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Reactions of the dirhenium(III,III) complex *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ that lead to the dirhenium(III,II) complexes $Re_2(\mu\text{-}O_2CMe)Cl_4(PR_3)_2$ and tetrarheniumcyclodiyne clusters of the type $Re_4(\mu\text{-}O)_4Cl_4(PR_3)_4$

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The reaction of *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ **1** with $P(C_6H_4OMe\text{-}p)_3$ gives the tetranuclear complex $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4$ **14** along with the salt $[(C_6H_4OMe\text{-}p)_3PMe]_2Re_2Cl_8$ **15**. Compound **14** is the first symmetrical, neutral, tetrarheniumcyclodiyne type cluster that contains phosphine ligands. Complexes of this same type with PPh_3 (**16**) and PMe_2Ph (**17**) have been prepared by alternative methods but have poor solubility properties. The paramagnetic complex $Re_2(\mu\text{-}O_2CMe)Cl_4(PPh_3)_2$ **2**, which is prepared from **1** by reaction with PPh_3, undergoes phosphine substitution reactions when treated with dichloromethane solutions of other phosphines. Simple non-redox reactions can occur upon reaction of **2** with monodentate and bridging bidentate phosphines to afford complexes of the types $Re_2(\mu\text{-}O_2CMe)Cl_4(PR_3)_2$ [$PR_3 = PBz_3$ **3**, $P(C_6H_4OMe\text{-}p)_3$ **4** or $PMePh_2$ **5**] and *trans*-$Re_2(\mu\text{-}O_2CMe)Cl_4(\mu\text{-}PP)_2$ [PP = dppm **9**, $Ph_2PNHPPh_2$ **10** or $(Ph_2P)_2C{=}CH_2$ **11**]. However, reactions that lead either to reduction to dirhenium(II) complexes or Re–Re bond cleavage are encountered in the case of the reactions of **2** with $PMePh_2$, PMe_2Ph, PCy_3 and dppe; these have led to the isolation of $Re_2Cl_4(PMePh_2)_4$ **6**, $Re_2Cl_4(PMe_2Ph)_4$ **7**, *mer-trans*-$ReOCl_3(PCy_3)_2$ **8**, α-$Re_2Cl_4(dppe)_2$ **12**, and *trans*-$[ReO_2(dppe)_2]Cl$ **13**. The structures of compounds **3**, **8**, **13**, **14** and **15** have been determined by X-ray crystallography.

Introduction

Several types of behavior have been encountered in the reactions of the dirhenium(III) carboxylate complex *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$[1] with the tertiary phosphines PMe_3, PMe_2Ph, $PMePh_2$ and PPh_3 in primary alcohol solvents.[2,3] The first three phosphines afford the two-electron reduced dirhenium(II) complexes of the type $Re_2Cl_4(PR_3)_4$, whereas PPh_3, which is the least basic of these phosphines, gives the dirhenium(IV,II) intramolecular disproportionation products $(RO)_2Cl_2ReReCl_2(PPh_3)_2$ (R = Me, Et or Pr^n).[2,3] More recently, we have examined the reactions of *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ towards an extensive range of triaryl phosphines (PAr_3) in methanol and isolated further examples of complexes of the type $(MeO)_2Cl_2ReReCl_2(PAr_3)_2$ [$PAr_3 = P(C_6H_4Me\text{-}p)_3$, $P(C_6H_4Me\text{-}m)_3$, $P(C_6H_4Cl\text{-}p)_3$ or $P(C_6H_4OMe\text{-}p]$.[3] Variations in the nature of the phosphine have led in several instances to the formation of unexpected reaction products under these same reaction conditions. Specifically, $Re_2(\mu\text{-}O_2CMe)Cl_3(OMe)(PCyPh_2)_2$ and $Re_2(\mu\text{-}O_2CMe)Cl_4(PBz_3)_2$ are the predominant products when $PCyPh_2$ and PBz_3 are used, while $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4$ is a major product in the reaction involving $P(C_6H_4OMe\text{-}p)_3$.[3] The paramagnetic complex $Re_2(\mu\text{-}O_2CMe)Cl_4(PBz_3)_2$ is similar to compounds of this type isolated previously with PPh_3 and PPh_2py.[4]

In the present report we address two important points raised by these earlier studies.[2–4] First, we have examined the substitutional lability of the PPh_3 ligands in $Re_2(\mu\text{-}O_2CMe)Cl_4(PPh_3)_2$ as a possible strategy for accessing other derivatives of the paramagnetic $[Re_2(\mu\text{-}O_2CMe)Cl_4]$ core. Second, since the tetranuclear complex $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4$ is the first example of a symmetrical tetrarhenium cyclodiyne type cluster containing phosphine ligands,[5] we have examined means by which this novel cluster chemistry can be developed.

Experimental

Starting materials and general procedures

Standard literature procedures were used to prepare the complexes *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ **1**[2b] and $Re_2(\mu\text{-}O_2CMe)Cl_4(PPh_3)_2$ **2**.[4] All phosphine ligands and common solvents were used as received from commercial sources. Reactions were performed under an atmosphere of dry dinitrogen, and solvents were deoxygenated by purging with dinitrogen prior to use. IR spectra, NMR spectra and cyclic voltammetric measurements were determined as described previously.[6] Elemental microanalyses were performed by Dr H. D. Lee of the Purdue University Microanalytical Laboratory.

Synthesis

$Re_2(\mu\text{-}O_2CMe)Cl_4(PBz_3)_2$ 3. A mixture of $Re_2(\mu\text{-}O_2CMe)Cl_4(PPh_3)_2$ **2** (127 mg, 0.116 mmol) and $P(CH_2Ph)_3$ (87 mg, 0.286 mmol) was stirred in dichloromethane (15 mL) for 6 h at room temperature. The solvent was removed under reduced pressure to leave an oily residue which was treated with diethyl ether (*ca.* 10 mL) and the mixture stirred. A red solid was filtered off, washed with diethyl ether (3 × 5 mL) and dried under a vacuum; yield 119 mg (87%). Calc. for $C_{44}H_{45}Cl_4O_2P_2Re_2$: C, 44.71; H, 3.84. Found: C, 44.77; H, 3.88%.

X-Ray quality single crystals of **3** were obtained by the diffusion of diethyl ether into a dichloromethane solution of the complex.

$Re_2(\mu\text{-}O_2CMe)Cl_4[P(C_6H_4OMe\text{-}p)_3]_2$ 4. A procedure similar to that described for **3** afforded the title complex when 130 mg (0.12 mmol) of **2** was reacted with 93 mg (0.26 mmol) of $P(C_6H_4OMe\text{-}p)_3$; yield 138 mg (90%). Calc. for $C_{44}H_{45}Cl_4O_8P_2Re_2$: C, 41.35; H, 3.55. Found: C, 41.28; H, 3.47%.

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$Re_2(\mu\text{-}O_2CMe)Cl_4(PMePh_2)_2$ 5 and $Re_2Cl_4(PMePh_2)_4$ 6. A dichloromethane solution (15 mL) of **2** (100 mg, 0.09 mmol) was treated with 0.1 mL of $PMePh_2$ and the mixture stirred for 8 h at room temperature. The reaction solvent was removed under reduced pressure and the residue washed with pentane (3 × 5 mL). The cyclic voltammogram showed the resulting solid (96 mg) to be a mixture of products, so it was extracted with benzene to leave an insoluble red paramagnetic solid (49 mg, 56%), identified as **5** by cyclic voltammetry (see Results and discussion), and a green benzene soluble product (44 mg, 37%) which was identified as **6** on the basis of its known spectroscopic and electrochemical properties.[7]

$Re_2Cl_4(PMe_2Ph)_4$ 7. The same procedure that was used to prepare **5**, along with $Re_2Cl_4(PMePh_2)_4$ **6**, was carried out with PMe_2Ph in place of $PMePh_2$. The product was exclusively $Re_2Cl_4(PMe_2Ph)_4$ **7**, which was identified based upon a comparison of its properties with those reported in the literature.[7,8] Yield: 90%.

***mer-trans*-$ReOCl_3(PCy_3)_2$ 8.** The reaction between **2** (81 mg, 0.074 mmol) and 70 mg (0.25 mmol) of PCy_3 in 15 mL of dichloromethane was carried out for 8 h, the solvent removed under reduced pressure, and diethyl ether (10 mL) added to afford a green precipitate which was recrystallized from dichloromethane–diethyl ether; yield 85 mg (70%). Calc. for $C_{36}H_{66}Cl_3OP_2Re$: C, 49.73; H, 7.65. Found: C, 50.09; H, 7.67%.

Crystals suitable for an X-ray diffraction study were grown by the slow diffusion of diethyl ether into a dichloromethane solution of the complex.

$Re_2(\mu\text{-}O_2CMe)Cl_4(\mu\text{-dppm})_2$ 9. A mixture of **2** (100 mg, 0.091 mmol) and bis(diphenylphosphino)methane (dppm) (85 mg, 0.22 mmol) was stirred in dichloromethane (15 mL) at room temperature for 8 h. The solvent was removed under reduced pressure and the oily residue treated with diethyl ether (10 mL) and stirred to afford **9** as a yellow solid; yield 116 mg (92%). The identity of this product was established by a comparison of its spectroscopic and electrochemical properties with literature data.[9]

$Re_2(\mu\text{-}O_2CMe)Cl_4(\mu\text{-dppa})_2$ 10. This complex was prepared by the reaction of **2** with $Ph_2PNHPPh_2$ (dppa) with the use of a procedure similar to that described above for its dppm analogue; yield 90%. The identity of **10** was based upon its spectroscopic and electrochemical properties.[10]

$Re_2(\mu\text{-}O_2CMe)Cl_4(\mu\text{-dppE})_2$ 11. A procedure similar to that described for **9** was used to prepare the title complex which contained the ligand $(Ph_2P)_2C{=}CH_2$ (dppE); yield 90%. Calc. for $C_{54}H_{47}Cl_4O_2P_4Re_2$: C, 47.48; H, 3.47. Found: C, 47.21; H, 3.58%.

α-$Re_2Cl_4(dppe)_2$ 12 and *trans*-$[ReO_2(dppe)_2]Cl$ 13. A procedure similar to that described for the preparation of **9**, employing 130 mg (0.12 mmol) of **2** and 104 mg (0.26 mmol) of $Ph_2P(CH_2)_2PPh_2$ (dppe), afforded a green solid that was shown by cyclic voltammetry to be a mixture of products. The reaction residue was dissolved in dichloromethane and diethyl ether allowed to slowly diffuse into this solution; this gave a separable mixture of green and yellow crystals. The green product (103 mg) was shown to be α-$Re_2Cl_4(dppe)_2$ **12** on the basis of its spectroscopic and electrochemical properties,[11] while the yellow crystals (35 mg) were found to be *trans*-$[ReO_2(dppe)_2]Cl$ **13** by a single crystal X-ray structure determination.

$Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4$ 14 and $[(C_6H_4OMe\text{-}p)_3PMe]_2\text{-}Re_2Cl_8$ 15. A sample of $P(C_6H_4OMe\text{-}p)_3$ (184 mg, 0.522 mmol) was heated in methanol (20 mL) until it had completely dissolved. A quantity of *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ **1** (113 mg, 0.169 mmol) was then added and the resulting mixture refluxed for 3 days. The crop of red crystalline **14** was filtered off, washed with a small volume of fresh methanol and diethyl ether and dried; yield 67 mg (48%). Calc. for $C_{86}H_{92}Cl_4O_{18}P_4Re_4$ (*i.e.* **14**·2MeOH): C, 42.61; H, 3.83; Cl, 5.85. Found: C, 41.38; H, 3.63; Cl, 6.35%. A suitable single crystal of composition **14**·2MeOH was selected from this batch for an X-ray structure analysis.

The filtrate from the above reaction was collected and the solvent removed under reduced pressure to afford an oily residue. The addition of diethyl ether (10 mL) gave a green solid which was filtered off, washed several times with this same solvent, redissolved in dichloromethane (3 mL) and diethyl ether allowed to diffuse slowly into this solution. After a period of two weeks, X-ray quality crystals of **15** were obtained: yield 32 mg (41%). Calc. for $C_{44}H_{48}Cl_8O_6P_2Re_2$: C, 38.00; H, 3.48. Found: C, 37.84; H, 3.42%. The identity of this product was confirmed by X-ray crystallography.

An alternative synthesis of the tetrarhenium complex **14** involved the reaction between $Re_2(\mu\text{-}O_2CMe)Cl_4[P(C_6H_4OMe\text{-}p)_3]_2$ **4** (116 mg, 0.091 mmol) and $LiOH{\cdot}2H_2O$ (10 mg, 0.24 mmol) in refluxing methanol (20 mL) for 2 days. The red microcrystalline product **14** was filtered off, washed with methanol (3 × 5 mL) and diethyl ether (2 × 5 mL) and dried under a vacuum; yield 28 mg (26%).

$Re_4(\mu\text{-}O)_4Cl_4(PPh_3)_4$ 16. A procedure similar to the alternative synthesis of **14** described above was used. The reaction between $Re_2(\mu\text{-}O_2CMe)Cl_4(PPh_3)_2$ **2** (130 mg, 0.12 mmol) and $LiOH{\cdot}2H_2O$ (12 mg, 0.28 mmol) afforded a small quantity of **16**; yield 21 mg (18%). Calc. for $C_{72}H_{60}Cl_4O_4P_4Re_4$: C, 43.24; H, 3.02. Found: C, 41.87; H, 3.47%.

$Re_4(\mu\text{-}O)_4Cl_4(PMe_2Ph)_4$ 17. A dichloromethane solution (15 mL) of **14** (60 mg, 0.025 mmol) was treated with 0.1 mL of PMe_2Ph and the mixture stirred for 8 h at room temperature. The orange solid was filtered off and washed with dichloromethane (2 × 5 mL); yield 29 mg (77%). The identity of **17** was based upon its electrochemical and IR spectral properties. A satisfactory microanalysis could not be obtained.

X-Ray crystallography

Crystals of the complexes $Re_2(\mu\text{-}O_2CMe)Cl_4(PBz)_2$ **3**, *mer-trans*-$ReOCl_3(PCy_3)_2$ **8**, *trans*-$[ReO_2(dppe)_2]Cl{\cdot}3CH_2Cl_2$ **13**, $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4{\cdot}2MeOH$ **14** and $[(C_6H_4OMe\text{-}p)_3PMe]_2Re_2Cl_8$ **15** were obtained as described in the appropriate sections detailing their syntheses.

The data were collected at 173 (±1) K for the crystals of **3**, **13** and **15**, 193 (± 1) K for **8**, and 296 (± 1) K for **14**. All measurements were carried out on a Nonius KappaCCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Crystal data and the relevant experimental details on data collection and refinement are given in Table 1. Lorentz and polarization corrections were applied to the data sets. The structures of **3**, **8**, **13** and **15** were solved using the structure solution program PATTY in DIRDIF92[12] while the structure of **14** was solved by direct methods using SIR97.[13] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with $U(H) = 1.3U_{eq}(C)$. An empirical absorption correction using SCALEPACK[14] was applied in all cases except **3** and **14** for which DELABS in PLATON[15] was used. The final refinements were performed by the use of the program SHELXL-97.[16] All non-hydrogen atoms were refined with anisotropic thermal parameters with the exception of atom O(1) of **8**.

In the crystal structure of **8**, the molecule sits on an inversion center and like its analogue *mer-trans*-$ReOCl_3(PMe_3)_2$[17] shows an orientational disorder involving the sets of *trans* O and Cl

Table 1 Crystallographic data for $Re_2(\mu\text{-}O_2CMe)Cl_4(PBz_3)_2$ **3**, *mer-trans*-$ReOCl_3(PCy_3)_2$ **8**, *trans*-$[ReO_2(dppe)_2]Cl\cdot 3CH_2Cl_2$ **13**, $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4\cdot 2MeOH$ **14** and $[(C_6H_4OMe\text{-}p)_3PMe]_2Re_2Cl_8$ **15**

	3	8	13	14	15
Formula	$C_{44}H_{45}Cl_4O_2P_2Re_2$	$C_{36}H_{66}Cl_3OP_2Re$	$C_{55}H_{54}Cl_7O_2P_4Re$	$C_{86}H_{92}Cl_4O_{18}P_4Re_4$	$C_{44}H_{48}Cl_8O_6P_2Re_2$
Formula weight	1182.01	869.43	1305.31	2424.19	1390.86
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	9.8942(5)	9.9534(5)	9.4968(3)	13.9995(7)	16.5256(3)
b/Å	13.5625(9)	10.2535(5)	12.9135(5)	23.5126(7)	18.6675(4)
c/Å	18.4975(12)	10.9010(5)	24.8886(10)	14.3633(7)	33.0129(4)
α/°	69.437(3)	114.311(3)	97.9692(19)	90.00	90.00
β/°	76.902(4)	107.608(3)	91.753(2)	114.1998(16)	100.5122(11)
γ/°	69.586(3)	93.089(3)	110.195(2)	90.00	90.00
Z	2	1	2	2	8
V/Å^3	2162.7(3)	945.76(19)	2826.8(4)	4312.4(6)	10013.3(6)
μ(Mo-Kα)/mm^{-1}	6.027	3.579	2.662	5.93	5.436
Reflections collected	17466	7186	19987	35082	75534
independent	9088	3917	11859	10854	15630
observed [$I > 2\sigma(I)$]	6436	3881	7006	7175	8019
No. of variables	489	201	625	550	1171
$R(F_o)^a$	0.041	0.043	0.061	0.062	0.053
$R_w(F_o^2)^b$	0.099	0.114	0.123	0.104	0.122
GOF	0.998	1.102	1.090	1.138	0.946

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. ^{b} $R_w = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

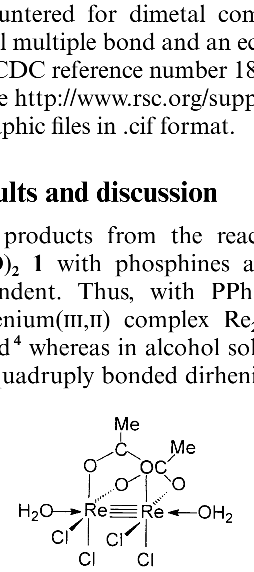
half atoms [*i.e.* O(1), Cl(1) and O(1)′, Cl(1)′]; these atoms are resolved in the refinement. In the refinement of **13**, the asymmetric unit was found to contain two independent Re cations located at inversion centers each at 0.5 occupancy, and three full molecules of lattice CH_2Cl_2. During the course of the refinement of the tetrarhenium complex **14**, the Re–Re units of the rectangular cluster were found to be disordered such that there are two incompletely occupied, approximately orthogonal sets, which to a first approximation share the same set of ligand atoms. The multiplicities of the major and minor forms are 0.949 and 0.051, respectively. This result is similar to that found during the solution of the structure of $(Bu^n{}_4N)_2[Re_4Cl_8(\mu\text{-}O)_2(\mu\text{-}OMe)_2]$[18] in which a disordered structure of this same type was encountered; in this instance the multiplicities were 0.96 and 0.04, respectively. Two molecules of methanol per tetrarhenium unit were found in the lattice. The refinement of the structure of **15** showed the presence of two pairs of independent cations and anions in the asymmetric unit. For each of the $[Re_2Cl_8]^{2-}$ anions, two sets of fractional Re–Re units were found to be present such that within each anion these units were perpendicular to one another and shared the same set of Cl ligands. These pairs refined satisfactorily to occupancies for Re(1A)/Re(2A) and Re(1B)/Re(2B) of 0.473 and 0.027, respectively, and for Re(3A)/Re(4A) and Re(3B)/Re(4B) of 0.432 and 0.068, respectively. This type of disorder is commonly encountered for dimetal complexes which contain a metal–metal multiple bond and an eclipsed M_2L_8 geometry.[19]

CCDC reference number 186/2199.

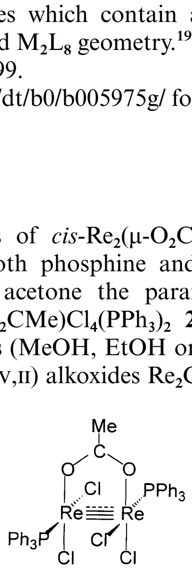
See http://www.rsc.org/suppdata/dt/b0/b005975g/ for crystallographic files in .cif format.

Results and discussion

The products from the reactions of *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ **1** with phosphines are both phosphine and solvent dependent. Thus, with PPh_3 in acetone the paramagnetic dirhenium(III,II) complex $Re_2(\mu\text{-}O_2CMe)Cl_4(PPh_3)_2$ **2** is produced[4] whereas in alcohol solvents (MeOH, EtOH or Pr^{n}OH) the quadruply bonded dirhenium(IV,II) alkoxides $Re_2Cl_4(OR)_2(PPh_3)_2$ are formed.[2,3] In the present study we have established that the coordinatively unsaturated complex **2** can be used as a convenient precursor to complexes of the types $Re_2(\mu\text{-}O_2CMe)Cl_4(PR_3)_2$ (PR_3 = monodentate tertiary phosphine) and $Re_2(\mu\text{-}O_2CMe)Cl_4(PP)_2$ (PP = bridging bidentate phosphine). These phosphine substitution reactions proceed in high yield when carried out in dichloromethane at room temperature. The monodentate phosphines PBz_3 (Bz = CH_2Ph) and $P(C_6H_4OMe\text{-}p)_3$ produced $Re_2(\mu\text{-}O_2CMe)Cl_4(PBz_3)_2$ **3** and $Re_2(\mu\text{-}O_2CMe)Cl_4[P(C_6H_4OMe\text{-}p)_3]_2$ **4**, respectively [Scheme 1(a)].



1



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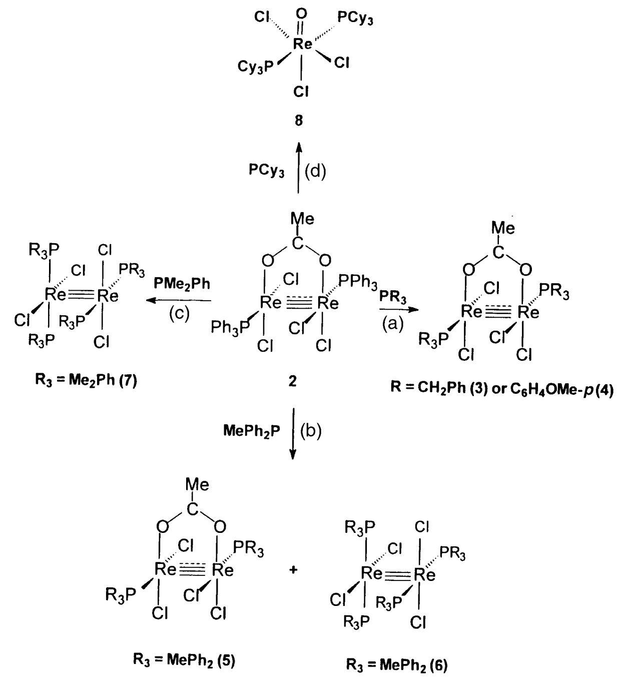

Scheme 1 Products from the reactions of $Re_2(\mu\text{-}O_2CMe)Cl_4(PPh_3)_2$ with monodentate phosphines.

Interestingly, **3** had been reported previously as the product when *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ **1** is reacted with PBz_3 in refluxing methanol,[3] while the use of methanol as the solvent in the reaction of **1** with $P(C_6H_4OMe\text{-}p)_3$ affords the tetranuclear complex **14** (*vide infra*). The properties of **3** isolated herein and those of samples reported previously are the same.[3] A single crystal X-ray structure determination of **3** confirms its close

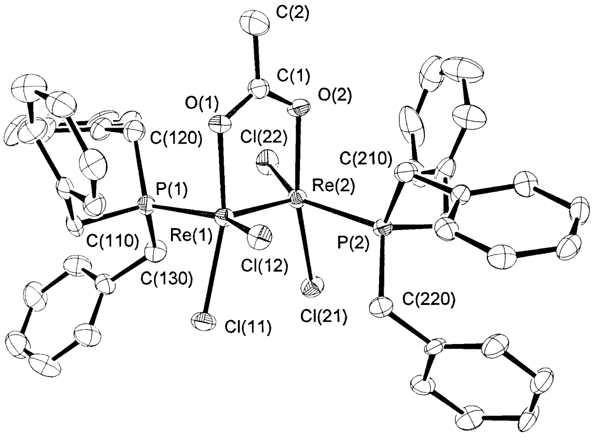

Fig. 1 ORTEP[20] representation of the structure of the dirhenium(III,II) complex $\mathrm{Re_2(\mu\text{-}O_2CMe)Cl_4(PBz_3)_2}$ **3**. Thermal ellipsoids are drawn at the 50% probability level.

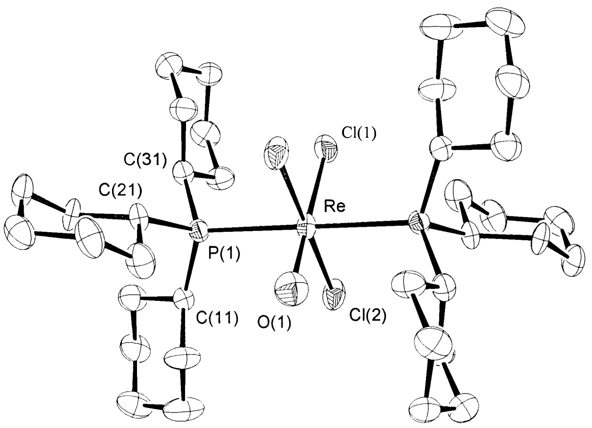

Fig. 2 ORTEP[20] representation of the structure of *mer-trans*-$\mathrm{ReOCl_3(PCy_3)_2}$ **8**. Only one-half of the orientational disorder involving the *trans* O and Cl ligands [O(1) and Cl(1)] is shown. Thermal ellipsoids are drawn at the 50% probability level.

Table 2 Important bond distances (Å) and angles (°) for $\mathrm{Re_2(\mu\text{-}O_2CMe)Cl_4(PBz_3)_2}$ **3**[a]

Re(1)–Re(2)	2.2166(4)	Re(2)–O(2)	2.106(5)
Re(1)–O(1)	2.076(5)	Re(2)–Cl(21)	2.3508(18)
Re(1)–Cl(11)	2.3462(18)	Re(2)–Cl(22)	2.3666(19)
Re(1)–Cl(12)	2.3730(19)	Re(2)–P(2)	2.4036(19)
Re(1)–P(1)	2.428(2)		
O(1)–Re(1)–Re(2)	90.61(15)	O(2)–Re(2)–Re(1)	89.70(16)
O(1)–Re(1)–Cl(11)	162.80(16)	O(2)–Re(2)–Cl(21)	165.74(16)
Re(2)–Re(1)–Cl(11)	106.53(5)	Re(1)–Re(2)–Cl(21)	104.54(5)
O(1)–Re(1)–Cl(12)	86.87(15)	O(2)–Re(2)–Cl(22)	84.91(16)
Re(2)–Re(1)–Cl(12)	114.60(5)	Re(1)–Re(2)–Cl(22)	117.28(5)
Cl(11)–Re(1)–Cl(12)	87.21(7)	Cl(21)–Re(2)–Cl(22)	87.79(7)
O(1)–Re(1)–P(1)	91.77(15)	O(2)–Re(2)–P(2)	94.41(15)
Re(2)–Re(1)–P(1)	94.57(5)	Re(1)–Re(2)–P(2)	96.12(5)
Cl(11)–Re(1)–P(1)	85.58(7)	Cl(21)–Re(2)–P(2)	84.97(7)
Cl(12)–Re(1)–P(1)	150.80(7)	Cl(22)–Re(2)–P(2)	146.56(7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3 Important bond distances (Å) and angles (°) for *mer-trans*-$\mathrm{ReOCl_3(PCy_3)_2}$ **8**[a]

Re–O(1)	1.699(14)	Re–Cl(2)	2.3822(16)
Re–Cl(1)	2.282(4)	Re–P(1)	2.5322(14)
O(1)–Re–Cl(1)	179.6(5)	Cl(1)–Re–Cl(2)	90.76(12)
O(1)–Re–Cl(2)	91.0(5)	P(1)–Re–Cl(1)	88.03(9)
O(1)–Re–Cl(2)	89.0(5)	P(1)–Re–O(1)	91.7(5)
Cl(1)–Re–Cl(2)	89.24(12)	P(1)–Re–Cl(2)	90.68(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

structural relationship to the analogous $\mathrm{PPh_3}$ complex **2**.[4] An ORTEP[20] representation of the structure of **3** is shown in Fig. 1 and important structural parameters are given in Table 2.

The structure of **3** resembles closely that of $\mathrm{Re_2(\mu\text{-}O_2CMe)Cl_4(PPh_3)_2}$. The Re–Re bond distance of 2.2166(4) Å is identical to that of 2.2165(7) Å in its $\mathrm{PPh_3}$ analogue, while the Re–Cl, Re–O and Re–P distances fall in very similar ranges for these two complexes. The rotational geometry is close to being fully eclipsed, with values for the torsional angles O(1)–Re(1)–Re(2)–O(2), Cl(11)–Re(1)–Re(2)–Cl(21), P(1)–Re(1)–Re(2)–Cl(22) and Cl(12)–Re(1)–Re(2)–P(2) of 3.8(2), 3.2(1), 11.5(1) and 11.4(1)°, respectively.

The properties of **3** and **4** are very similar. The cyclic voltammograms of solutions of **4** in 0.1 M $\mathrm{Bu^n{}_4NPF_6}$–$\mathrm{CH_2Cl_2}$ reveal a one-electron oxidation at $E_{1/2} = +0.47$ V and a one-electron reduction at $E_{1/2} = -0.67$ V *vs.* Ag–AgCl; these processes have ΔE_p values ($E_{p,a} - E_{p,c}$) of 60–65 mV at $v = 200$ mV s^{-1}. This behavior resembles closely the CVs of **3**[3] and its $\mathrm{PPh_3}$ and $\mathrm{PPh_2py}$ analogues.[4] Like these paramagnetic $[\mathrm{Re_2}]^{5+}$ complexes, **4** shows only very broadened peaks in its ^1H NMR spectrum and no resonances in its ^{31}P NMR spectrum.

When **2** is reacted with phosphines that are less sterically demanding than $\mathrm{PBz_3}$ and $\mathrm{P(C_6H_4OMe\text{-}}p)_3$, we observed behavior different than just substitution of the $\mathrm{PPh_3}$ ligands of **2**. With $\mathrm{PMePh_2}$, which has a similar basicity to $\mathrm{P(C_6H_4\text{-}OMe\text{-}}p)_3$ but possesses a smaller cone angle (136 *vs.* 145°), a separable mixture of $\mathrm{Re_2(\mu\text{-}O_2CMe)Cl_4(PMePh_2)_2}$ **5** and $\mathrm{Re_2Cl_4(PMePh_2)_4}$ **6** was obtained {both complexes were unambiguously identified by their cyclic voltammetric properties) [Scheme 1(b)]}. Solutions of the red paramagnetic complex **5** in 0.1 M $\mathrm{Bu^n{}_4NPF_6}$–$\mathrm{CH_2Cl_2}$ showed reversible processes at $E_{1/2}(\mathrm{ox}) = +0.48$ V and $E_{1/2}(\mathrm{red}) = -0.65$ V *vs.* Ag–AgCl in the CV, with ΔE_p values of 70 mV at $v = 200$ mV s^{-1}. These characteristics are similar to those displayed in the CVs of **3** and **4** (*vide supra*). The dirhenium(II) complex **6** is a known compound that has been characterized previously.[7] The addition of an excess of $\mathrm{PMePh_2}$ to a dichloromethane solution of **5** led to mixtures of **5** and **6** as monitored by CV. Accordingly, it is reasonable to conclude that **5** is the intermediate in the conversion of **2** to **6**. For the reaction of **2** with the phosphine $\mathrm{PMe_2Ph}$, which is more basic than $\mathrm{PMePh_2}$ and has a significantly smaller cone angle, the dirhenium(III,II) intermediate $\mathrm{Re_2(\mu\text{-}O_2CMe)Cl_4(PMe_2Ph)_2}$ could not be isolated; instead, the dirhenium(II) complex $\mathrm{Re_2Cl_4(PMe_2Ph)_4}$ **7** was obtained in almost quantitative yield [Scheme 1(c)]. This behavior reflects the greater propensity of the $[\mathrm{Re_2}]^{5+}$ core to be reduced to $[\mathrm{Re_2}]^{4+}$ in the presence of $\mathrm{PMe_2Ph}$, a phosphine which is also less sterically demanding than the phosphines which afford stable $\mathrm{Re_2(\mu\text{-}O_2CMe)Cl_4(PR_3)_2}$ compounds.

The reaction of **2** with $\mathrm{PCy_3}$, which is the most basic of the phosphines we studied and also possesses the largest cone angle (170°), resulted in the substitution of the $\mathrm{PPh_3}$ ligands and also the cleavage of the Re–Re multiple bond. This led to the product *mer-trans*-$\mathrm{ReOCl_3(PCy_3)_2}$ **8** (*ca.* 70% yield) along with some unidentified Re-containing species [Scheme 1(d)]. The source of oxygen is presumably small amounts of adventitious O_2 and/or H_2O. Complex **8** possesses a ν(Re=O) mode in its IR spectrum (KBr disc) at 971 cm^{-1} and a singlet in its $^{31}P\{^1H\}$ NMR spectrum (recorded in $\mathrm{CDCl_3}$) at δ −26.0. The CV of **8** recorded on a solution in 0.1 M $\mathrm{Bu^n{}_4NPF_6}$–$\mathrm{CH_2Cl_2}$ shows irreversible processes at $E_{p,c} = +1.39$ V and $E_{p,a} = -0.97$ *vs.* Ag–AgCl with $v = 200$ mV s^{-1}. The identity of this green complex was confirmed by a single crystal X-ray structure determination. The ORTEP[20] representation of **8** is shown in Fig. 2 and important structural parameters are listed in Table 3.

As described in the Experimental section, the *mer-trans*-$\mathrm{ReOCl_3(PCy_3)_2}$ molecule shows an orientational disorder in the crystal similar to that found in *mer-trans*-$ReOCl_3(PMe_3)_2$,[17] so that there are two sets of *trans* O and Cl half atoms; only one of these sets is shown in Fig. 2. In spite of this disorder the pairs of disordered atoms O(1)/Cl(1) can be resolved; the Re–O distance in **8** [1.699(14) Å] is similar to that observed in *mer-trans*-$ReOCl_3(PPh_3)_2$[21] and *mer-trans*-$ReOCl_3(PEt_2Ph)_2$.[22]

The substitutional lability of the PPh_3 ligands of **2** towards bridging bidentate ligands is illustrated by the high yield conversion of **2** (⩾ 90% yield) to *trans*-$Re_2(\mu\text{-}O_2CMe)Cl_4(\mu\text{-}PP)_2$, where PP = dppm (**9**), dppa (**10**) or dppE (**11**). Compounds **9** and **10** have been prepared previously,[9,10] but the dppE analogue **11** is new. The CV of a solution of **11** in 0.1 M $Bu^n{}_4NPF_6$–CH_2Cl_2 shows processes with $E_{1/2}(ox) = +0.45$ V ($\Delta E_p = 60$ mV) and $E_{p,c} = -0.54$ V *vs.* Ag–AgCl, which are very similar to the CVs reported for **9** and **10**.[9,10] An alternative synthesis of **11**, utilizing the reaction between *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ **1** and dppE, was unsuccessful since this afforded $Re_2Cl_4(\mu\text{-dppE})_2$.[23] However, an analogous strategy works well for the preparation of **9** and **10**.[9,10]

The conformational requirements of two bridging $Ph_2PCH_2CH_2PPh_2$ (dppe) ligands in a [Re(μ-dppe)$_2$Re] unit favors a staggered rotational geometry,[24] thereby destabilizing a complex such as $Re_2(\mu\text{-}O_2CMe)Cl_4(\mu\text{-dppe})_2$, in which the acetate-containing [Re(μ-O_2CMe)Re] unit should be approximately planar. Accordingly, in the reaction between **2** and dppe, although both PPh $_3$ ligands are displaced, the reaction is quite complicated and a mixture of the triply bonded dirhenium(II) complex α-$Re_2Cl_4(dppe)_2$ **12**, which contains *chelating* dppe ligands,[11] and *trans*-$[ReO_2(dppe)_2]Cl$ **13** was obtained. The formation of **12** derives formally from the reductive elimination of $MeCO_2^{\bullet}$ from the unstable intermediate {$Re_2(\mu\text{-}O_2CMe)Cl_4(\mu\text{-dppe})_2$}. Compound **13** probably arises from a competing disruption of the Re–Re multiple bond and the reaction of a coordinatively unsaturated intermediate with adventitious O_2. However, an alternative oxygen source, such as the acetate ligands, cannot be ruled out. Compound **12** does not convert to **13** under our experimental conditions. The structure of the $[ReO_2(dppe)_2]^+$ cation present in **13** was confirmed by X-ray crystallography, but since this structure is essentially identical to that present in the previously characterized $[ReO_4]^-$, $[I]^-$ and $[PF_6]^-$ salts of this cation,[25,26] further discussion of the structure is unnecessary (see supplementary material for further details).

In addition to the phosphine ligand substitution reactions of **2** that lead to complexes of the types $Re_2(\mu\text{-}O_2CMe)Cl_4(PR_3)_2$ and $Re_2(\mu\text{-}O_2CMe)Cl_4(PP)_2$ (*vide supra*), and reactions (with PCy_3 and dppe) which can result in disruption of the Re–Re multiple bond, a third type of reaction was encountered in the present study. This involved non-redox transformations of the type $[Re_2]^{6+} \longrightarrow [Re_4]^{12+}$.

We had described previously how the $[Re_2]^{5+}$ core complex $Re_2(\mu\text{-}O_2CMe)Cl_4(PBz_3)_2$ **3** can be prepared both through the reduction of *cis*-$Re_2(O_2CMe)_2Cl_4(H_2O)_2$ **1** by PBz_3 (see ref. 3) and the non-redox substitution reaction of **2** with PBz_3 (this work). While $P(C_6H_4OMe\text{-}p)_3$ reacts with **2** to give $Re_2(\mu\text{-}O_2CMe)Cl_4[P(C_6H_4OMe\text{-}p)_3]_2$ **4**, which is structurally analogous to **3**, the reaction of this phosphine with **1** in refluxing methanol affords the novel tetranuclear complex $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4$ **14**. This reaction course not only differs from that between **1** and PBz_3 (*vide supra*) but also from those involving the triaryl phosphines PAr_3 (Ar = Ph, C_6H_4Me-*p*, C_6H_4Me-*m* and C_6H_4Cl-*p*) all of which produce the quadruply bonded 'mixed-valence' dirhenium (IV,II) complexes $Cl_2(MeO)_2ReReCl_2(PAr_3)_2$ under these same conditions.[2,3] For reasons that are not entirely clear, the phosphine $P(C_6H_4OMe\text{-}p)_3$ is unique in affording this unusual tetranuclear rhenium cluster by this procedure. Complex **14** is the first *symmetrical* tetrarheniumcyclodiyne type cluster containing phosphine ligands. While the dimerization of quadruply bonded dimetal complexes is well established in Mo and W chemistry,[27,28] it has rarely been encountered in Re chemistry.[19,29]

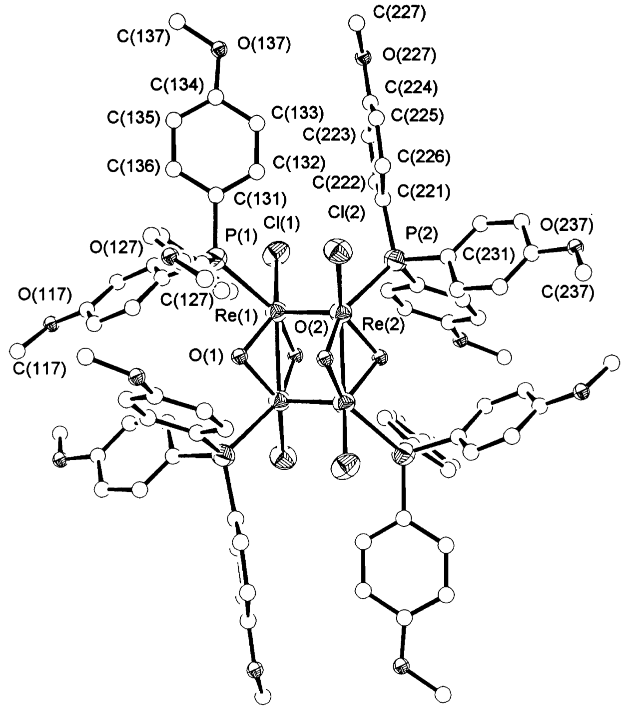

Fig. 3 ORTEP[20] representation of the structure of the tetranuclear cluster $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4$ in crystals of **14**·2MeOH. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the phosphine ligands which are circles of arbitrary radii. Unlabeled atoms are related to the labeled atoms by an inversion center. The four Re atoms shown are those of the primary form of a disorder in which a secondary and very minor form, sharing the same ligand atoms, is in a plane orthogonal to the primary form.

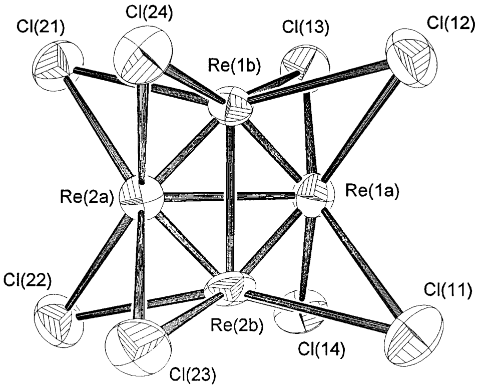

Fig. 4 ORTEP[20] representation of the structure of the $[Re_2Cl_8]^{2-}$ anion present in the crystals of **15** showing one of the two crystallographically independent anions with a two-fold orientational disorder of the Re–Re unit [Re(1a)/Re(2a) and Re(1b)/Re(2b)]. Thermal ellipsoids are drawn at the 50% probability level.

Compound **14** could be reproducibly obtained in yields that approached 50%, so that a considerable quantity of Re was originally not accounted for.[5] However, work-up of the reaction filtrate yielded the phosphonium salt $[(C_6H_4OMe\text{-}p)_3PMe]_2Re_2Cl_8$ **15** in isolated yields exceeding 40%, thereby accounting for most of the Re. Accordingly, it is reasonable to propose the following reaction stoichiometry (where Ar = C_6H_4OMe-*p*):

$$3\ \underset{\mathbf{1}}{cis\text{-}Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2} + 6\ PAr_3 + 4MeOH$$

$$\longrightarrow \underset{\mathbf{14}}{Re_4(\mu\text{-}O)_4Cl_4(PAr_3)_4} + \underset{\mathbf{15}}{(Ar_3PMe)_2Re_2Cl_8} +$$

$$2MeCO_2Me + 8H_2O$$

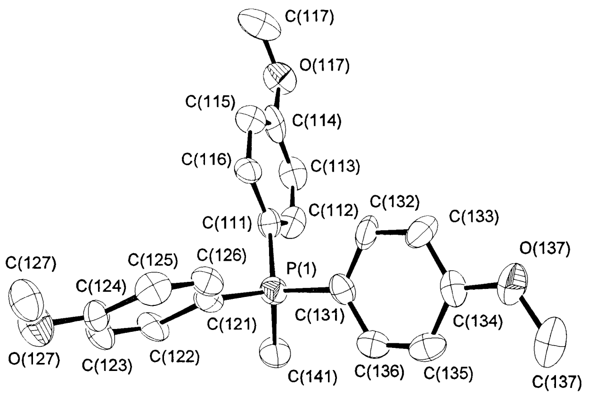

Fig. 5 ORTEP[20] representation of one of the two crystallographically independent $[(C_6H_4OMe\text{-}p)_3PMe]^+$ cations present in the crystals of **15**. Thermal ellipsoids are drawn at the 50% probability level.

Table 4 Important bond distances (Å) and bond angles (°) for $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4{\cdot}2MeOH$ **14**[a,b]

Re(1)–Re(2)	2.2726(5)	Re(2)–P(2)	2.524(2)
Re(1)–Re(2)′	2.5388(5)	Re(1)–O(1)	1.943(5)
Re(1)–Cl(1)	2.350(2)	Re(1)–O(2)	1.995(5)
Re(2)–Cl(2)	2.359(2)	Re(2)–O(1)	1.960(5)
Re(1)–P(1)	2.521(2)	Re(2)–O(2)	1.988(5)
Re(1)–Re(2)–Re(1)′	90.099(16)	O(1)–Re(2)–Cl(2)	146.77(17)
Re(2)′–Re(1)–Re(2)	89.901(16)	O(2)–Re(2)–Cl(2)	87.30(15)
Re(2)–Re(1)–O(1)	99.50(17)	O(1)–Re(2)–P(2)	77.66(15)
Re(2)–Re(1)–O(2)	101.77(17)	O(2)–Re(2)–P(2)	152.26(18)
O(1)–Re(1)–Cl(1)	146.48(17)	Cl(2)–Re(2)–P(2)	84.41(7)
O(2)–Re(1)–Cl(1)	87.12(16)	O(1)–Re(1)–O(2)	96.0(2)
O(1)–Re(1)–P(1)	77.08(15)	O(1)–Re(2)–O(2)	95.7(2)
O(2)–Re(1)–P(1)	151.08(18)	Re(1)–O(1)–Re(2)′	81.15(19)
Cl(1)–Re(1)–P(1)	84.16(7)	Re(1)–O(2)–Re(2)′	79.19(19)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] The four Re atoms shown in Fig. 4 are those of the primary form of a disorder in which a secondary form [atoms Re(3) and Re(4)] appears to share the same ligand atoms and is in a plane approximately orthogonal to the primary form. The distances Re(3)–Re(4) and Re(3)–Re(4)′ are 2.275(8) and 2.528(8) Å, respectively, and the major and minor forms of this disorder have occupancies of 94.9 and 5.1%, respectively.

The origin of the oxygen that is incorporated into the tetranuclear cluster **14** is most likely the methanol solvent, based on the observations by Cotton and co-workers[18,29] who isolated the mixed oxide/methoxide species $[Re_4(\mu\text{-}O)_2(\mu\text{-}OMe)_2Cl_8]^{2-}$ and $[Re_4(\mu\text{-}O)_2(\mu\text{-}OMe)(\mu\text{-}Cl)Cl_8]^{2-}$.

The structures of **14** and **15** were confirmed by X-ray crystallography. The ORTEP[20] representations of the Re containing species are given in Figs. 3 and 4, and a representation of the structure of the cation that is present in **15** is shown in Fig. 5. Important bond distances and angles are listed in Tables 4 and 5. The structure of the tetranuclear complex **14** (Fig. 3) consists of a rectangular cluster of metal atoms with two Re≡Re bonds linked by two Re–Re single bonds, each of which is bridged by a pair of O^{2-} ligands. The bare Re_4 cluster arises formally from the [2 + 2] cycloaddition of two Re≡Re units (originating from two molecules of **1**) by loss of their *δ* components. The cluster possesses a crystallographic inversion center and Re≡Re and Re–Re bond distances of 2.2726(5) and 2.5388(5) Å (Table 4), respectively, which are very similar in magnitude to the analogous distances encountered in salts of the $[Re_4(\mu\text{-}O)_2(\mu\text{-}OMe)_2Cl_8]^{2-}$, $[Re_4(\mu\text{-}O)_2(\mu\text{-}OMe)(\mu\text{-}Cl)Cl_8]^{2-}$ and $[Re_4(\mu\text{-}O)_2(\mu\text{-}Cl)_2Cl_8]^{2-}$ anions that have been reported previously by Cotton and co-workers.[18,29] The structural identification of **14** is noteworthy in that it is the first *neutral* tetrarheniumcyclodiyne type cluster possessing the $[Re_4(\mu\text{-}O)_4]^{4+}$ core, and the first to contain phosphine ligands. This cluster represents an extreme in the chemistry of metal rectangles that range from those in which there are four separate ligand-bridged metal centers[32] to those with pairs of ligand-bridged multiply bonded M_2 units which may or may not be linked by M–M bonds within the rectangular cluster.[33]

For **15**, the presence of the $[(C_6H_4OMe\text{-}p)_3PMe]^+$ cation was confirmed, and the $[Re_2Cl_8]^{2-}$ anion was found to have a twofold orientational disorder of the Re–Re unit within the cube of eight Cl ligands. Two sets of crystallographically independent cations and anions were present so that the complete set of four Re_2 units, labeled Re(1a)/Re(2a), Re(1b)/Re(2b), Re(3a)/Re(4a) and Re(3b)/Re(4b), have occupancies of 47.3, 2.7, 43.2 and 6.8%, respectively. The Re–Re distances for the two major pairs [Re(1a)/Re(2a) and Re(3a)/Re(4a)] are 2.2231(6) and 2.2157(7) Å respectively; these values are typical for the quadruply bonded $[Re_2Cl_8]^{2-}$ anion,[30] and are similar to those encountered in other salts possessing this type of crystallo-

Table 5 Important bond distances (Å) and bond angles (°) for $[(C_6H_4OMe\text{-}p)_3PMe]_2Re_2Cl_8$ **15**[a,b]

Re(1A)–Re(2A)	2.2231(6)	Re(2A)–Cl(22)	2.326(3)	Re(2B)–Cl(11)	2.339(8)	P(1)–C(131)	1.800(11)
Re(1A)–Cl(11)	2.319(3)	Re(2A)–Cl(24)	2.330(3)	Re(2B)–Cl(14)	2.345(8)	P(1)–C(141)	1.808(10)[c]
Re(1A)–Cl(12)	2.320(3)	Re(1B)–Re(2B)	2.207(11)	Re(2B)–Cl(23)	2.351(8)	P(2)–C(211)	1.770(11)
Re(1A)–Cl(14)	2.325(3)	Re(1B)–Cl(12)	2.314(9)	Re(2B)–Cl(22)	2.383(9)	P(2)–C(221)	1.778(13)
Re(1A)–Cl(13)	2.339(3)	Re(1B)–Cl(24)	2.332(7)	P(1)–C(121)	1.784(12)	P(2)–C(231)	1.783(12)
Re(2A)–Cl(21)	2.324(3)	Re(1B)–Cl(13)	2.388(7)	P(1)–C(111)	1.784(11)	P(2)–C(241)	1.783(10)[c]
Re(2A)–Cl(23)	2.326(3)	Re(1B)–Cl(21)	2.397(8)				
Re(2A)–Re(1A)–Cl(11)	104.17(8)	Cl(23)–Re(2A)–Cl(22)	86.74(11)	Re(1B)–Re(2B)–Cl(11)	101.4(4)	Re(2A)–Cl(22)–Re(2B)	39.3(2)
Re(2A)–Re(1A)–Cl(12)	103.62(7)	Re(1A)–Re(2A)–Cl(24)	102.33(7)	Re(1B)–Re(2B)–Cl(14)	101.6(3)	Re(2A)–Cl(23)–Re(2B)	39.56(19)
Cl(11)–Re(1A)–Cl(12)	87.69(11)	Cl(21)–Re(2A)–Cl(24)	86.79(10)	Cl(11)–Re(2B)–Cl(14)	86.1(3)	Re(2A)–Cl(24)–Re(1B)	39.3(2)
Re(2A)–Re(1A)–Cl(14)	102.65(7)	Cl(23)–Re(2A)–Cl(24)	86.73(10)	Re(1B)–Re(2B)–Cl(23)	101.7(4)	C(121)–P(1)–C(111)	111.7(5)
Cl(11)–Re(1A)–Cl(14)	87.04(10)	Cl(22)–Re(2A)–Cl(24)	153.50(10)	Cl(11)–Re(2B)–Cl(23)	91.2(3)	C(121)–P(1)–C(131)	107.9(5)
Cl(12)–Re(1A)–Cl(14)	153.71(10)	Re(2B)–Re(1B)–Cl(12)	103.6(4)	Cl(14)–Re(2B)–Cl(23)	156.7(4)	C(111)–P(1)–C(131)	108.6(5)
Re(2A)–Re(1A)–Cl(13)	104.18(7)	Re(2B)–Re(1B)–Cl(24)	102.7(4)	Re(1B)–Re(2B)–Cl(22)	101.8(4)	C(121)–P(1)–C(141)	108.1(6)
Cl(11)–Re(1A)–Cl(13)	151.64(10)	Cl(12)–Re(1B)–Cl(24)	89.4(3)	Cl(11)–Re(2B)–Cl(22)	156.8(4)	C(111)–P(1)–C(141)	110.3(5)
Cl(12)–Re(1A)–Cl(13)	85.87(11)	Re(2B)–Re(1B)–Cl(13)	102.6(4)	Cl(14)–Re(2B)–Cl(22)	88.6(3)	C(131)–P(1)–C(141)	110.3(5)
Cl(14)–Re(1A)–Cl(13)	86.64(10)	Cl(12)–Re(1B)–Cl(13)	84.9(3)	Cl(23)–Re(2B)–Cl(22)	84.9(3)	C(211)–P(2)–C(221)	109.6(5)
Re(1A)–Re(2A)–Cl(21)	104.20(7)	Cl(24)–Re(1B)–Cl(13)	154.6(4)	Re(1A)–Cl(11)–Re(2B)	39.5(2)	C(211)–P(2)–C(231)	112.9(6)
Re(1A)–Re(2A)–Cl(23)	103.90(7)	Re(2B)–Re(1B)–Cl(21)	102.2(4)	Re(1B)–Cl(12)–Re(1A)	38.86(19)	C(221)–P(2)–C(231)	107.2(5)
Cl(21)–Re(2A)–Cl(23)	151.89(10)	Cl(12)–Re(1B)–Cl(21)	154.2(4)	Re(1A)–Cl(13)–Re(1B)	38.05(19)	C(211)–P(2)–C(241)	108.5(5)
Re(1A)–Re(2A)–Cl(22)	104.17(7)	Cl(24)–Re(1B)–Cl(21)	85.1(3)	Re(1A)–Cl(14)–Re(2B)	39.4(2)	C(221)–P(2)–C(241)	109.8(6)
Cl(21)–Re(2A)–Cl(22)	86.97(10)	Cl(13)–Re(1B)–Cl(21)	89.4(3)	Re(2A)–Cl(21)–Re(1B)	38.73(19)	C(231)–P(2)–C(241)	108.9(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Data are given for one of the two crystallographically independent molecules of **15**. The pairs Re(1A)/Re(2A) and Re(1B)/Re(2B) are the two disordered Re_2 units represented in Fig. 5. Full data are available as supplementary material. [c] Distance involving the methyl carbon atom of the phosphonium cation.

graphic disorder.[30,31] The spectroscopic and electrochemical properties of **15** confirmed the purity of the bulk product. The ^1H NMR spectral resonances for the $[(C_6H_4OMe\text{-}p)_3PMe]^+$ cation (recorded in CD_2Cl_2) are at δ +7.7–7.5(m) and δ +7.2–7.1(m) (12H, C_6H_4), δ +3.92(s) (9H, OMe) and δ +2.75(d) (3H, Me), while a singlet at δ +19.1 is observed in the $^{31}P\{^1H\}$ NMR spectrum (recorded in CD_2Cl_2). The cyclic voltammetric properties of a solution of **15** in 0.1 M $Bu^n{}_4NPF_6$–CH_2Cl_2 (recorded with a scan rate of 200 mV s^{-1} at a Pt-bead electrode) show reversible one-electron processes at $E_{1/2}(ox) = +1.21$ V and $E_{1/2}(red) = -0.87$ V *vs.* Ag–AgCl that are characteristic of the $[Re_2Cl_8]^{2-}$ anion.[19]

While the tetrarhenium complex **14** was the only tetranuclear cluster we isolated from the reactions of *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ with triaryl phosphines in methanol, two other derivatives of the type $Re_4(\mu\text{-}O)_4Cl_4(PR_3)_4$ were obtained by the use of other methods. The triphenylphosphine complex $Re_4(\mu\text{-}O)_4Cl_4(PPh_3)_4$ **16** was obtained in low yield (*ca.* 20%) upon heating $Re_2(\mu\text{-}O_2CMe)Cl_4(PPh_3)_2$ **2** in methanol in the presence of $LiOH{\cdot}2H_2O$ but the absence of added phosphine. The use of LiOH as a source of O^{2-} is known in the literature as, for example, in the synthesis of tetrahedral $[M_4(\mu_4\text{-}O)]^{n+}$ clusters.[34] A similar procedure with the use of **4** {*i.e.* $Re_2(\mu\text{-}O_2CMe)Cl_4[P(C_6H_4OMe\text{-}p)_3]_2$} in place of **2** provided an alternative means of obtaining **14** but in a lower yield (26%). The substitutional lability of the $P(C_6H_4OMe\text{-}p)_3$ ligands of **14** was established by the conversion of this complex to $Re_4(\mu\text{-}O)_4Cl_4(PMe_2Ph)_4$ **17** upon its treatment with an excess of PMe_2Ph.

The identities of **16** and **17** were established through a comparison of their electrochemical properties and far-IR spectra, but their poor solubility properties limited their full characterization. Furthermore, our inability to recrystallize these products is probably a factor in the poor C and H microanalytical data that were obtained. The crystallographically characterized complex **14** shows well defined NMR spectral properties (recorded in CD_2Cl_2), with multiplets at δ +8.15, +7.58, +6.90, +6.80, +6.33 and +6.22 for the C_6H_4 rings of the phosphine ligands, singlets at δ +3.87, +3.84 and +3.58 for the OMe substituents, and δ +3.42(s) for the lattice methanol. The $^{31}P\{^1H\}$ NMR spectrum of **14** consists of a singlet at δ +13.6. The compounds **16** and **17** were not soluble enough to obtain satisfactory NMR spectra. However, the single scan CVs of dilute solutions of **14**, **16** and **17** in 0.1 M $Bu^n{}_4NPF_6$–CH_2Cl_2 (Pt-bead electrode, scan rate 200 mV s^{-1}) were very similar, with a single irreversible oxidation at $E_{p,a} = +0.98$, +1.00 and +1.40 V *vs.* Ag/AgCl, respectively, in the potential range +1.6 to −1.5 V. Equally diagnostic were their low-frequency IR spectra (Nujol mulls 550–250 cm^{-1}), which were remarkably similar with bands at 339m, 328ms and 277mw cm^{-1} for **16**, and 340m, 327s and 277mw cm^{-1} for **17**, which are in the region expected for ν(Re–Cl) and other ν(M–L) vibrations.

Concluding remarks

While PPh_3 is known to react with the dirhenium(III) synthon *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_4(H_2O)_2$ **1** to afford the paramagnetic dirhenium(III,II) complex $Re_2(\mu\text{-}O_2CMe)Cl_4(PPh_3)_2$ **2**,[4] the reaction of **1** with the triarylphosphine $P(C_6H_4OMe\text{-}p)_3$ in methanol affords the novel tetranuclear complex $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4$ **14**, along with the dirhenium(III) salt $[(C_6H_4OMe\text{-}p)_3PMe]_2Re_2Cl_8$. While no other phosphine-containing tetranuclear complexes of this type can be synthesized by this particular route,[3] the clusters $Re_4(\mu\text{-}O)_4Cl_4(PPh_3)_4$ **15** and $Re_4(\mu\text{-}O)_4Cl_4(PMe_2Ph)_4$ **16** have been obtained by the alternative methods of reacting **2** with LiOH, and the substitution of the phosphine ligands in **14** by PMe_2Ph.

The non-redox substitutional lability of the PPh_3 ligands of $Re_2(\mu\text{-}O_2CMe)Cl_4(PPh_3)_2$ **2** towards both monodentate and bidentate phosphines has been demonstrated for PBz_3, $P(C_6H_4OMe\text{-}p)_3$, $PMePh_2$, $Ph_2PCH_2PPh_2$, $Ph_2PNHPPh_2$ and $Ph_2PC(=CH_2)PPh_2$; these reactions afford complexes of the types $Re_2(\mu\text{-}O_2CMe)Cl_4(PR_3)_2$ [$PR_3 = PBz_3$, $P(C_6H_4OMe\text{-}p)_3$ or $PMePh_2$] and *trans*-$Re_2(\mu\text{-}O_2CMe)Cl_4(\mu\text{-}PP)_2$ (PP = bridging bidentate phosphine), generally in very high yield. The reaction of **2** with $PMePh_2$ is complicated by a redox reaction which produces a considerable quantity of the dirhenium(II) complex $Re_2Cl_4(PMePh_2)_4$, while the more basic and least sterically demanding phosphine PMe_2Ph gives exclusively $Re_2Cl_4(PMe_2Ph)_4$. With the use of certain phosphines, specifically PCy_3 and $Ph_2PCH_2CH_2Ph_2$, which are either very sterically demanding or prefer a chelating coordination mode to Re, the Re–Re multiple bond is cleaved to produce mononuclear species. For PCy_3, the complex *mer-trans*-$ReOCl_3(PCy_3)_2$ is formed, whereas $Ph_2PCH_2CH_2PPh_2$ gives a mixture of dinuclear α-$Re_2Cl_4(dppe)_2$ (chelating phosphine, Re≡Re bond) and *trans*-$[ReO_2(dppe)_2]Cl$.

Future studies are now being directed at examining the carboxylate substitution chemistry of $Re_2(\mu\text{-}O_2CMe)Cl_4(PR_3)_2$, *trans*-$Re_2(\mu\text{-}O_2CMe)Cl_4(\mu\text{-}dppm)_2$ and *cis*-$Re_2(\mu\text{-}O_2CMe)_2Cl_2(\mu\text{-}dppm)_2$,[9] a strategy which we have found can be used to synthesize $[Re_2]_n$ (n = 2, 3 or 4) clusters.

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