

# The first symmetrical tetraheniumcycloidyne type cluster containing phosphine ligands: $\text{Re}_4(\mu\text{-O})_4\text{Cl}_4[\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3]_4$

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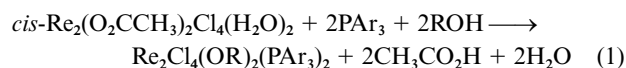
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Received 28th April 1999, Accepted 27th May 1999

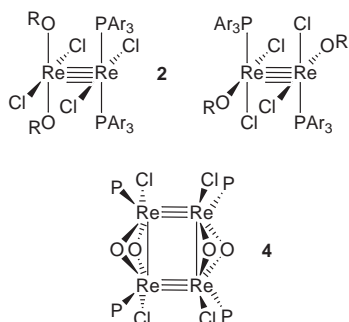
The reactions of methanol solutions of *cis*- $\text{Re}_2(\mu\text{-O}_2\text{-CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$  with  $\text{PAR}_3$  (Ar = Ph,  $\text{C}_6\text{H}_4\text{Me-}p$ ,  $\text{C}_6\text{H}_4\text{Me-}m$  or  $\text{C}_6\text{H}_4\text{Cl-}p$ ) afford the quadruply bonded dirhenium(IV,II) complexes  $\text{Cl}_2(\text{MeO})_2\text{ReReCl}_2(\text{PAR}_3)_2$ , whereas  $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$  gives the complex  $\text{Re}_4(\mu\text{-O})_4\text{Cl}_4[\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3]_4$ , which X-ray crystallography has shown is the first symmetrical, neutral, tetraheniumcycloidyne type cluster containing phosphine ligands.

The reactions of the dirhenium(III) carboxylate complex *cis*- $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$  (**1**) with triphenylphosphine in primary alcohol solvents are unusual in that they afford the unsymmetrical, quadruply bonded, alkoxide complexes  $\text{Re}_2\text{Cl}_4(\text{OR})_2(\text{PAR}_3)_2$  (**2**), Ar = Ph [eqn. (1)], which are formally

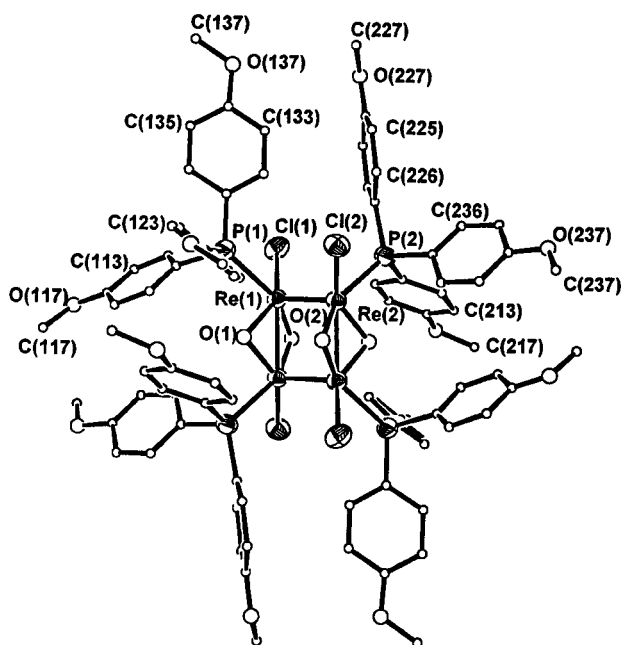


$\text{Re(IV)-Re(II)}$  species that are derived from the  $\text{Re(III)-Re(III)}$  core by an intramolecular disproportionation.<sup>1</sup> Subsequently, Chisholm and co-workers<sup>2</sup> discovered the remarkable compound  $\text{Mo}_2(\text{OPr}^i)_4(\text{dmpe})_2$  ( $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ) which is formally a  $\text{Mo(IV)-Mo(0)}$  complex, *i.e.*  $(\text{Pr}^i\text{O})_4\text{Mo-Mo}(\text{dmpe})_2$ , and retains a metal-metal multiple bond.<sup>3,4</sup>

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**,<sup>†</sup> have led us to study the reactions of the synthon *cis*- $\text{Re}_2(\mu\text{-O}_2\text{-CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ <sup>5</sup> with triarylphosphines which vary in basicity and cone angle. We report in the present communication our findings concerning the reaction of **1** with  $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$  in methanol which affords a route to the prototype of a new class of neutral, symmetrical, tetraheniumcycloidyne type of cluster, *viz.*,  $\text{Re}_4(\mu\text{-O})_4\text{Cl}_4[\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3]_4$  (**4**).



Although methanol solutions of **1** react with  $\text{PAR}_3$  (Ar = Ph,  $\text{C}_6\text{H}_4\text{Me-}p$ ,  $\text{C}_6\text{H}_4\text{Me-}m$  or  $\text{C}_6\text{H}_4\text{Cl-}p$ ) to yield methoxide complexes of type **2**, reactions with  $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$  afford the red complex **4** under these same conditions.<sup>‡</sup> 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  $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4[\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3]_2$ ,<sup>6§</sup> along with small amounts of  $\text{Re}_2\text{Cl}_6[\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3]_2$  and  $\text{Re}_2\text{Cl}_4(\text{OEt})_2$ -



**Fig. 1** ORTEP<sup>13</sup> representation of the structure of the tetranuclear cluster  $\text{Re}_4(\mu\text{-O})_4\text{Cl}_4[\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3]_4$  in crystals of 4·2MeOH. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the  $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$  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 (°):  $\text{Re}(1)\text{-Re}(2)$  2.2726(5),  $\text{Re}(1)\text{-Re}(2')$  2.5388(5),  $\text{Re}(1)\text{-Cl}(1)$  2.350(2),  $\text{Re}(2)\text{-Cl}(2)$  2.359(2),  $\text{Re}(1)\text{-P}(1)$  2.521(2),  $\text{Re}(2)\text{-P}(2)$  2.524(2),  $\text{Re}(1)\text{-O}(1)$  1.943(5),  $\text{Re}(1)\text{-O}(2)$  1.995(5),  $\text{Re}(2)\text{-O}(1)$  1.960(5),  $\text{Re}(2)\text{-O}(2)$  1.988(5);  $\text{Re}(1)\text{-Re}(2)\text{-Re}(1)'$  90.099(16),  $\text{Re}(2)\text{-Re}(1)\text{-Re}(2)$  89.901(16),  $\text{Cl}(1)\text{-Re}(1)\text{-P}(1)$  84.16(7),  $\text{Cl}(2)\text{-Re}(2)\text{-P}(2)$  84.41(7),  $\text{O}(1)\text{-Re}(1)\text{-O}(2)$  96.0(2),  $\text{O}(1)\text{-Re}(2)\text{-O}(2)$  95.7(2),  $\text{Re}(1)\text{-O}(1)\text{-Re}(2)$  81.15(19),  $\text{Re}(2)\text{-O}(2)\text{-Re}(1)$  79.19(19). The four Re atoms shown are those of the primary form of a disorder in which a secondary form (atoms  $\text{Re}(3)$  and  $\text{Re}(4)$ ), appearing to share the same ligand atoms, is in a plane approximately orthogonal to the primary form. The distances  $\text{Re}(3)\text{-Re}(4)$  and  $\text{Re}(3)\text{-Re}(4)'$  are 2.275(8) Å and 2.528(8) Å, respectively.

$[\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3]_2$ . The substitution of the pyridine analogue *cis*- $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\text{py})_2$  for **1** in the reaction with  $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$  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  $\{\text{Re}_4(\mu\text{-O})_4\}$  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.

The diamagnetic complex **4** was shown by X-ray crystallography to contain a rectangular cluster of metal atoms with two  $\text{Re}=\text{Re}$  bonds and two  $\text{Re}-\text{Re}$  bonds.¶ Formally, this unit arises from the  $[2 + 2]$  cycloaddition of two  $\text{Re}\equiv\text{Re}$  units (derived from two molecules of **1**) by loss of their  $\delta$  components. An ORTEP representation of the structure of **4** is shown in Fig. 1. This centrosymmetric cluster possesses  $\text{Re}-\text{Re}$

bond distances of 2.273(1) Å and 2.539(1) Å, the longer distance being associated with the [Re( $\mu$ -O)<sub>2</sub>Re] units. These Re=Re and Re–Re bond distances are similar to those encountered in the [Bu<sub>4</sub><sup>n</sup>N]<sup>+</sup> salts of the [Re<sub>4</sub>( $\mu$ -O)<sub>2</sub>( $\mu$ -OMe)<sub>2</sub>Cl<sub>8</sub>]<sup>2-</sup>, [Re<sub>4</sub>( $\mu$ -O)<sub>2</sub>( $\mu$ -OMe)( $\mu$ -Cl)Cl<sub>8</sub>]<sup>2-</sup> and [Re<sub>4</sub>( $\mu$ -O)<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>Cl<sub>8</sub>]<sup>2-</sup> anions that have been structurally characterized by Cotton and co-workers.<sup>7,8</sup> Unlike the latter species, compound **4** is neutral, contains phosphine ligands, and is the first tetrarheniumcycloidyne type cluster with a [Re<sub>4</sub>( $\mu$ -O)<sub>4</sub>]<sup>4+</sup> 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<sup>9</sup> 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.<sup>10</sup>

While this type of dimerization of quadruply bonded dimetal complexes were first encountered by McCarley and co-workers many years ago,<sup>11</sup> and has subsequently been developed quite extensively in Mo and W chemistry,<sup>12</sup> it is rare in Re chemistry.<sup>7,8</sup> 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<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>3</sub> ligands are substitutionally labile as shown by the conversion of **4** to Re<sub>4</sub>( $\mu$ -O)<sub>4</sub>Cl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>4</sub> upon its reaction with PMe<sub>2</sub>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<sub>3</sub>P)(RO)Cl<sub>2</sub>ReReCl<sub>2</sub>(OR)(PAR<sub>3</sub>) arrangement of ligands, are of course possible.

‡ Synthesis of **4**: a sample of P(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>3</sub> (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<sub>86</sub>H<sub>92</sub>Cl<sub>4</sub>O<sub>18</sub>P<sub>4</sub>Re<sub>4</sub> (*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):  $\nu$ (Re–Cl) 326ms and 276m cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  C<sub>6</sub>H<sub>4</sub> of C<sub>6</sub>H<sub>4</sub>OMe-*p* +8.15m, +7.58m, +6.90m, +6.80m, +6.33m, +6.22m; OMe of C<sub>6</sub>H<sub>4</sub>OMe-*p* +3.87s, +3.84s; +3.58s; MeOH +3.42s. <sup>31</sup>P-<sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  +13.6s. Cyclic voltammogram (0.1 M Bu<sub>4</sub><sup>n</sup>NPF<sub>6</sub> CH<sub>2</sub>Cl<sub>2</sub>, Pt-bead electrode, scan rate 200 mV s<sup>-1</sup>, potential range +1.5 to -1.5 V, potentials vs. Ag–AgCl): E<sub>p,a</sub> = +0.98 V.

§ This product has properties very similar to those of the structurally characterized complex Re<sub>2</sub>( $\mu$ -O<sub>2</sub>CCH<sub>3</sub>)Cl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>.<sup>6</sup>

¶ Crystal data: 4·2MeOH (C<sub>86</sub>H<sub>92</sub>Cl<sub>4</sub>O<sub>18</sub>P<sub>4</sub>Re<sub>4</sub>, *M* = 2424.19) at 296 K: space group *P*2<sub>1</sub>/*c* with *a* = 13.9995(7), *b* = 23.5126(7), *c* = 14.3633(7) Å,  $\beta$  = 114.1998(16)°, *U* = 4312.4(6) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.867 g cm<sup>-3</sup>,  $\mu$ (Mo–K $\alpha$ ) = 5.937 mm<sup>-1</sup>. Data collection performed on a Nonius Kappa-CCD and the structure solved by direct methods using SIR97<sup>13</sup> and refined through the use of SHELX-97:<sup>13</sup> 35082 reflections measured, 10854 unique (*R*<sub>int</sub> = 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*<sub>o</sub>) = 0.062, *R*<sub>w</sub>(*F*<sub>o</sub><sup>2</sup>) = 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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Communication 9/03367J