydrogen atoms were refined anisotropically; corrections for anomalous scattering were applied to all atoms so refined [17]. The highest peak in the final difference Fourier map was 1.03 e/Å^3 and did not appear to be of any chemical significance.

Table 2 lists the atomic positional parameters and their errors, while Tables 3 and 4 provide the more important intramolecular bond distance and angles for the dirhenium cation. See also 'Supplementary Material'.

TABLE 2. Positional parameters for non-hydrogen atoms and their e.s.d.s[a]

Atom	x	y	z	B (Å^2)
Re(1)	1	1/2	0.86104(3)	2.65(2)
Re(2)	1	1/2	0.76835(3)	2.84(2)
Cl(1)	1	1/2	0.9656(2)	3.6(1)
Cl(2)	0.9564(3)	0.3710(3)	0.7376(2)	4.0(1)
P(1)	0.8551(3)	0.4596(3)	0.8691(2)	2.9(1)
P(2)	1.1440(3)	0.4639(3)	0.7586(2)	3.3(1)
N(1)	1.0187(9)	0.3792(9)	0.8673(5)	2.9(4)
C(2)	1.034(1)	0.310(1)	0.8746(9)	4.2(5)
C(3)	1.037(1)	0.220(1)	0.885(1)	5.4(6)
C(4)	1.107(2)	0.204(2)	0.918(1)	11(1)
C(B)	0.805(1)	0.464(1)	0.8019(7)	3.1(4)
C(111)	0.841(1)	0.359(1)	0.8917(7)	3.6(4)*
C(112)	0.846(1)	0.342(1)	0.9502(8)	4.3(4)*
C(113)	0.838(1)	0.265(1)	0.970(1)	5.3(6)*
C(114)	0.825(1)	0.200(1)	0.9369(9)	4.9(5)*
C(115)	0.806(2)	0.217(2)	0.880(1)	6.9(7)*
C(116)	0.820(1)	0.293(2)	0.857(1)	5.6(6)*
C(121)	0.784(1)	0.517(1)	0.9169(8)	4.2(5)*
C(122)	0.707(1)	0.491(2)	0.9143(9)	5.5(5)*
C(123)	0.647(1)	0.537(1)	0.9479(9)	5.6(6)*
C(124)	0.669(2)	0.605(2)	0.972(1)	6.7(7)*
C(125)	0.753(1)	0.627(2)	0.973(1)	5.9(6)*
C(126)	0.813(1)	0.586(1)	0.9459(9)	4.9(5)*
C(211)	1.183(1)	0.480(1)	0.6921(8)	4.7(5)*
C(212)	1.264(1)	0.491(1)	0.6811(8)	5.1(5)*
C(213)	1.292(2)	0.508(2)	0.6292(9)	5.8(5)*
C(214)	1.245(2)	0.505(2)	0.589(1)	9.3(8)*
C(215)	1.160(2)	0.486(2)	0.589(1)	6.9(7)*
C(216)	1.128(2)	0.477(1)	0.6450(9)	6.2(6)*
C(221)	1.187(1)	0.365(1)	0.7762(8)	3.0(4)*
C(222)	1.252(2)	0.360(2)	0.807(1)	7.6(7)*
C(223)	1.292(2)	0.282(2)	0.816(1)	6.9(7)*
C(224)	1.256(1)	0.212(2)	0.800(1)	5.7(6)*
C(225)	1.181(1)	0.212(2)	0.771(1)	6.1(6)*
C(226)	1.153(1)	0.298(1)	0.755(1)	5.4(6)*
P(1000)	1/2	1/2	1/2	7.0(3)
P(2000)	1/2	1/2	0.7873(9)	8.2(6)
F(1001)	1/2	1/2	0.561(1)	22(1)
F(1002)	0.590(1)	0.479(1)	0.504(1)	14.7(8)
F(2001)	1/2	1/2	0.735(2)	24(3)
F(2002)	0.525(4)	0.590(3)	0.780(3)	25(3)
F(2003)	0.424(3)	0.546(4)	0.791(2)	22(2)
F(2004)	1/2	1/2	0.836(3)	30(4)
Cl(1001)	0.795(1)	0.458(1)	1.0839(6)	17.8(5)*
Cl(1002)	0.731(1)	0.589(1)	1.1199(8)	25.4(8)*
C(1000)	0.876(7)	0.538(7)	1.093(4)	43(5)*

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Values marked with an asterisk are for isotropically refined atoms.

Physical Measurements

Infrared 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, $E_{1/2} = +0.47$ V versus Ag/AgCl for the ferrocenium/ferrocene couple.

TABLE 3. Some important bond distances (Å)[a]

Re(1)–Re(2)	2.2661(9)	P(1)–C(121)	1.90(2)
Re(1)–Cl(1)	2.556(4)	P(2)–C(B)	1.81(2)
Re(1)–P(1)	2.479(5)	P(2)–C(211)	1.77(2)
Re(1)–N(1)	2.01(1)	P(2)–C(221)	1.82(2)
Re(2)–Cl(2)	2.361(4)	N(1)–C(2)	1.18(2)
Re(2)–P(2)	2.451(5)	C(2)–C(3)	1.51(3)
P(1)–C(B)	1.84(2)	C(3)–C(4)	1.42(3)
P(1)–C(111)	1.76(2)		

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

Voltammetric experiments were performed with a Bioanalytical Systems Inc. Model CV-1A instrument in conjuction with a Hewlett-Packard Model 7035B x–y recorder. Conductivity measurements were performed on 1×10^{-3} M solutions of the complexes with the use of an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. ^{31}P{^{1}H} 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$_3$PO$_4$ as an external standard. ^{1}H NMR spectra were obtained on a Varian XL-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent.

Analytical Procedures

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

Results and Discussion

Synthesis of Re$_2$X$_4$(dppm)$_2$(PMe$_3$) (X = Cl or Br) and Re$_2$Cl$_4$(dppm)$_2$[P(OR)$_3$] (R = Me, Et or Ph)

The aforementioned complexes were prepared by the direct reaction of Re$_2$X$_4$(dppm)$_2$ [1–3] with stoichiometric proportions of PMe$_3$ or P(OR)$_3$ in dichloromethane (or acetone) at room temperature. These 1:1 adducts are the first complexes of this type prepared with ligands other than the π-acceptors CO and RNC [4, 9–11], with the single exception of the very unstable complex Re$_2$Cl$_4$(dppm)$_2$(NCEt) [7]. The reaction of Re$_2$Cl$_4$(dppm)$_2$ with an excess of PMe$_3$ affords the previously isolated complex Re$_2$Cl$_4$(dppm)(PMe$_3$)$_2$ [18].

Solutions of Re$_2$Cl$_4$(dppm)$_2$(PMe$_3$) and Re$_2$Cl$_4$(dppm)$_2$[P(OMe)$_3$] in DMF have conductivities typical of non-electrolytes. Cyclic voltammetric (CV) measurements on solutions of all the complexes in 0.1 M TBAH–CH$_2$Cl$_2$ show that they have very similar redox characteristics (Table 5 and Fig. 1), with a reversible one-electron oxidation having an associated $E_{1/2}$ value of between +0.29 and +0.43 V versus Ag/AgCl. A second oxidation with an $E_{\mathrm{p,a}}$ value > + 1.2 V is also present; only in the case of Re$_2$Cl$_4$(dppm)$_2$[P(OR)$_3$] (R = Et or Ph) is there a coupled reduction wave (Table 5), and in both instances $i_{\mathrm{p,c}} \ll i_{\mathrm{p,a}}$. This redox behavior is typical of complexes that contain the triply bonded Re$_2$$^{4+}$ core [4, 19]; for example, Re$_2$Cl$_4$(dppm)$_2$ possesses two reversible one-electron oxidations with $E_{1/2}$ values of +0.27 and +0.80 V versus SCE in its CV [20].

The ^{1}H NMR spectra of the chloride and bromide complexes Re$_2$X$_4$(dppm)$_2$(PMe$_3$) are very similar. Solutions of the chloride complex in CD$_2$Cl$_2$ show a series of well resolved phenyl resonances (all multiplets) at $\delta \simeq +8.0$, $\delta \simeq +7.55$, $\delta \simeq +7.35$ and $\delta \simeq +7.2$, a complex multiplet at δ +5.7 assignable to the

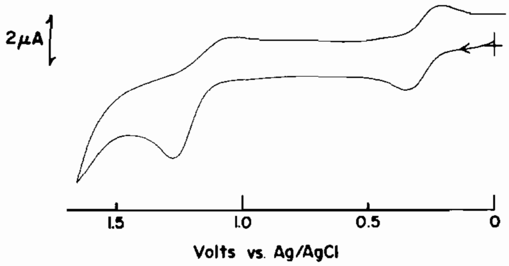


Fig. 1. Single sweep cyclic voltammogram of a solution of Re$_2$Cl$_4$(dppm)$_2$(PMe$_3$) in 0.1 M TBAH–CH$_2$Cl$_2$ recorded at 200 mV s^{-1} with the use of a Pt-bead electrode.

TABLE 4. Some important bond angles (°)[a]

Re(2)–Re(1)–Cl(1)	180.0	Re(1)–Re(2)–Cl(2)	108.6(1)
Re(2)–Re(1)–P(1)	94.5(1)	Re(1)–Re(2)–P(2)	95.6(1)
Re(2)–Re(1)–N(1)	94.3(4)	Cl(2)–Re(2)–Cl(2)	142.9(3)
Cl(1)–Re(1)–P(1)	85.5(1)	Cl(2)–Re(2)–P(2)	92.6(2)
Cl(1)–Re(1)–N(1)	85.7(4)	Cl(2)–Re(2)–P(2)	83.9(2)
P(1)–Re(1)–P(1)	170.9(2)	P(2)–Re(1)–P(2)	168.8(2)
P(1)–Re(1)–N(1)	82.9(4)	Re(1)–N(1)–C(2)	174(2)
P(1)–Re(1)–N(1)	96.4(4)	N(1)–C(2)–C(3)	169(2)
N(1)–Re(1)–N(1)	171.3(8)	C(2)–C(3)–C(4)	107(2)

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 5. Cyclic voltammetry properties for $Re_2X_4(dppm)_2(PMe_3)$ and $Re_2Cl_4(dppm)_2[P(OR)_3]$

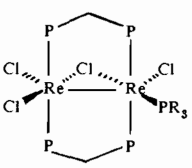
Complex	CV half-wave potentials (V)[a]	
	$E_{p,a}$	$E_{1/2}(ox)$[b]
$Re_2Cl_4(dppm)_2(PMe_3)$	+1.29	+0.30(100)
$Re_2Br_4(dppm)_2(PMe_3)$	+1.31	+0.38(120)
$Re_2Cl_4(dppm)_2[P(OMe)_3]$	+1.39	+0.31(90)
$Re_2Cl_4(dppm)_2[P(OEt)_3]$	+1.41[c]	+0.29(120)
$Re_2Cl_4(dppm)_2[P(OPh)_3]$	+1.66[d]	+0.43(140)

[a] vs. Ag/AgCl. Recorded on solutions in 0.1 M TBAH–CH_2Cl_2 by the use of a Pt-bead electrode. Data obtained at 200 mV s^{-1}. [b] Value of ΔE_p (i.e. $E_{p,a}-E_{p,c}$) given in parentheses. [c] Coupled reduction wave at +1.05 V ($i_{p,c} < i_{p,a}$). [d] Coupled reduction wave at +1.16 ($i_{p,c} < i_{p,a}$).

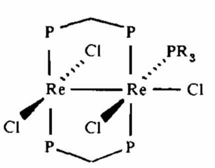
bridgehead $-CH_2-$ groups of the dppm ligands, and a broad doublet at δ +1.40 due to the P–CH_3 resonances (J(P–H) = 6.4 Hz) of the PMe_3 ligand. The $^{31}P\{^1H\}$ NMR spectrum (in CD_2Cl_2) of $Re_2Cl_4(dppm)_2(PMe_3)$ is typical of an AA'BB'X spin system and shows a triplet at δ −28.8 (J(P–P) ≃ 13 Hz, relative intensity 1) assignable to the PMe_3 ligand, together with complex multiplets (relative intensities 2:2), whose most intense components are at δ −17.1 and δ −12.4, that arise from the dppm ligands. In the related spectrum of $Re_2Br_4(dppm)_2(PMe_3)$, the most intense components of the three multiplets are at δ −34.3, δ −26.2 and δ −20.8, respectively.

The $^{31}P\{^1H\}$ NMR spectra of $Re_2Cl_4(dppm)_2[P(OR)_3]$ (R = Me or Et) in CD_2Cl_2 are remarkably similar and resemble those of the PMe_3 derivatives in their general features. Each shows a triplet for the phosphite resonance (δ +102.3 for R = Me, δ +100.2 for R = Et; J(P–P) ≃30 and ≃28 Hz, respectively) and a pair of complex multiplets for the inequivalent pairs of phosphorus atoms of the dppm ligands (δ −22.9 and δ +0.9 for the most intense components when R = Me, δ −22.1 and δ −1.6 when R = Et). While the related spectrum of $Re_2Cl_4(dppm)_2[P(OPh)_3]$ was of a poor quality because of its low solubility in CD_2Cl_2, nonetheless, multiplets at δ +81.8, δ −0.5 and δ −23.2 were observed.

The $^{31}P\{^1H\}$ NMR spectral properties of these complexes are in accord with an A-frame-like structure **I***, similar to that found for the analogous carbonyl and isocyanide complexes [9–11], or a more open structure **II***, in which there are no bridging ligands other than the two μ-dppm bridges. While we favor **I** as being the more likely structure of the two, we have been unsuccessful in our attempts to obtain single crystals suitable for a definitive X-ray structure determination.



(I)



(II)

Reactions of $Re_2Cl_4(dppm)_2(PMe_3)$ with Nitriles

The title complex was reacted with organic nitriles R'CN (R' = Me, Et, CH_2Ph or Ph) in dichloromethane in the presence of $TlPF_6$ in an attempt to prepare derivatives of the type $[Re_2Cl_3(dppm)_2(PMe_3)(NCR')_x]PF_6$ (x = 1 or 2). Instead, the bis-nitrile complexes $[Re_2Cl_3(dppm)_2(NCR')_2]PF_6$ are formed in high yield, reflecting the lability of the PMe_3 ligand. Consequently, we did not examine the reactions of nitriles with the 1:1 phosphite ligand adducts.

Of the four bis-nitrile adducts that were isolated, only the benzylnitrile derivative had not been isolated previously. The other derivatives had electrochemical and spectroscopic properties (IR, ^1H NMR and $^{31}P\{^1H\}$ NMR) that were in good agreement with the data from their previous characterization [7]. In the case of $[Re_2Cl_3(dppm)_2(NCCH_2Ph)_2]PF_6$, its solutions in 0.1 M TBAH–CH_2Cl_2 have a CV displaying a reversible oxidation at $E_{1/2}$ = +0.66 V ($E_{p,a} - E_{p,c}$ = 170 mV) and an irreversible reduction at $E_{p,c}$ = −1.50 V versus Ag/AgCl. The IR spectrum of this complex has a characteristic ν(P–F) mode at 839(vs) cm^{-1}, due to the $[PF_6]^-$ anion, but the nitrile ν(C≡N) mode was too weak to be observed. The ^1H NMR spectrum of a $CDCl_3$ solution of this complex showed a broad resonance at δ +5.8 due to the bridgehead $-CH_2-$ groups of the dppm ligands, and two broad resonances at δ +3.3 and δ +2.8 that arise from the methylene resonances of the $PhCH_2CN$ ligands (the protons of the methylene groups are prochiral).

During the course of this investigation we isolated single crystals of the propionitrile complex $[Re_2Cl_3(dppm)_2(NCEt)_2]PF_6$ and determined its structure using X-ray crystallography. This was deemed important in view of the disorder problem previously encountered in solving the structure of the benzonitrile derivative $[Re_2Cl_3(dppm)_2(NCPh)_2]PF_6$ [7]. The two complexes possess essentially isostructural dirhenium cations, although no disorder was encountered involving the cation in the present structure determination. An ORTEP representation of the structure of the dirhenium cation is shown in Fig. 2. The dirhenium unit has crystallographically imposed two-fold symmetry. The Re–Re distance of 2.2661(9) Å is essentially identical to that in the benzonitrile complex (2.270(1) Å) [7]. There is a similar disparity in these two structures between the long, axial Re(1)–Cl(1) bond (colinear with the Re–Re unit) and the pair of shorter 'equatorial' Re(2)–Cl(2)

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*For this structure there is of course more than one isomer that is possible.

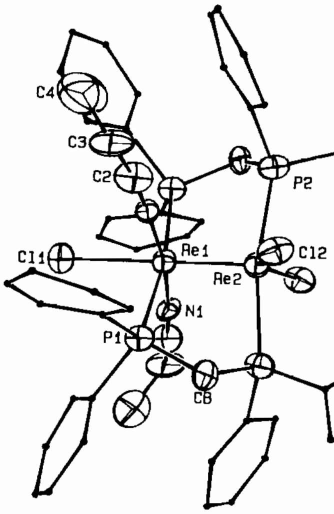

Fig. 2. ORTEP representation of the structure of the $[Re_2Cl_3(dppm)_2(NCEt)_2]^+$ cation showing the atomic numbering scheme for the non phenyl group atoms. The thermal ellipsoids are drawn at the 50% probability level.

bonds; in the propionitrile complex these distances are 2.556(4) and 2.361(4) Å, respectively. All other bond lengths (including Re–N and Re–P) in this molecule are normal, and merit little further consideration. The bond angles are also comparable between the two structures; for example, an Cl(2)–Re(2)–Cl(2) angle of 142.9(3)° can be compared with a corresponding angle of 140.5(3) in $[Re_2Cl_3(dppm)_2(NCPh)_2]^+$, while the N(1)–Re(1)–N(1) angles for the two cations are 171.3(8) and 169.6(5)°, respectively. The torsion angle P(1)–Re(1)–Re(2)–P(2) is 30.6°, and N(1)–Re(1)–Re(2)–Cl(2) is 27.5° for the propionitrile complex; these values reflect a staggered rotational geometry of a type that is often encountered in triply bonded Re_2^{4+} complexes [21].

Concluding Remarks

The ability of the complexes $Re_2X_4(dppm)_2$ to form fairly stable 1:1 adducts with PMe_3 and phosphite ligands expands the scope of their reaction chemistry to include stronger σ-donors ligands; previously their reactions with the π-acceptor ligands CO and RNC have been well documented [4, 5]. In the case of the reaction between $Re_2Cl_4(dppm)_2$ and PMe_3, it appears that $Re_2Cl_4(dppm)_2(PMe_3)$ is an intermediate in the formation of $Re_2Cl_4(dppm)(PMe_3)_2$ when an excess of PMe_3 is used [18]. The lability of the PMe_3 ligand of $Re_2Cl_4(dppm)_2(PMe_3)$ is noteworthy in that it leads smoothly to the formation of the bis-nitrile complexes $[Re_2Cl_3(dppm)_2(NCR)_2]PF_6$. Our structure determination of the propionitrile derivative is only the second one on a complex of this type.

Supplementary Material

Tables of anisotropic thermal parameters (S1), full listings of bond distances (S2) and bond angles (S3), and observed and calculated structure factors are available on request from R.A.W. Details concerning the data set and the structure solution and refinement may be obtained from Dr P. E. Fanwick.

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