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Reactions of Alkynes with Binuclear Platinum Hydrides

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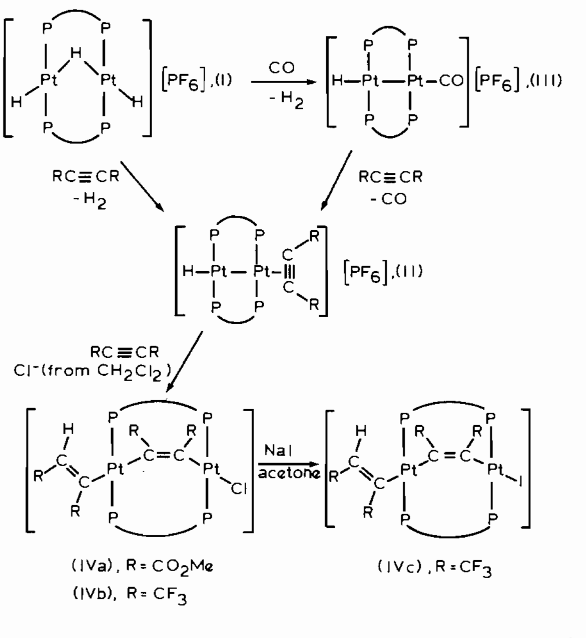
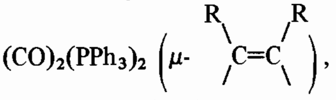
Insertion reactions of alkenes and alkynes into metal–hydride bonds are necessary in several metal catalysed reactions, and these reactions have been studied in great detail for mononuclear platinum hydrides from both experimental and theoretical viewpoints [1, 2]. However such insertion reactions with binuclear hydridoplatinum complexes have not been reported [3].

The binuclear hydride $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$, (I), dppm = $Ph_2PCH_2PPh_2$ [4], does not react under mild conditions with ethylene, propyne, 1,3-butadiene or diphenylacetylene but it reacts readily with alkynes bearing electronegative substituents, RC≡CR, R = $-CF_3$ or $-CO_2Me$. Using excess alkyne in dichloromethane solution the final products were formed as yellow solids having structure (IV), Scheme 1. The initial reaction occurs with effervescence and, when R = CO_2Me, the gaseous product was identified as H_2 formed in 60% yield. This observation suggests that the initial step in the reaction sequence involves alkyne induced reductive elimination of hydrogen from (I) to give intermediate (II) [5]. Support for this hypothesis is given by the observation that the same products are formed on reaction of alkynes with $[Pt_2H(CO)(\mu\text{-dppm})_2][PF_6]$, (III), Scheme 1 [6]. The formation of (IV) from (II) involves *cis*-insertion of alkyne into the remaining terminal Pt–H bond, *cis*-insertion of alkyne into the Pt–Pt bond and then abstraction of Cl^- from the solvent. Attempts are being made to confirm this sequence of reactions by characterisation of intermediates which can be detected and isolated by using stoichiometric quantities of alkyne or by using non-chlorinated solvents (*e.g.* benzene or methanol).



Scheme I. Proposed Reactions of Alkynes with Binuclear Platinum Hydrides, P⌒P = dppm.

The complexes (IV) were characterised by elemental analysis and by spectroscopic methods. For example, (IVb) gave a parent ion in the mass spectrum with the expected isotope pattern centred at m/e 1518, and peaks at 1355 ($P-C_4F_6H$), 1320 ($P-C_4F_6H-Cl$) and 1158 ($P-C_4F_6H-Cl-C_4F_6$) and gave peaks in the IR spectrum at 1600 cm^{-1} and 1530 cm^{-1} assigned as C=C stretching modes due to the terminal vinyl group and the bridging C_4F_6 group respectively [7]. More positive structural information was obtained from the ^1H, ^{19}F and ^{31}P NMR spectra. Thus the $^{31}P\text{-}\{^1H\}$ NMR spectrum of (IVb) appeared as an AA′BB′ multiplet, indicating bridging dppm groups in an unsymmetrical molecule [$\delta(P_{A,A'})$ −7.23 ppm (from trimethylphosphate reference), $^1J(PtP)$ 3110 Hz, $^2J(PtP)$ 100 Hz; $\delta(P_{B,B'})$ −9.63 ppm, $^1J(PtP)$ 2940 Hz, $^2J(PtP)$ 90 Hz] and the magnitudes of $^1J(PtP)$ indicate mutually ***trans*** phosphorus atoms at each platinum centre [8, 9]. The ^{19}F and ^1H NMR spectra characterise the $Pt-C(CF_3)=C(CF_3)H$ group positively since such groupings are well known in mononuclear complexes. Two quartets due to the CF_3 groups with $^5J(FF)$ 12 Hz establishes the *cis*-stereochemistry at the vinyl group, and in the ^1H NMR spectrum the magnitude of the coupling constant between platinum and the vinylic proton [δ(=CH) 6.30 ppm, $^3J(PtH)$ 56.0 Hz] confirms this point [10]. The presence of the C_4F_6 group bridging between non-equivalent platinum centres is indicated by an A_3B_3 multiplet in the ^{19}F NMR spectrum centred at δ −50.16 ppm from $CFCl_3$ reference. The addition of hexafluorobut-2-yne to the Pd–Pd bond of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ to give a similar $\mu\text{-}C_4F_6$ unit has been reported recently [11] and a similar functional group is also found in the complex [Pt₂-



$[Pt_2(CO)_2(PPh_3)_2(\mu\text{-}RC{=}CR)]$, R = CO_2Me [12]. In the complex (IVb), the protons of the CH_2 group of each dppm ligand are non-equivalent and they appear in the ^1H NMR spectrum as an AB pattern. This effect has been observed previously in other complexes with the $[Pt_2(\mu\text{-}X)(\mu\text{-dppm})_2]$ grouping [13] and further supports the presence of the μ-C_4F_6 group in (IVb). The combined NMR data allows the structures of these complex molecules to be deduced with confidence. Spectral properties of (IVa) and (IVc) will be discussed in detail elsewhere, but are also fully consistent with the proposed structures.

The detailed mechanism of these reactions is being studied, since the reactions involving two platinum centres may be closely related to the processes involved in hydrogenation of alkynes using a platinum metal catalyst.

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References

1 T. G. Attig, H. C. Clark and C. S. Wong, *Canad. J. Chem., 55,* 189 (1977).

2 D. L. Thorn and R. Hoffman, *J. Am. Chem. Soc., 100,* 2079 (1978).

3 Binuclear platinum hydrides are now well known, see G. Minghetti, G. Banditelli and A. L. Bandini, *J. Organometal. Chem., 139,* C80 (1977); G. Bracher, D. M. Grove, P. S. Pregosin and L. M. Venanzi, *Angew. Chem. Int. Ed. Engl., 18,* 155 (1979); T. H. Tulip, T. Yamagata, T. Yoshida, R. D. Wilson, J. A. Ibers and S. Otsuka, *Inorg. Chem., 18,* 2239 (1979); H. C. Clark, A. B. Goel, R. G. Goel and W. O. Ogini, *J. Organometal. Chem., 157,* C16 (1978).

4 M. P. Brown, R. J. Puddephatt, M. Rashidi and K. R. Seddon, *Inorg. Chim. Acta, 23,* L29 (1977); *idem, J. Chem. Soc. Dalton,* 516 (1978).

5 M. P. Brown, J. R. Fisher, Lj. Manojlović-Muir, K. W. Muir, R. J. Puddephatt, M. A. Thomson and K. R. Seddon, *J. Chem. Soc. Chem. Comm.,* 931 (1979).

6 M. P. Brown, J. R. Fisher, R. J. Puddephatt and M. A. Thomson, *Inorg. Chim. Acta,* in press.

7 A. Johnson and R. J. Puddephatt, *J. Chem. Soc. Dalton,* 980 (1978).

8 M. P. Brown, R. J. Puddephatt, M. Rashidi and K. R. Seddon, *J. Chem. Soc. Dalton,* 1540 (1978).

9 M. P. Brown, S. J. Cooper, R. J. Puddephatt, M. A. Thomson and K. R. Seddon, *J. Chem. Soc. Chem. Comm.,* 1117 (1979). $[\delta(MeO)_3PO = 1.72$ ppm from 85% $H_3PO_4]$.

10 H. C. Clark and W. S. Tsang, *J. Am. Chem. Soc., 89,* 533 (1967); B. E. Mann, B. L. Shaw and N. I. Tucker, *J. Chem. Soc. Chem. Comm.,* 1333 (1970).

11 A. L. Balch, C-L. Lee, C. H. Lindsay and M. M. Olmstead, *J. Organometal. Chem., 177,* C22 (1979).

12 Y. Koie, S. Shinoda. Y, Saito, B. J. Fitzgerald and C. G. Pierpoint, *Inorg. Chem., 19,* 770 (1980).

13 M. P. Brown, J. R. Fisher, R. J. Puddephatt and K. R. Seddon, *Inorg. Chem., 18,* 2808 (1979).