

Synthesis and Crystal Structure of the Novel Cyclometallophosphine Complex $\text{Re}_4\text{Cl}_2(\text{CO})_{15}\{\text{MePP}(\text{Me})\text{PMe}\}$

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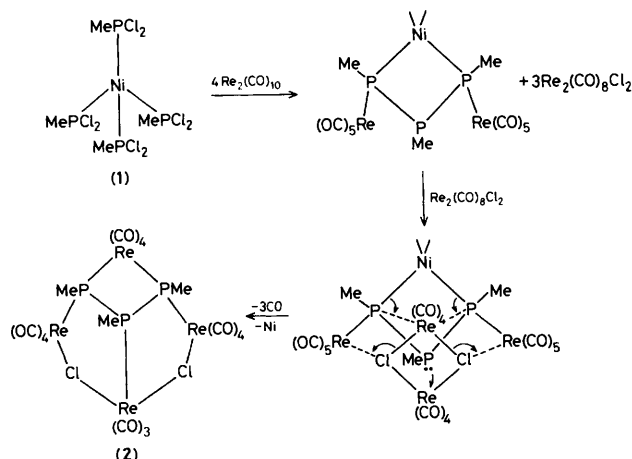
Pyrolysis of tetrakis(methyldichlorophosphine)nickel(0) with decacarbonyldirhenium leads to the formation of the tetranuclear complex $\text{Re}_4\text{Cl}_2(\text{CO})_{15}\{\text{MePP}(\text{Me})\text{PMe}\}$, the eight-electron donor triphosphine ligand forming a four-membered cyclorhenatriphosphine ring.

The thermal stability of tetrakis(methyldichlorophosphine)nickel(0) (**1**)[†] (decomp. $\sim 180^\circ\text{C}$) has prompted us to explore the possibility of dehalogenating the metal-bound ligands *in situ* before Ni-P bond cleavage as a possible source of

phosphinidene fragments for metal carbonyl cluster building. To this end, (**1**) was heated with decacarbonyldirhenium (1:5 mole ratio) to 175°C under argon at atmospheric pressure.[‡] After 1 h, the temperature was allowed to rise to 220°C during

[†] Complex (**1**) was easily prepared by refluxing nickel shot or powder in methyldichlorophosphine.

[‡] In view of the amount of CO evolved, sealed-tube reactions are potentially hazardous.



Scheme 1

2 h and this temperature maintained until CO evolution had ceased. The system was then evacuated to remove any unchanged $\text{Re}_2(\text{CO})_{10}$ by sublimation. Upon cooling, the mixture was extracted with toluene. This solution contained a number of as yet uncharacterized products as well as a significant quantity of $\text{Re}_2(\text{CO})_8\text{Cl}_2$. (^{31}P N.m.r. indicates the presence of several probable phosphinidene resonances in the +350–450 p.p.m. range.) The remaining air-stable white crystals (2) [~30% yield based on (1)] were recrystallized from tetrahydrofuran (THF) [$\nu(\text{CO}; \text{THF})$: 2109w, 2101s, 2086m, 2040s, 2007vsbr, 1986m, 1961sbr, 1950sh, and 1909m cm^{-1}].

A single-crystal X-ray analysis \S has revealed that (2) (Figure 1) has the novel tetranuclear cyclometallophosphine structure $\text{Re}_4\text{Cl}_2(\text{CO})_{15}\{\text{MePP}(\text{Me})\text{PMe}\}$. Complex (2) has crystallographically imposed mirror symmetry such that the nine unique carbonyl groups are consistent with the nine-band i.r. spectrum. The structure is essentially 'bowl-shaped' with the rhenium and chlorine atoms forming the rim while the eight-electron donor triphosphine ligand $\text{MePP}(\text{Me})\text{PMe}$ occupies the base. Complex (2) cannot be considered a cluster since the shortest Re–Re contact [$\text{Re}(2) \cdots \text{Re}(3)$ 4.318(1) Å] is definitely non-bonding nor are any such bonds required to satisfy the electron-counting rules. Previous attempts to synthesize cyclometallo-phosphines and -arsines have involved reaction of a metal carbonyl with $(\text{RX})_n$ ($n = 4, 5$, or 6; $\text{X} = \text{As}$ or P). A three-membered MAS_2 ring is found in $\text{Fe}(\text{CO})_4(\text{AsC}_6\text{F}_5)_2$ ¹ whilst MX_4 rings occur in $[\text{Fe}(\text{CO})_3]_2(\text{RX})_4$ ($\text{X} = \text{P}$ or As),^{2–4} and MAS_5 rings in $[\text{Mn}(\text{CO})_4]_2(\text{MeAs})_5$ and $[\text{Mn}(\text{CO})_3]_2(\text{MeAs})_8$.³ Structure (2) represents the first MP_3 four-membered ring system as well as a cyclometallophosphine exercising maximum electron donation.

\S Crystal Data: $\text{C}_{18}\text{H}_9\text{Cl}_2\text{O}_{15}\text{P}_3\text{Re}_4$, $M = 1379.92$; orthorhombic, $a = 13.784(2)$, $b = 18.111(2)$, $c = 12.406(3)$ Å, $U = 3097.1(9)$ Å³; space group, $Pnma$; $Z = 4$; $D_m = 2.95$, $D_c = 2.946$ g cm^{-3} ; $F(000) = 2464$; $\lambda = 0.71069$ Å; $\mu(\text{Mo-K}\alpha) = 168.57$ cm^{-1} . From 2831 diffractometer (Syntex P2₁) measured data ($2\theta \leq 50^\circ$) obtained using a crystal of dimensions 0.10 × 0.11 × 0.12 mm, the structure was solved by Patterson and Fourier techniques using 1628 absorption-corrected reflections with $I \geq 3\sigma(I)$. The structure was refined to a conventional R of 0.033 ($R_w = 0.036$). The atomic co-ordinates for this structure are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

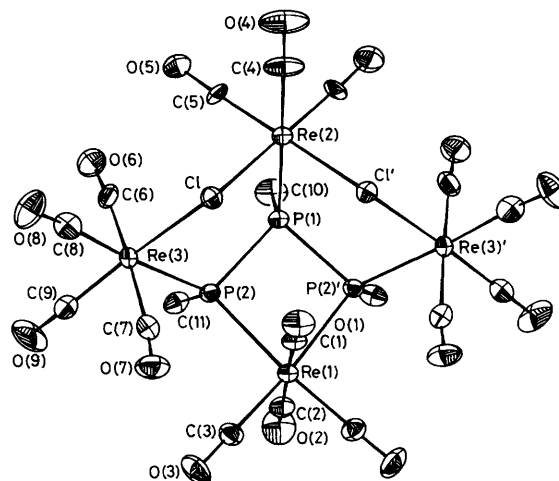


Figure 1. ORTEP plot of the structure of $\text{Re}_4\text{Cl}_2(\text{CO})_{15}\{\text{MePP}(\text{Me})\text{PMe}\}$ $\text{Re}(1)\text{--P}(2)$, 2.508(4); $\text{Re}(2)\text{--Cl}$, 2.519(4); $\text{Re}(2)\text{--P}(1)$, 2.446(5); $\text{Re}(3)\text{--Cl}$, 2.520(4); $\text{Re}(3)\text{--P}(2)$, 2.493(4); $\text{P}(1)\text{--P}(2)$, 2.231(5) Å.

The ^{31}P n.m.r. spectrum of (2) in $\text{THF}/[^2\text{H}_6]\text{acetone}$ exhibits the expected two-bands with $\text{P}(1)$ at +150 (t) and $\text{P}(2)$ at –132 p.p.m. (d) with $J_{\text{P--P}}$ 102 Hz. Whilst the $\text{P}(1)$ resonance is typical of monodentate phosphines with relatively electronegative substituents, the large upfield shift of $\text{P}(2)$ is related to the extreme phosphido-bridge angle [$\text{Re}(1)\text{--P}(2)\text{--Re}(3)$, $124.6(1)^\circ$] and long $\text{Re}(1) \cdots \text{Re}(3)$ bridged distance [4.429(1) Å]. By comparison, the ^{31}P resonance in the phosphido-bridged dimer $\text{Re}_2(\text{CO})_8(\mu\text{-PPh}_2)_2$ ⁵ ($\text{Re} \cdots \text{Re}$, 3.930 Å; Re--P--Re , 102.4°) is at –150 p.p.m. and in the rhenium-rhenium bonded trimer $\text{Re}_3(\text{CO})_{12}(\mu\text{-PPh}_2)_5$ (Re--Re , 3.038 Å; Re--P--Re , 77.9°) +40 p.p.m.

A mechanism for the formation of (2) is by nature rather speculative considering the conditions employed but it would seem unlikely that the ligand $\text{MePP}(\text{Me})\text{PMe}$ could be derived from MeP fragments in a metal-carbonyl-rich environment. Although (1) begins to dissociate to nickel metal and methylchlorophosphine at ~180 °C, direct reaction of $\text{Re}_2(\text{CO})_{10}$ with this phosphine gives predominantly $\text{ReCl}(\text{CO})_3(\text{MePCl}_2)_2$ with no evidence of (2) being present.⁵ More realistically, this ligand is most probably formed on the nickel atom surface as indicated in the tentative mechanism in Scheme 1.

Although (2) is a very stable complex (decomp. ~230 °C), it does appear that the triphosphine moiety can be degraded to form phosphinidene–metal carbonyl clusters, the chemistry of which is currently being studied.

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