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The first symmetrical tetrarheniumcyclodiyne type cluster containing phosphine ligands: $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4$

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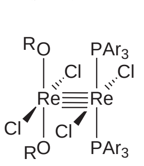
The reactions of methanol solutions of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$ with PAr_3 (Ar = Ph, C_6H_4Me-*p*, C_6H_4Me-*m* or C_6H_4Cl-*p*) afford the quadruply bonded dirhenium(IV,II) complexes $Cl_2(MeO)_2ReReCl_2(PAr_3)_2$, whereas $P(C_6H_4OMe\text{-}p)_3$ gives the complex $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4$, which X-ray crystallography has shown is the first symmetrical, neutral, tetrarheniumcyclodiyne type cluster containing phosphine ligands.

The reactions of the dirhenium(III) carboxylate complex *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$ (**1**) with triphenylphosphine in primary alcohol solvents are unusual in that they afford the unsymmetrical, quadruply bonded, alkoxide complexes $Re_2Cl_4(OR)_2(PAr_3)_2$ (**2**), Ar = Ph [eqn. (1)], which are formally

$$cis\text{-}Re_2(O_2CCH_3)_2Cl_4(H_2O)_2 + 2PAr_3 + 2ROH \longrightarrow Re_2Cl_4(OR)_2(PAr_3)_2 + 2CH_3CO_2H + 2H_2O \quad (1)$$

Re(IV)–Re(II) species that are derived from the Re(III)–Re(III) core by an intramolecular disproportionation.[1] Subsequently, Chisholm and co-workers[2] discovered the remarkable compound $Mo_2(OPr^i)_4(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) which is formally a Mo(IV)–Mo(0) complex, *i.e.* $(Pr^iO)_4Mo\text{-}Mo(dmpe)_2$, and retains a metal–metal multiple bond.[3,4]

Our interest in probing the factors which favor the stability of unsymmetrical structures such as **2**, coupled with attempts to design synthetic strategies to the symmetrical isomer **3**,† have led us to study the reactions of the synthon *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$[5] with triarylphosphines which vary in basicity and cone angle. We report in the present communication our findings concerning the reaction of **1** with $P(C_6H_4OMe\text{-}p)_3$ in methanol which affords a route to the prototype of a new class of neutral, symmetrical, tetrarheniumcyclodiyne type of cluster, *viz.*, $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4$ (**4**).



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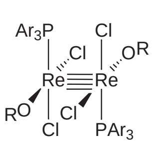

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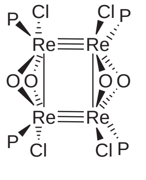

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Although methanol solutions of **1** react with PAr_3 (Ar = Ph, C_6H_4Me-*p*, C_6H_4Me-*m* or C_6H_4Cl-*p*) to yield methoxide complexes of type **2**, reactions with $P(C_6H_4OMe\text{-}p)_3$ afford the red complex **4** under these same conditions.‡ This compound could be isolated reproducibly in yields of *ca.* 35%. The use of refluxing ethanol as the reaction solvent produced only very small quantities of **4**; the major product was the dirhenium(III,II) complex $Re_2(\mu\text{-}O_2CCH_3)Cl_4[P(C_6H_4OMe\text{-}p)_3]_2$,[6]§ along with small amounts of $Re_2Cl_6[P(C_6H_4OMe\text{-}p)_3]_2$ and $Re_2Cl_4(OEt)_2[P(C_6H_4OMe\text{-}p)_3]_2$. The substitution of the pyridine analogue *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(py)_2$ for **1** in the reaction with $P(C_6H_4OMe\text{-}p)_3$ in refluxing methanol afforded **4** in low yield (<10%). While the reaction temperature may be important in the formation of **4**, the origin of the oxygen in the $\{Re_4(\mu\text{-}O)_4\}$ core of **4** is probably the alcohol solvent and not coordinated or adventitious water since the addition of varying amounts of water did not increase the yield of this product.

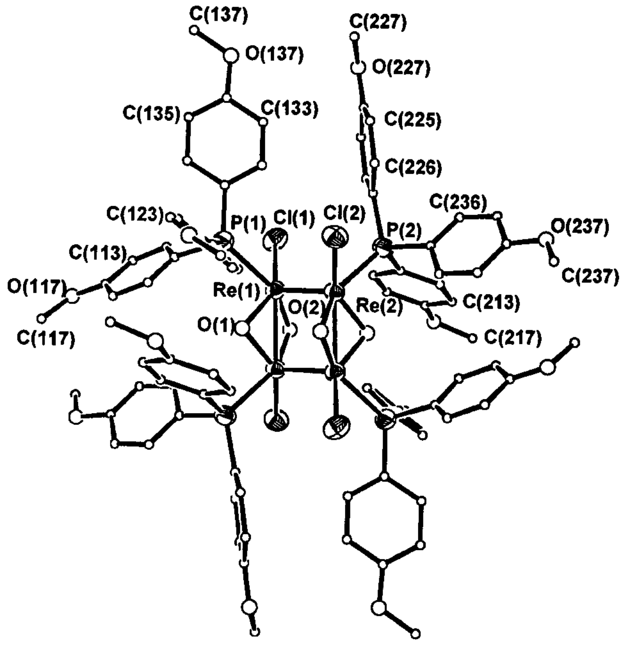

Fig. 1 ORTEP[13] representation of the structure of the tetranuclear cluster $Re_4(\mu\text{-}O)_4Cl_4[P(C_6H_4OMe\text{-}p)_3]_4$ in crystals of **4**·2MeOH. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the $P(C_6H_4OMe\text{-}p)_3$ ligands which are circles of arbitrary radius. Unlabeled atoms are related to the labeled atoms by an inversion center. Selected bond distances (Å) and bond angles (°): Re(1)–Re(2) 2.2726(5), Re(1)–Re(2)′ 2.5388(5), Re(1)–Cl(1) 2.350(2), Re(2)–Cl(2) 2.359(2), Re(1)–P(1) 2.521(2), Re(2)–P(2) 2.524(2), Re(1)–O(1) 1.943(5), Re(1)–O(2) 1.995(5), Re(2)–O(1) 1.960(5), Re(2)–O(2) 1.988(5); Re(1)–Re(2)–Re(1)′ 90.099(16), Re(2)′–Re(1)–Re(2) 89.901(16), Cl(1)–Re(1)–P(1) 84.16(7), Cl(2)–Re(2)–P(2) 84.41(7), O(1)–Re(1)–O(2) 96.0(2), O(1)–Re(2)–O(2) 95.7(2), Re(1)–O(1)–Re(2) 81.15(19), Re(2)–O(2)–Re(1) 79.19(19). The four Re atoms shown are those of the primary form of a disorder in which a secondary form (atoms Re(3) and Re(4)), appearing to share the same ligand atoms, 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) Å and 2.528(8) Å, respectively.

The diamagnetic complex **4** was shown by X-ray crystallography to contain a rectangular cluster of metal atoms with two Re≡Re bonds and two Re–Re bonds.¶ Formally, this unit arises from the [2 + 2] cycloaddition of two Re≣Re units (derived from two molecules of **1**) by loss of their δ components. An ORTEP representation of the structure of **4** is shown in Fig. 1. This centrosymmetric cluster possesses Re–Re bond distances of 2.273(1) Å and 2.539(1) Å, the longer distance being associated with the [Re(μ-O)$_2$Re] units. These Re≡Re and Re–Re bond distances are similar to those encountered in the $[Bu_4^nN]^+$ 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 structurally characterized by Cotton and co-workers.[7,8] Unlike the latter species, compound **4** is neutral, contains phosphine ligands, and is the first tetrarheniumcyclodiyne type cluster with a $[Re_4(\mu\text{-}O)_4]^{4+}$ core. This compound represents one extreme in the chemistry of molecular rectangles (cyclic quartets) which range from those which contain four separate ligand-bridged metal centers[9] to those with pairs of ligand-bridged multiply bonded dimetal units which may or may not be linked by metal–metal bonds within the rectangular cluster.[10]

While this type of dimerization of quadruply bonded dimetal complexes were first encountered by McCarley and co-workers many years ago,[11] and has subsequently been developed quite extensively in Mo and W chemistry,[12] it is rare in Re chemistry.[7,8] Our work expands this field and provides an interesting and potentially useful synthon for further reactivity studies. While **4** does not possess any readily accessible *reversible* redox chemistry, the P(C$_6$H$_4$OMe-*p*)$_3$ ligands are substitutionally labile as shown by the conversion of **4** to $Re_4(\mu\text{-}O)_4Cl_4(PMe_2Ph)_4$ upon its reaction with PMe$_2$Ph. Further studies are underway to develop the reaction chemistry of this new cluster and ones like it.

Notes and references

† Other isomers, based upon a (Ar$_3$P)(RO)Cl$_2$ReReCl$_2$(OR)(PAr$_3$) arrangement of ligands, are of course possible.

‡ Synthesis of **4**: a sample of P(C$_6$H$_4$OMe-*p*)$_3$ (184 mg, 0.522 mmol) was heated in methanol (20 mL) until it had completely dissolved, whereupon a quantity of **1** (113 mg, 0.169 mmol) was added *via* an addition sidearm. The resulting reaction mixture was then refluxed for 3 days, and the crop of red crystalline **4** was filtered off, washed with methanol and diethyl ether; yield 67 mg (33%). Calc. for $C_{86}H_{92}Cl_4O_{18}P_4Re_4$ (*i.e.* **4**·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 **4**·2MeOH was selected from this batch for an X-ray structure analysis. Far IR spectrum (Nujol mull): *ν*(Re–Cl) 326ms and 276m cm^{-1}. ^{1}H NMR spectrum (CD$_2$Cl$_2$): *δ* C$_6$*H*$_4$ of C$_6$H$_4$OMe-*p* +8.15m, +7.58m, +6.90m, +6.80m, +6.33m, +6.22m; O*Me* of C$_6$H$_4$OMe-*p* +3.87s, +3.84s; +3.58s; *Me*OH +3.42s. ^{31}P-{^{1}H} NMR spectrum (CD$_2$Cl$_2$): *δ* +13.6s. Cyclic voltammogram (0.1 M $Bu_4^nNPF_6$ CH$_2$Cl$_2$, Pt-bead electrode, scan rate 200 mV s^{-1}, potential range +1.5 to −1.5 V, potentials *vs.* Ag–AgCl): $E_{p,a}$ = +0.98 V.

§ This product has properties very similar to those of the structurally characterized complex $Re_2(\mu\text{-}O_2CCH_3)Cl_4(PPh_3)_2$.[6]

¶ Crystal data: **4**·2MeOH ($C_{86}H_{92}Cl_4O_{18}P_4Re_4$, *M* = 2424.19) at 296 K: space group $P2_1/c$ with *a* = 13.9995(7), *b* = 23.5126(7), *c* = 14.3633(7) Å, *β* = 114.1998(16)°, U = 4312.4(6) Å^3, *Z* = 2, D_c = 1.867 g cm^{-3}, μ(Mo-Kα) = 5.937 mm^{-1}. Data collection performed on a Nonius Kappa-CCD and the structure solved by direct methods using SIR97[13] and refined through the use of SHELX-97:[13] 35082 reflections measured, 10854 unique (R_{int} = 0.101). Hydrogen atoms included but constrained to ride on the atom to which they are bonded. A cut-off $F_o^2 > 2\sigma(F_o^2)$ used for *R*-factor calculations to give $R(F_o) = 0.062$, $R_w(F_o^2) = 0.104$, and GOF = 1.138. Disorder involving the four Re atoms of the rectangular cluster 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 primary and secondary forms are 0.949 and 0.051, respectively. CCDC reference number 186/1485. See http://www.rsc.org/suppdata/dt/1999/2273/ for crystallographic files in .cif format.

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