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On the Mechanism of Reductive Elimination of Hydrogen from a Binuclear Platinum Hydride

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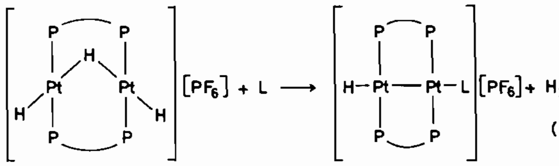
The mechanism of reductive elimination of H_2 from binuclear or polynuclear metal hydrides has not been investigated, although considerable work has been done on reductive elimination of H_2 from mononuclear hydrides (eqns. 1 and 2, L = tertiary phosphine or phosphite) [1, 2].

$$[IrH_2(CO)_2L_2]^+ + L \longrightarrow [Ir(CO)_2L_3]^+ + H_2 \qquad (1)$$

$$[CoH_2L_4]^+ + L \longrightarrow [CoL_5]^+ + H_2 \qquad (2)$$

In each case, the rate determining step involves intramolecular *cis*-reductive elimination of H_2, followed by trapping of the 16-electron intermediate by free L. The mechanism is thus dissociative and the rate is generally independent of the nature and concentration of L, so long as its concentration is high enough to trap the intermediate effectively [1, 2]. The discovery of facile binuclear reductive elimination of H_2 from complex (Ia) according to eqn. (3), $\widehat{P\,P}$ = $Ph_2PCH_2PPh_2$, dppm, allows a comparison of the mechanisms of the binuclear and mononuclear reductive eliminations to be made [3].



(3)

(Ia)

(IIa), L = PPh₃

(IIb), L = η'-dppm

The following mechanistic data are found:

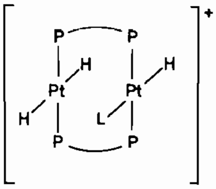
1. The reactions involve intramolecular reductive elimination, since reaction of a mixture of (Ia) and $[Pt_2D_3(\mu\text{-dppm})_2][PF_6]$, (Ib), with PPh_3 gave a mixture of H_2 and D_2 with only traces of HD.

2. No intermediates are formed in concentrations detectable using ^{31}P NMR spectroscopy. When L = PPh_3, reaction (3) occurred slowly at –30 °C but only spectra of (Ia) and (IIa) were observed at intermediate stages*. With the smaller ligands L = $PMePh_2$ and PMe_2Ph reaction was rapid at –78 °C.

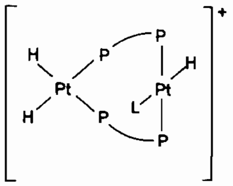
3. A kinetic study of reaction (3) was carried out in 1,2-dichloroethane solution at 21 °C, monitoring reactions by UV-visible spectrophotometry, under conditions with a large excess of ligand L. The reactions when L = dppm or PPh_3 followed the kinetic law $-d[Ia]/dt = k_2[Ia][L]$ with k_2 = 10.9 and 1.60 $l\ mol^{-1}\ sec^{-1}$ respectively under these conditions. We were unable to follow the kinetics with the smaller ligands $PMePh_2$ or PMe_2Ph since, with excess ligand present, displacement of dppm from platinum occurs as well as rapid reductive elimination of H_2.

4. Similar kinetic studies were carried out with (Ib). By comparison with rates for (Ia), the reactions with dppm and PPh_3 gave primary kinetic isotope effects, k_H/k_D, of 3.46 and 3.52 respectively. These may be compared with similar isotope effects of 2.1 for loss of H_2 from $[IrH_2(CO)_2L_2]^+$, 1.22 for addition of H_2 to *trans*-$[IrCl(CO)(PPh_3)_2]$ and 3.3 for reductive elimination of CH_4 (or CH_3D) from *cis*-$[PtH(\text{or } D)Me(PPh_3)_2]$ [1, 4, 5].

The kinetics of reaction (3) show an associative mechanism and an intermediate or transition state [Ia•L] is clearly involved, in striking contrast with the mechanisms for reactions (1) and (2). If an intermediate is formed it is expected to have structure (III) or (IV), since each platinum centre can attain the 16-electron count without a bridging hydride present.



(III)



(IV)

The intermediate is not formed in detectable amounts, and its formation could be rate-determining. This would be consistent with the observation that smaller phosphine ligands L give an overall higher rate, although bulkier ligands L should facilitate reductive elimination from (III) or (IV) [6, 7]. The high kinetic isotope effect indicates that Pt–H bond cleavage is involved in the transition state. If formation of (III) or (IV) is rate determining, then the

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*A trace of a side-product was formed, but it remained at the end of the reaction and was clearly not an intermediate. The UV studies also show that no intermediates are formed in detectable amounts. The NMR experiments were carried out with the $[BPh_4]^-$ salt of cation (Ia).

isotope effect must be associated with transformation of the bridging hydride to a terminal hydride, rather than with the reductive elimination step.*

Although the detailed mechanism must be regarded as tentative, the demonstration of an associative mechanism is important in allowing an understanding of the rapid *ligand-induced* reductive elimination. Thus complex (I) is not decomposed in pyridine, acetonitrile or methanol solvents at 100 °C, yet efficient reductive elimination of H_2 from (Ia) induced by CO is a necessary step in the catalysis of the Water Gas Shift reaction catalyzed by (Ia) [8]. Preliminary studies show that photolysis of (I) in acetonitrile occurs very readily and its nature is under investigation.** The reductive elimination of H_2 appears to be involved, and this opens up the possibility of photocatalysis by (Ia) in systems where ligand-induced reductive elimination of H_2 does not occur easily.***

The ligand-induced reductive elimination may prove to be general in polynuclear complexes. For example, although the mechanism has not been studied, the reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with CO to give first $[Os_3H(\mu\text{-}H)(CO)_{11}]$ and then $[Os_3(CO)_{12}]$ and H_2 could occur in a similar way [9, 10].

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*Alternatives would involve a rapid pre-equilibrium, giving undetectably small amounts of (III) or (IV), followed by slow loss of H_2, with the overall rate dominated by the equilibrium constant for formation of (III) or (IV), or a mechanism in which phosphine addition and H_2 loss occurred synchronously. The latter is difficult to envisage since the hydride ligands in (I) are far apart.

**The photodecomposition of (Ia) was conducted at 362 ± 8 nm in a JASCO spectroirradiator. The kinetics, which will be discussed in our full paper, are complicated by light absorption by the product and its subsequent transformations, but the quantum yield is over 50%. We thanks Ms. J. Taylor for assistance with the photochemistry.

***Photolysis of mononuclear transition metal hydrides occurs readily, but this appears to be a unique case in binuclear or polynuclear hydrides.