

Preliminary communication

PREPARATION AND X-RAY STRUCTURE OF $[\text{ReCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$

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Summary

$[\text{ReCl}(\text{dppe})_2]$ (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) has been prepared by photolysis of *trans*- $[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ and shown to have a trigonal bipyramidal structure by X-ray analysis; it adds CNMe to give the corresponding isocyanide complex.

The recent report that $[\text{ReCl}(\text{dppe})_2]$ is a highly reactive intermediate formed during the photolysis of *trans*- $[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ in benzene or methanol [1], prompts us to present our structural characterisation of this electronically unsaturated compound.

During our investigations of the reactions of *trans*- $[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ in toluene under photolysis [2] we have isolated dark brown crystals in low yield, we have identified these as $[\text{ReCl}(\text{dppe})_2]$ and determined the molecular structure.

Crystal data: $\text{C}_{52}\text{H}_{43}\text{ClP}_4\text{Re}\cdot\text{C}_7\text{H}_8$, $M = 1110.6$, triclinic, space group $P1$ (No. 2), a 13.062(2), b 13.266(2), c 16.282(4) Å, α 101.35(2), β 95.88(2), γ 111.81(2)°, U 2519.9 Å³, $Z = 2$, $D_c = 1.464$ g cm⁻³, $F(000) = 1124$, $\lambda(\text{Mo-K}\alpha) 0.71069$ Å, $\mu(\text{Mo-K}\alpha) 26.6$ cm⁻¹ **.

The structure was solved by the heavy atom method. Full-matrix least-squares refinement using 6569 reflections yielded a conventional R value of

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** Atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, Great Britain. Any request should be accompanied by a full literature citation for this communication.

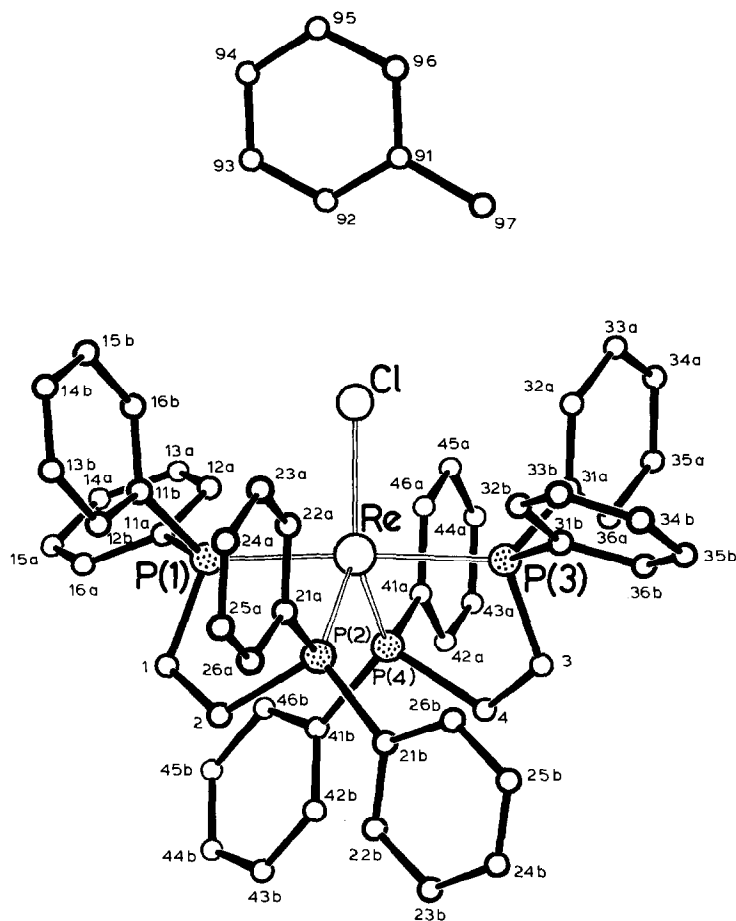


Fig. 1. Molecular structure of $[\text{ReCl}(\text{Ph}, \text{PCH}_2\text{CH}_2\text{PPh}_2)_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$. Coordination dimensions about the Re atom: Distances (Å), with e.s.d.'s in parentheses: Re—P(1) 2.366(1); Re—P(2) 2.269(1); Re—P(3) 2.380(1); Re—P(4) 2.256(1); Re—Cl 2.403(1). Angles ($^\circ$) (e.s.d.'s are all less than 0.1°): P(1)—Re—P(2) 79.8; P(1)—Re—P(3) 175.3; P(1)—Re—P(4) 95.8; P(2)—Re—P(3) 99.4; P(2)—Re—P(4) 93.7; P(3)—Re—P(4) 79.5; Cl—Re—P(1) 91.7; Cl—Re—P(2) 135.8; Cl—Re—P(3) 92.1; Cl—Re—P(4) 130.5.

0.033. Figure 1 shows the approximately trigonal bipyramidal coordination about the rhenium atom, with the chloride in an equatorial position and the two dppe ligands each straddling an apical and an equatorial position. There is a pseudo two-fold symmetry axis along the Re—Cl bond; a view almost down this bond is shown in Fig. 2. A molecule of toluene crystallises with the complex and is located close to the plane of Cl, P(1) and P(3), above the Cl atom (Fig. 1).

The structure is particularly compact, with the ethane C—C torsion angles close to zero. The Re—P axial distances are some 0.1 Å longer than the equatorial distances, as might be expected, but all distances appear to be short. Generally in 5- or 6-coordinate complexes of Re^{V} or Re^{I} [3], $d(\text{Re—P})$ is of the order of 2.46 ± 0.02 Å, the distances observed here are 0.1–0.2 Å less, presumably as a consequence of the electron-deficiency of the formally 16-electron Re centre.

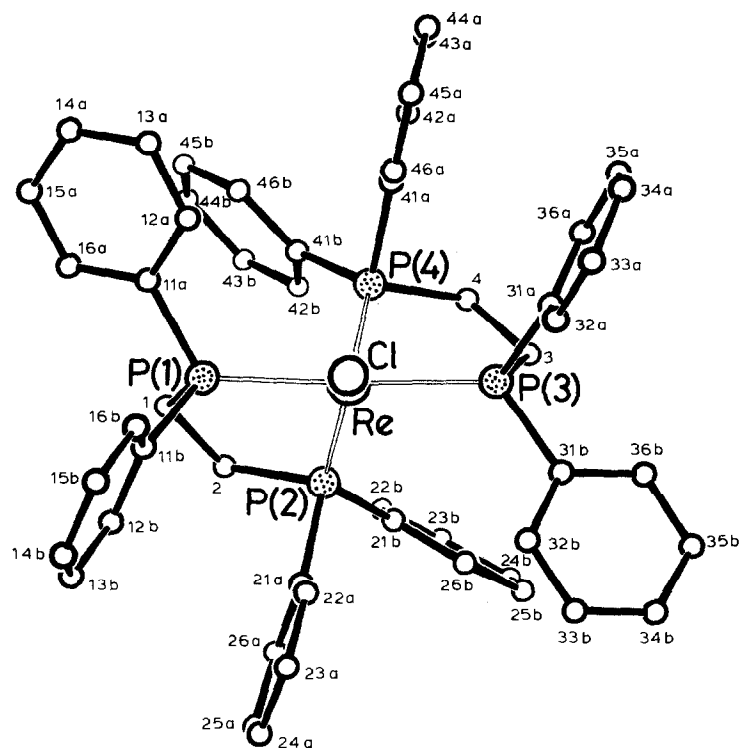


Fig. 2. View of $[\text{ReCl}(\text{dppe})_2]$ looking down the $\text{Re}-\text{Cl}$ bond.

The ^{31}P NMR spectrum of $[\text{ReCl}(\text{dppe})_2]$ is a doublet in agreement with the presence of two non-equivalent phosphorus atoms in the structure.

Kinetic studies have indicated that the unsaturated intermediate $[\text{Mo}(\text{N}_2)(\text{dppe})_2]$, in which the metal is in a d^6 configuration and which is isoelectronic with $[\text{ReCl}(\text{dppe})_2]$, is formed in the reactions of *trans*- $[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$ with species such as isocyanides [4] or organic halides [5], but its lifetime is short because of its high reactivity towards nucleophiles, and this prevents its isolation.

The complex $[\text{ReCl}(\text{dppe})_2]$ reacts with CNMe to give the known [2] complex *trans*- $[\text{ReCl}(\text{CNMe})(\text{dppe})_2]$ and also tends to undergo intramolecular *ortho*-metallation in solution, but surprisingly, appears not to react with N_2 . We are investigating these properties in more detail.

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