Dirhenium complexes of the tripodal phosphine $CH_3C(CH_2PPh_2)_3$ (triphos). The isolation and characterization of the confacial bioctahedral species $[(triphos)Re(\mu\text{-}X)_3Re(triphos)]^{n+}$ ($n = 1$ or 0)

Michael T. Costello, Paul W. Schrier, Phillip E. Fanwick and Richard A. Walton*
Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393 (USA)

(Received January 27, 1993; revised April 30, 1993)

Abstract

The reactions of $Re_2(O_2CCH_3)_2X_4L_2$ (X = Cl or Br; L = py or H_2O) with the tripodal phosphine $CH_3C(CH_2PPh_2)_3$ (triphos) in refluxing ethanol provide a route to the confacial bioctahedral dirhenium(II) complexes $[Re_2(\mu\text{-}X)_3(triphos)_2]Y$, where Y = Cl, Br or BPh_4. The structural identity of the dirhenium cation has been established by X-ray crystallography on a crystal of composition $[Re_2Cl_3(triphos)_2]Cl$. Crystal data at +20 °C: triclinic space group $P\bar{1}$ (No. 2), $a = 12.868(2)$, $b = 13\,174(1)$, $c = 25.432(3)$ Å, $\alpha = 94.761(8)$, $\beta = 96.76(1)$, $\gamma = 114.235(8)°$, $V = 3862(2)$ Å^3, $Z = 2$. The structure was refined by full-matrix least-squares to $R = 0.040$ ($R_w = 0.058$) for 7523 data with $I > 3\sigma(I)$. The confacial bioctahedral dirhenium(II) cation has a surprisingly long Re–Re distance (3.199(1) Å), which implies the absence of an Re–Re bond. The paramagnetism of these complexes accords with this result; all show well-defined contact-shifted ^1H NMR spectra and are ESR silent. The cations display four metal centered redox processes (two one-electron oxidations, two one-electron reductions); the first reduction can be accessed by cobaltocene to form the neutral complexes $Re_2(\mu\text{-}X)_3(triphos)_2$ in which there is an Re_2^{3+} core present.

Introduction

Polydentate phosphines (three to six P donor atoms) form a vast array of mononuclear and polynuclear complexes with the transition metals [1]. However, to date, comparatively few such complexes have been isolated within which there is multiple bonding between the metal atoms.

We recently embarked on a study of rhenium polyhydride complexes that contain the tripodal phosphine ligand $CH_3C(CH_2PPh_2)_3$ (1,1,1-tris(diphenylphosphino)methyl)ethane; abbreviated triphos) [2] with an important goal being the synthesis and characterization of mononuclear compounds such as ReH_5(triphos), whose properties could be compared with those that contained a less rigid ReP_3 skeleton, i.e. $ReH_5(PR_3)_3$ (PR_3 represents a monodentate phosphine). During the course of this work we discovered a novel thermal reaction in which mononuclear ReH_5(triphos) is converted into dinuclear $Re_2H_4(triphos)_2$ [2]. The latter compound very readily oxidizes to the paramagnetic cation $[Re_2H_4(triphos)_2]^+$. The structural characterization of salts of the latter species showed [2] that this cation possesses the unsymmetrical structure $[(triphos)HRe(\mu\text{-}H)_3Re(triphos)]^+$. This finding has led us to examine further the chemistry of dirhenium complexes that contain the triphos ligand. We have found that the reactions of quadruply bonded dirhenium(III) complexes of the type *cis*-$Re_2(O_2CCH_3)_2X_4L_2$ (X = Cl or Br; L = H_2O or py) [3, 4] with triphos afford a route to the novel dirhenium(II) cations $[Re_2(\mu\text{-}X)_3(triphos)_2]^+$ (X = Cl or Br). The present report provides details of some of our initial findings.

Experimental

Starting materials

The dirhenium(III) complexes *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ and *cis*-$Re_2(O_2CCH_3)_2X_4(py)_2$ (X = Cl or Br) were prepared according to reported methods [4]. The triphos ligand was purchased from Strem Chemicals and used without further purification. The other reagents and solvents were obtained from commercial sources and were used without further purification. Solvents were deoxygenated prior to use.

Reaction procedures

All reactions were performed under an atmosphere of nitrogen gas with the use of standard Schlenk techniques.

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

A. Reactions of 1,1,1-tris(diphenylphosphinomethyl)ethane with cis-$Re_2(O_2CCH_3)_2X_4L_2$. Synthesis of [Re_2(μ-X)$_3$(triphos)$_2$]X

(i) From $Re_2(O_2CCH_3)_2Cl_4(py)_2$. A mixture of $Re_2(O_2CCH_3)_2Cl_4(py)_2$ (0.200 g, 0.253 mmol) and triphos (0.313 g, 0.506 mmol) was combined with 15 ml of ethanol and refluxed for 3 days in the presence of a pine applicator stick. A black crystalline product deposited on the applicator stick as the reaction progressed. The product was harvested from the stick upon completion of the reflux. The reaction filtrate was set aside for 1 day to afford additional black crystals; total yield 0.052 g (12%). *Anal.* Calc. for $C_{82}H_{78}Cl_4P_6Re_2$: Cl, 8.04. Found: Cl, 7.42%.

(ii) From $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$. A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.200 g, 0.299 mmol) and triphos (0.374 g, 0.599 mmol) in 10 ml of ethanol was reacted under reflux for 24 h, with use of a procedure similar to A(i), to afford a crop of black crystals; yield 0.120 g (23%). This product was shown to be [Re_2(μ-Cl)$_3$(triphos)$_2$]Cl on the basis of its electrochemical and spectroscopic properties which were identical to those found for the product in A(i).

(iii) From $Re_2(O_2CCH_3)_2Br_4(py)_2$. A similar reaction to A(i), but with the use of $Re_2(O_2CCH_3)_2Br_4(py)_2$, led to a black micro-crystalline product; yield (13%). The product was concluded to be [Re_2(μ-Br)$_3$(triphos)$_2$]Br on the basis of its cyclic voltammetric and ^{1}H NMR spectroscopic properties which were similar to those of [Re_2(μ-Cl)$_3$(triphos)$_2$]Cl. *Anal.* Calc. for $C_{82}H_{78}Br_4P_6Re_2$: Br, 16.46. Found: Br, 15.95%.

B. Synthesis of [Re_2(μ-X)$_3$(triphos)$_2$]BPh_4

(i) [Re_2(μ-Cl)$_3$(triphos)$_2$]BPh_4. A sample of [Re_2(μ-Cl)$_3$(triphos)$_2$]Cl (0.075 g, 0.0425 mmol) was dissolved in 10 ml of THF. The solution was filtered and $NaBPh_4$ (0.10 g, 0.292 mmol) was added to the filtrate, and the resulting mixture was stirred for 1 h. The dark purple solid was filtered off and washed with THF and diethyl ether; yield 0.081 g (92%).

This same compound can be prepared by the use of reaction A(i) when it is carried out in the presence of $NaBPh_4$ (0.087 g, 0.253 mmol) and with a reflux time of 24 h. The dark olive green solution was evaporated to dryness and the residue stirred with 20 ml of THF. After 1 day a dark purple solid was filtered off and washed with THF and diethyl ether; yield 0.070 g (13%). This product was shown to be [Re_2(μ-Cl)$_3$(triphos)$_2$]BPh_4 by cyclic voltammetry and ^{1}H NMR spectroscopy.

(ii) [Re_2(μ-Br)$_3$(triphos)$_2$]BPh_4. This compound was obtained in 89% yield from the reaction of [Re_2(μ-Br)$_3$(triphos)$_2$]Br with $NaBPh_4$.

C. Reduction reactions of [Re_2(μ-X)$_3$(triphos)$_2$]BPh_4. Synthesis of Re_2(μ-X)$_3$(triphos)$_2$

(i) Re_2(μ-Cl)$_3$(triphos)$_2$. A mixture of [Re_2(μ-Cl)$_3$(triphos)$_2$]BPh_4 (0.100 g, 0.0483 mmol) and (η^5-C_5H_5)$_2$Co (0.009 g, 0.048 mmol) in 10 ml of acetone was stirred for 30 min. The resulting orange–yellow solid was filtered off, and washed with acetone and diethyl ether; yield 0.074 g (89%).

(ii) Re_2(μ-Br)$_3$(triphos)$_2$. This orange complex was obtained from the reaction between [Re_2(μ-Br)$_3$(triphos)$_2$]BPh_4 (0.100 g, 0.0454 mmol) and (η^5-C_5H_5)$_2$Co (0.010 g, 0.053 mmol) in 10 ml of acetone; yield 0.068 g (80%).

X-ray crystallography

A suitable crystal of the complex of composition [Re_2Cl_3(triphos)$_2$]Cl was obtained directly from one of the reactions that afforded this compound (see A(i)). The structure of the crystal was determined by the application of standard procedures. The basic crystallographic parameters for this complex are listed in Table 1. The cell constants are based on 25 reflections with $18 < \theta < 21°$. The crystal was found to belong to the triclinic space group $P\bar{1}$ (No. 2). Three standard reflections were measured after every 5000 s of beam exposure during data collection. There were no systematic variations in intensity. Lorentz and polarization corrections were applied to the data set. An empirical absorption correction [5] was applied and the linear absorption coefficient used was 34.45 cm^{-1}. No corrections for extinction were applied. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package.

The structure was solved by use of the Enraf-Nonius structure solution procedure MolEN and refined by full-matrix least-squares where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. The hydrogen atoms of the triphos ligands were included at fixed positions with $B(H) = 1.3B(C)$. The non-hydrogen atoms of the dirhenium cation were refined anisotropically; corrections for anomalous scattering were applied to these atoms [6]. The highest peak in the final difference Fourier had a height of 2.10 e/Å^3 and the final residuals were $R = 0.040$ ($R_w = 0.058$) for 7523 data with $I > 3\sigma(I)$.

The one problem encountered during the structure solution involved the unambiguous identification and refinement of the anion. Following location of all non-hydrogen atoms of the dirhenium cation, two regions

TABLE 1 Crystallographic data and data collection parameters for $[Re_2(\mu\text{-}Cl)_3(triphos)_2]Cl$

Formula	$Re_2Cl_4P_6C_{82}H_{78}$
Formula weight	1763.59
Space group	$P\bar{1}$(No. 2)
a (Å)	12.868(2)
b (Å)	13.174(1)
c (Å)	25.432(3)
α (°)	94.761(8)
β (°)	96.76(1)
γ (°)	114.235(8)
V (Å^3)	3862(2)
Z	2
D_c (g cm^{-3})	1.517
Crystal dimensions (mm)	0.25×0.24×0.15
Temperature (°C)	20
Radiation (wavelength)	Mo Kα (0.71073 Å)
Monochromator	graphite
Linear absorption coefficient (cm^{-1})	34.45
Absorption correction applied	empirical[a]
Transmission factors: min., max.	0 86, 1.00
Diffractometer	Enraf-Nonius CAD4
Scan method	ω–2θ
h, k, l Limits	−13 to 13, −14 to 14, 0 to 27
2θ Range (°)	4.00–45.00
Scan width (°)	0.69+0.35 tan(θ)
Take-off angle (°)	2 95
Programs used	Enraf-Nonius MolEN
F(000)	1762.0
p-Factor used in weighting	0.040
Data collected	10055
Unique data	10055
Data with $I>3.0\sigma(I)$	7523
No. variables	846
Largest shift/e.s.d. in final cycle	0.08
R[b]	0.040
R_w[c]	0.058
GOF[d]	1.448

[a]See ref. 5. [b]$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [c]$R_w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/\sigma^2(F_o)$. [d]Goodness of fit$=[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

of electron density (each ~8e) remained that were located about an inversion center. Refinement of each as a chloride ion at one-half occupancy seemed the most reasonable assumption based upon the known stoichiometry of this product and the clear chemical evidence for the presence of Cl^- in the bulk samples. Nonetheless, the refinement of Cl(A) and Cl(B) was not entirely satisfactory since at convergence these 'atoms' still possessed large thermal parameters. However, we found no alternative model which would give a more satisfactory solution or one that was chemically more reasonable, and since these uncertainties did not in any way affect the refinement and structural significance of the cation the refinement was terminated at this stage.

Table 2 lists the atomic positional parameters and their errors for the non-hydrogen atoms, while Table 3 provides the more important intramolecular bond distances and angles for the structure. See also 'Supplementary material'.

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 carried out on dichloromethane solutions that contained 0.1 M tetra-n-butylammonium hexafluorophosphate (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. Voltammetric experiments were performed with a BAS Inc. model CV-27 instrument in conjunction with a BAS model RXY recorder. ^1H NMR spectra were recorded on CD_2Cl_2 solutions of the compounds with use of a Varian Gemini-200 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. Conductivity measurements were performed on c. 10^{-3} M acetone, acetonitrile

TABLE 2 Positional parameters for the non-phenyl group atoms of $[Re_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ and their e.s.d.s[a]

Atom	x	y	z	B (Å^2)
Re(1)	0.07372(3)	0.28338(3)	0.18555(2)	1.822(9)
Re(2)	0.03232(3)	0.23631(3)	0.30446(2)	1.788(9)
Cl(1)	0.1602(2)	0.1974(2)	0.2486(1)	2.24(6)
Cl(2)	−0.1017(2)	0.1700(2)	0.2191(1)	2.49(6)
Cl(3)	0.1008(2)	0.4133(2)	0.2664(1)	2.52(6)
P(11)	0.0445(2)	0.1421(2)	0.1155(1)	2.23(6)
P(12)	0.2450(2)	0.4037(2)	0.1561(1)	2.22(7)
P(13)	−0.0180(2)	0.3614(2)	0.1265(1)	2.45(7)
P(21)	−0.1008(2)	0.2717(2)	0.3504(1)	2.28(7)
P(22)	−0.0277(2)	0.0595(2)	0.3343(1)	2.19(6)
P(23)	0.1665(2)	0.3121(2)	0.3849(1)	2.31(7)
C(11)	0.0430(9)	0.1938(9)	0.0498(4)	2.5(3)
C(12)	0.2346(9)	0.3608(8)	0.0842(4)	2.4(3)
C(13)	0.0515(9)	0.3907(9)	0.0666(4)	2.7(3)
C(1A)	0.1144(9)	0.3194(9)	0.0499(4)	2.5(3)
C(1B)	0.133(1)	0.335(1)	−0.0074(5)	3.8(3)
C(21)	−0.0874(9)	0.2468(9)	0.4206(5)	2.9(3)
C(22)	−0.0694(9)	0.0626(9)	0.4007(5)	2.6(3)
C(23)	0.1103(9)	0.2432(9)	0.4423(5)	2.8(3)
C(2A)	−0.0222(9)	0.1761(9)	0.4383(4)	2.6(3)
C(2B)	−0.045(1)	0.150(1)	0.4947(5)	4.0(3)
Cl(A)	0.441(2)	0.383(2)	0.0172(9)	16(1)*
Cl(B)	0.464(2)	0.533(2)	0.026(1)	17(1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\gamma)\beta(1,2)+ac(\cos\beta)\beta(1,3)+bc(\cos\alpha)\beta(2,3)]$ For parameters for the phenyl group carbon atoms see 'Supplementary material'.

TABLE 3 Some important bond distances (Å) and bond angles (°) for the $[Re_2(\mu\text{-}Cl)_3(triphos)_2]^+$ cation[a]

Bond distances			
Re(1)–Re(2)	3.199(1)	P(12)–C(12)	1.84(1)
Re(1)–Cl(1)	2.451(3)	P(13)–C(13)	1.84(1)
Re(1)–Cl(2)	2.440(3)	P(21)–C(21)	1.84(1)
Re(1)–Cl(3)	2.457(3)	P(22)–C(22)	1.83(1)
Re(1)–P(11)	2.344(3)	P(23)–C(23)	1.85(1)
Re(1)–P(12)	2.376(3)	C(11)–C(1A)	1.53(2)
Re(1)–P(13)	2.353(3)	C(12)–C(1A)	1.54(2)
Re(2)–Cl(1)	2.471(3)	C(13)–C(1A)	1.53(2)
Re(2)–Cl(2)	2.452(3)	C(1A)–C(1B)	1.52(2)
Re(2)–Cl(3)	2.458(3)	C(21)–C(2A)	1.55(2)
Re(2)–P(21)	2.357(3)	C(22)–C(2A)	1.55(2)
Re(2)–P(22)	2.356(3)	C(23)–C(2A)	1.55(2)
Re(2)–P(23)	2.361(3)	C(2A)–C(2B)	1.53(2)
P(11)–C(11)	1.86(1)	C(2A)–C(2B)	1.53(2)
Bond angles			
Cl(1)–Re(1)–Cl(2)	82.5(1)	Cl(1)–Re(2)–P(21)	174.8(1)
Cl(1)–Re(1)–Cl(3)	82.8(1)	Cl(1)–Re(2)–P(22)	92.6(1)
Cl(1)–Re(1)–P(11)	91.1(1)	Cl(1)–Re(2)–P(23)	97.8(1)
Cl(1)–Re(1)–P(12)	98.3(1)	Cl(2)–Re(2)–Cl(3)	81.5(1)
Cl(1)–Re(1)–P(13)	177.2(1)	Cl(2)–Re(2)–P(21)	93.0(1)
Cl(2)–Re(1)–Cl(3)	81.8(1)	Cl(2)–Re(2)–P(22)	96.1(1)
Cl(2)–Re(1)–P(11)	93.7(1)	Cl(2)–Re(2)–P(23)	176.2(1)
Cl(2)–Re(1)–P(12)	176.4(1)	Cl(3)–Re(2)–P(21)	95.8(1)
Cl(2)–Re(1)–P(13)	94.6(1)	Cl(3)–Re(2)–P(22)	174.6(1)
Cl(3)–Re(1)–P(11)	172.8(1)	Cl(3)–Re(2)–P(23)	94.7(1)
Cl(3)–Re(1)–P(12)	94.9(1)	P(21)–Re(2)–P(22)	89.1(1)
Cl(3)–Re(1)–P(13)	96.7(1)	P(21)–Re(2)–P(23)	87.2(1)
P(11)–Re(1)–P(12)	89.7(1)	P(22)–Re(2)–P(23)	87.7(1)
P(11)–Re(1)–P(13)	89.3(1)	Re(1)–Cl(1)–Re(2)	81.07(8)
P(12)–Re(1)–P(13)	84.5(1)	Re(1)–Cl(2)–Re(2)	81.66(9)
Cl(1)–Re(2)–Cl(2)	81.9(1)	Re(1)–Cl(3)–Re(2)	81.22(8)
Cl(1)–Re(2)–Cl(3)	82.35(9)		

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

or nitromethane solutions by using an Industrial Instruments Inc. model RC-16B2 conductivity bridge.

Results and discussion

The bidentate (chelating or bridging) phosphines $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2PCH_2CH_2PPh_2$ (dppe) react in refluxing ethanol with *cis*-$Re_2(O_2CCH_3)_2X_4L_2$ (X = Cl or Br; L = H_2O, py, or some other neutral monodentate ligand) to afford the dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ and β-$Re_2X_4(dppe)_2$ in moderate to good yield [7]. While the analogous reductive decarboxylation reactions with the tripodal phosphine triphos proceed to produce dirhenium(II) species, the product yields are low (<25%) and the structures of the products are quite different from those of the triply bonded compounds $Re_2X_4(\mu\text{-dppm})_2$ and β-$Re_2X_4(dppe)_2$. Nonetheless, these complexes, which contain the $[Re_2(\mu\text{-}X)_3(triphos)_2]^+$ cations, are of special interest since they represent the first examples of their type in dirhenium(II) chemistry [4].

The formulation of these products as the dinuclear dirhenium(II) complexes $[Re_2(\mu\text{-}X)_3(triphos)_2]X$ (X = Cl or Br) is based upon the single crystal X-ray structure analyses of the chloro complex, and a variety of other characterization studies. Although we were unable to obtain satisfactory carbon and hydrogen elemental analyses for these compounds, satisfactory halogen analyses were obtained. The carbon and hydrogen microanalyses were consistently 6–12% low because of the incomplete combustion of both compounds at temperatures up to 950 °C*.

Solutions of both complexes in acetone and acetonitrile had conductivities in accord with them being 1:1 electrolytes. For the chloro complex, the Λ_m values were 96 and 98 Ω^{-1} cm^2 mol^{-1} for solutions in acetone and acetonitrile (*c.* 1×10^{-3} M), respectively, while for $[Re_2(\mu\text{-}Br)_3(triphos)_2]Br$, $\Lambda_m = 101$ Ω^{-1} cm^2 mol^{-1} for a solution in acetone. Cyclic voltammetric measurements on solutions of both complexes in 0.1 M TBAH–CH_2Cl_2 were very similar and showed, in addition to four metal-

---

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

based redox processes (Table 4), irreversible oxidations that were characteristic of an outer-sphere halide anion [8]. For $[Re_2(\mu\text{-}Cl)_3(triphos)_2]Cl$, the $E_{p,a}$ value for Cl^- was +1.1 V versus Ag/AgCl, whereas for the analogous bromo complex there were two characteristic oxidation processes at $E_{p,a} = +1.0$ and +0.8 V versus Ag/AgCl for the Br^- anion. Further support for this formulation is provided by the anion exchange reactions of $[Re_2(\mu\text{-}X)_3(triphos)_2]X$ with $NaBPh_4$ to afford the salts $[Re_2(\mu\text{-}X)_3(triphos)_2]BPh_4$ (X = Cl or Br). The behavior of these compounds as 1:1 electrolytes was shown by a conductivity measurement on a 1×10^{-3} M solution of the chloro complex in acetone ($\Lambda_m = 102$ Ω^{-1} cm^2 mol^{-1}), and the cyclic voltammetric properties of both complexes confirmed their identity. Solutions of these complexes in 0.1 M TBAH–CH_2Cl_2 possessed CVs that were essentially the same as those of the halide salts (Table 4) with the exception of the presence of an irreversible process at $E_{p,a} = +0.90$ V versus Ag/AgCl which is characteristic of the $[BPh_4]^-$ anion.

In order to establish the structure of the dirhenium cation we carried out an X-ray structure analysis on a crystal we had expected to be of composition $[Re_2Cl_3(triphos)_2]Cl$. However, while the structure of the cation was readily established, the unambiguous identification of the anion *in this particular crystal* was complicated by a disorder problem. An ORTEP representation of the dirhenium cation is shown in Fig. 1, in which the phenyl group atoms have been omitted for clarity, while a view of the confacial bioctahedral $[Re_2(\mu\text{-}Cl)_3P_6]$ skeleton along the Re–Re vector is provided in Fig. 2. Important bond distances and angles for the cation are listed in Table 3. This cation bears a close structural relationship to the previously characterized diosmium(II) complex $[Os_2(\mu\text{-}Cl)_3(PEt_3)_6]PF_6$ [9].

The most interesting and significant aspect of the structure of the $[Re_2(\mu\text{-}Cl)_3(triphos)_2]^+$ cation is the very long Re–Re distance (3.199(1) Å), a clear indication of the absence of a strong metal–metal interaction. This result is surprising given the propensity of the Re_2^{4+} core to form compounds in which there is an electron-rich metal–metal triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration) [10]. The Re–Cl distances in the $Re(\mu\text{-}Cl)_3Re$ unit average to 2.455 Å, significantly longer than the terminal Re–Cl distances present in the compound *fac*-$ReCl_3(triphos)$ (av. 2.358 Å) [2]. The Re–P distances in $[Re_2(\mu\text{-}Cl)_3(triphos)_2]^+$ (av. 2.358 Å) are significantly shorter than are those in *fac*-$ReCl_3(triphos)$ (av. 2.448 Å). The shortening of the Re–P bonds in the dirhenium(II) cation may reflect both the influence of a structural *trans* effect (the Re–Cl bonds *trans* to Re–P are longer and weaker in the cation) and an enhanced degree of $Re(d_\pi) \rightarrow P(d_\pi)$ bonding in this lower valent dirhenium(II) species.

The structural parameters for the triphos ligands in the $[Re_2(\mu\text{-}Cl)_3(triphos)_2]^+$ cation are similar to those found for the compounds $ReCl_3(triphos)$ [2] and $[Re_2H_4(triphos)_2]ReO_4$ [2]. The overall geometry about each of the Re atoms in $[Re_2(\mu\text{-}Cl)_3(triphos)_2]^+$ is the same as that present in *fac*-$ReCl_3(triphos)$ [2]. However, the Cl–Re–Cl and P–Re–P angles in these two structures differ as a consequence of the Re–Cl bonds being terminal in one structure and bridging in the other. While the Cl–Re–Cl angles are, as expected, larger in mononuclear *fac*-$ReCl_3(triphos)$ [2] (i.e. 87.1° (av.) versus 82.1° (av.) in $[Re_2(\mu\text{-}Cl)_3(triphos)_2]^+$) the reverse is true for the P–Re–P angles, which average to 85.5° in the structure of *fac*-$ReCl_3(triphos)$ [2] and 87.9° in $[Re_2(\mu\text{-}Cl)_3(triphos)_2]^+$.

There are comparatively few d^5–d^5 confacial bioctahedral species, most of which appear to be diruthenium(III) compounds [11]. In the case of $[Re_2(\mu\text{-}X)_3(triphos)_2]^+$, we might have anticipated the presence of a net Re–Re single bond ($\sigma^2\pi^4\pi^{*4}$ configuration) [11], but while the Re–Re distance of 3.20 Å is appreciably shorter than that present in the d^6–d^6 system $[Os_2(\mu\text{-}Cl)_3(PEt_3)_6]^+$ (3.45 Å) [9] it still does not accord with a strong Re···Re interaction being present. Accordingly, we would expect the salts of the $[Re_2(\mu\text{-}$

TABLE 4. Cyclic voltammetric data for dirhenium(II) complexes of the type $[Re_2(\mu\text{-}X)_3(triphos)_2]Y$[a]

Complex		Dirhenium cation				Anion	
X	Y	$E_{1/2}(ox)(2)$	$E_{1/2}(ox)(1)$	$E_{1/2}(red)(1)$	$E_{1/2}(red)(2)$	$E_{p,a}(1)$	$E_{p,a}(2)$
Cl	Cl	+1.16	+0.52	−0.43	−0.91	+1.1	
Cl	BPh_4	+1.21	+0.55	−0.41	−0.90	+0.90	
Br	Br	+1.20	+0.54	−0.37	−0.85	+0.8	+1.0
Br	BPh_4	+1.20	+0.54	−0.38	−0.86	+0.90	
Cl		+1.18	+0.54	−0.42[b]	−0.90		
Br		+1.18	+0.54	−0.38[b]	−0.85		

[a] Measurements carried out on 0.1 M TBAH–CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode with a scan rate (ν) of 200 mV/s at a Pt-bead electrode. Under our experimental conditions $E_{1/2} = +0.47$ V vs. Ag/AgCl for the ferrocenium/ferrocene couple. Values of ΔE_p (i.e. $E_{p,a} - E_{p,c}$) were in the range 70–80 mV. [b] $E_{1/2}(ox)$ value.

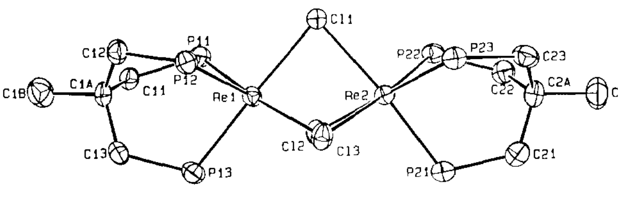

Fig. 1 ORTEP representation of the structure of the $[Re_2(\mu\text{-}Cl)_3(triphos)_2]^+$ cation with the phenyl group atoms omitted. The thermal ellipsoids are drawn at the 50% probability level.

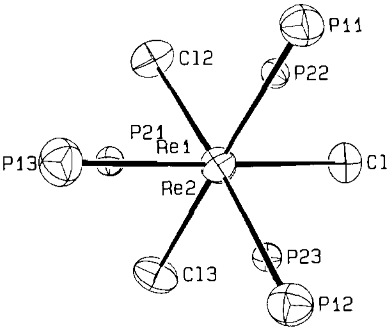

Fig. 2 View of the confacial bioctahedral $Re_2Cl_3P_6$ skeleton along the Re–Re vector. The thermal ellipsoids are drawn at the 50% probability level.

$X)_3(triphos)_2]^+$ cations to be paramagnetic and this is indeed the case. While none of the compounds are ESR-active (X-band measurements in CH_2Cl_2 glasses at −160 °C), temperature range magnetic susceptibility measurements on a sample of $[Re_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ (SQUID technique)* showed that the μ_{eff} value of 1.33 BM at 380 K decreased to 0.35 BM at 60 K. All four complexes showed very similar contact-shifted ^1H NMR spectra, but we observed no resonances in the ^{31}P NMR spectra. These properties are consistent with a metal-based antiferromagnetic paramagnetism being present. The ^1H NMR spectra of CD_2Cl_2 solutions of the complexes gave sharp resonances. For example, the complex $[Re_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ showed phenyl resonances centered at δ +6.95(m), δ +6.78(d) and δ +6.68 (^2J(H–H) = 7.5 Hz) and $-CH_2-$ and $-CH_3$ resonances for the triphos ligands as singlets at δ +8.73 and δ +5.13, respectively. The spectrum of $[Re_2(\mu\text{-}Cl)_3(triphos)_2]BPh_4$ was very similar to that of the chloride, except for the presence of additional multiplets at δ +7.34 and δ +7.05 that are assigned to the $[BPh_4]^-$ anion. The relative intensity ratio of the $-CH_3$, $-CH_2-$ and $-C_6H_5$ resonances was in good agreement with the expected ratio (obs. 1.0:1.9:14.3; calc. 1:2:13.3). For the chloride salt we found the corresponding intensity ratio to be 1.0:1.8:10.0 (calc. 1:2:10). The ^1H NMR spectral data for the bromo complexes are very similar to those obtained for their chloro analogues.

A variable temperature ^1H NMR spectral study of a CD_2Cl_2 solution of $[Re_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ was carried out over the temperature range +22 to −79 °C. The $-CH_3$ and $-CH_2-$ resonances of the triphos ligands shifted upfield upon lowering the temperature, with the former shifting from δ +5.13 to δ +3.86 and the latter from δ +8.73 to δ +6.47. We attempted to fit this behavior within the models [12, 13] that have been utilized to explain the temperature dependences of NMR resonances in other paramagnetic dinuclear systems. With a diamagnetic chemical shift of +1.2 ppm for the $-CH_3$ resonance of triphos** and a hyperfine coupling constant (A) of 0.2 MHz, we obtained a 'best fit' [12] for the exchange integral (J) of between 190 and 210 cm^{-1}. However, our failure to achieve better agreement with the calculated behavior [12] may reflect inadequacies in our model. Further studies of these properties are in order.

Finally, we should comment upon an observation that was made during the course of our earlier studies on the polyhydrido complexes $ReH_5(triphos)$ and $[Re_2H_4(triphos)_2]^+$ [2]. When $ReCl_3(PPh_3)_2(NCCH_3)$ is refluxed in benzene with triphos, the complex $ReCl_3(triphos)$ is produced. If the reactants are reacted for a short period of time, a mixture of $ReCl_3(triphos)$ and an impurity is produced [14]. The impurity and $ReCl_3(triphos)$ proved difficult to separate, but when this mixture was refluxed in ethanol with $NaBH_4$, and then exposed to air, the product $ReCl_3(triphos)$ reacted to form the soluble species $[Re_2H_4(triphos)_2]^+$ while the impurity remained intact. The orange impurity could then be isolated free of the main product. The cyclic voltammetric properties of this material [14] were identical to those of the $[Re_2(\mu\text{-}Cl)_3(triphos)_2]Y$ salts (Table 4) with the exception that the process at $E_{1/2}$ *c.* −0.42 V corresponded to a one-electron *oxidation* of the complex. This implies that the orange material is $Re_2(\mu\text{-}Cl)_3(triphos)_2$, and therefore a rare example of a compound that contains the Re_2^{3+} core. In accord with this conclusion, we have found that the cobaltocene reduction of $[Re_2(\mu\text{-}Cl)_3(triphos)_2]BPh_4$ produces this exact same compound. A similar cobaltocene reduction of $[Re_2(\mu\text{-}Br)_3(triphos)_2]BPh_4$ gives $Re_2(\mu\text{-}Br)_3(triphos)_2$. The electrochemical properties of both compounds are presented in Table 4. Neither compound is soluble in acetone and both decompose in acetonitrile. Although they also decompose in nitromethane, freshly prepared solutions in this solvent (*c.* 1×10^{-3} M) had

---

*This measurement was carried out on a Quantum Design MPMS susceptometer housed in the Physics and Astronomy Department at Michigan State University. We thank Professor Kim R. Dunbar and Mr Stuart L. Bartley for obtaining these results for us.

**This value for the diamagnetic chemical shift was based upon the spectral properties for the triphos ligands in the diamagnetic complex $Re_2H_4(triphos)_2$ [14].

low conductivities ($\Lambda_m = 16$ and 10 Ω^{-1} cm^2 mol^{-1} for X = Cl and Br, respectively), in accord with their nonionic nature. These compounds are ESR inactive, and both gave contact-shifted ^{1}H NMR spectra; the $-CH_2-$ and $-CH_3$ resonances of the triphos ligands were observed as broad singlets at δ +11.8 and δ +5.48 for X = Cl and δ +8.90 and δ +4.04 for X = Br. Further studies of these neutral compounds are planned including their complete structural characterization.

Supplementary material

Tables of positional parameters for the hydrogen atoms, anisotropic thermal parameters, full listings of bond distances and bond angles, and observed and calculated structure factors are available on request from author R.A.W. Further details concerning the structure determination can be obtained from Dr P.E. Fanwick of this department.

Acknowledgement

Support from the National Science Foundation (Grant CHE91-07578 to R.A.W.) is gratefully acknowledged.

References

1 F.A. Cotton and B Hong, *Prog Inorg Chem.*, *40* (1992) 179–289.

2 M.T. Costello, P.E. Fanwick, M A. Green and R.A. Walton, *Inorg. Chem*, *31* (1992) 2359.

3 A.R. Chakravarty, F.A. Cotton, A.R Cutler and R.A Walton, *Inorg Chem*, *25* (1986) 3619.

4 F.A Cotton and R.A. Walton, *Multiple Bonds Between Metal Atoms*, Oxford University Press, Oxford, 2nd edn., 1993.

5 N. Walker and D. Stuart, *Acta Crystallogr., Sect A*, *39* (1983) 158.

6 D.T. Cromer, *International Tables for X-ray Crystallography*, Vol IV, Kynoch, Birmingham, UK, 1974, (a) Table 2.3.1; (b) Table 2.2B.

7 A.R. Cutler, D.R. Derringer, P.E. Fanwick and R A. Walton, *J. Am Chem Soc*, *110* (1988) 5024.

8 V. Srinivasan and R.A. Walton, *Inorg. Chem*, *19* (1980) 1635.

9 P.E. Fanwick, I.F. Fraser, S.M. Tetrick and R.A. Walton, *Inorg Chem*, *26* (1987) 3786

10 F.A Cotton and R.A. Walton, *Multiple Bonds Between Metal Atoms*, Oxford University Press, Oxford, 2nd edn., 1993, Section 2.1.6, pp. 60–111.

11 F A. Cotton and R.A. Walton, *Multiple Bonds Between Metal Atoms*, Oxford University Press, Oxford, 2nd edn., 1993, Section 9.4.1, pp. 600–606.

12 T.W. Coffindaffer, G P. Niccolai, D. Powell, I.P. Rothwell and J C. Huffman, *J Am Chem. Soc*, *107* (1985) 3572.

13 F.A Cotton, H. Chen, L.M. Daniels and X. Feng, *J. Am Chem Soc*, *114* (1992) 8980.

14 M.T. Costello, *Ph D. Theses*, Purdue University, 1992.