Phosphorus Chemistry: Reaction Between White Phosphorus and Bis-π-cyclopentadienylmolybdenum Dihydride Forming a MoP_2H_2 System

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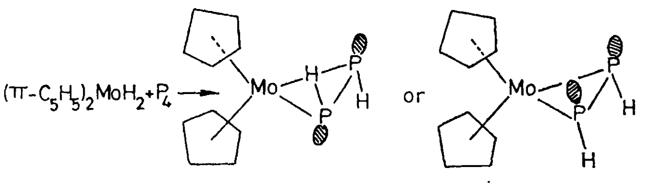
Summary White phosphorus reacts with bis-π-cyclopentadienylmolybdenum dihydride giving the diphosphane derivative $(\pi\text{-}C_5H_5)_2MoP_2H_2$.

It is well known that white phosphorus reacts with aqueous sodium hydroxide forming phosphine and diphosphine, as well as oxyacid salts. Also, it has been shown that the P_4 molecule may act as a ligand in some manner in complexes such as $RhCl(P_4)(PPh_3)_2$.[1] These and other observations led us to study reactions between transition-metal hydrides and white phosphorus.

Treatment of the dihydride $(\pi\text{-}C_5H_5)_2MoH_2$ (I) in toluene with excess of white phosphorus at 90° causes smooth reaction and, following purification by chromatography on alumina, a deep red crystalline compound (II) is isolated. Analysis, the mass spectrum, and molecular weight determination show the compound (II) to have the stoicheiometry corresponding to the formulation $(\pi\text{-}C_5H_5)_2MoP_2H_2$ [*m/e*, 292 $C_{10}H_{12}{}^{98}MoP_2{}^{+}$, *M*(cryoscopic in benzene), 270 (reqd. 290)]. The compound (II) is soluble in benzene and the solutions are readily decomposed by oxygen. The ^1H and ^{31}P n.m.r. spectra suggest a structure for the complex (II) in which each of the two $(\pi\text{-}C_5H_5)$ groups, the two phosphorus atoms, and two P-hydrogens are equivalent respectively {^1H n.m.r., δ [$(CD_3)_2SO$; 60 MHz; external Me_4Si]: 5·88 [10H, t, $J(^{31}P\text{–}\pi\text{-}C_5H_5)$ 1·0 Hz, 2 × $\pi\text{-}C_5H_5$] and 0·19 (2H, complex m, symmetrical band typical of an AA′XX′ system). The separation between the two outer, most intense bands is 160 Hz, and this value may be assigned to $J_{PH} + J_{PH'}$. ^{31}P n.m.r. [$(CD_3)_2SO$; 36·43 MHz; external H_3PO_4]: 203 p.p.m., complex symmetrical band typical of AA′XX′ system. The i.r. spectrum (mulls) shows a band



trans-
(IIa)

cis-
(IIb)

typical of a $(\pi\text{-}C_5H_5)_2Mo$ system and a strong, sharp band at 2240 cm^{-1} which may be assigned to ν_{P-H}. The data do not permit distinction between the *trans*- or fluxional *cis*-configurations (IIa or IIb respectively); a structure with a planar MoP_2H_2 system is also consistent with the spectra. The latter, however, seems less likely since phosphorus normally has an essentially tetrahedral distribution of electron pairs. The P_2H_2 molecule, and di-imine N_2H_2, are isoelectronic with ethylene so that we prefer to propose that compound (II) is similar to the ethylene derivative $(\pi\text{-}C_5H_5)_2Mo(C_2H_4)$.[2]

The compound (II) clearly provides a model for di-imine-metal derivatives, which have been envisaged to occur as intermediates in dinitrogen fixation.

(*Received*, 13*th December* 1973; *Com.* 1688.)

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