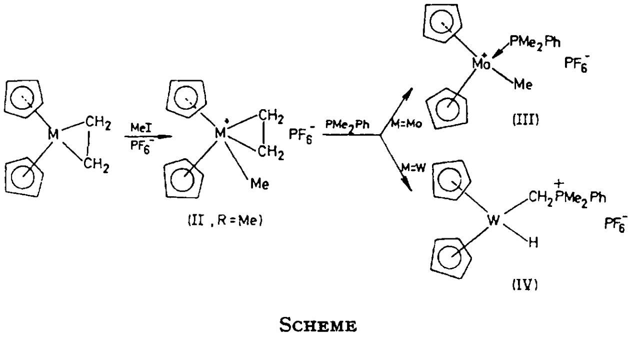
Formation of a Tungsten-substituted Quarternary Phosphonium Derivative by an Unexpected Route

By N. John Cooper and Malcolm L. H. Green*
(*Inorganic Chemistry Laboratory, South Parks Road, Oxford* OX1 3QR)

Summary Treatment of the ethylenemethyl compound $[(\pi\text{-}C_5H_5)_2W(C_2H_4)Me]^+$ PF_6^- with dimethylphenylphosphine gives the compound $[(\pi\text{-}C_5H_5)_2W(CH_2PMe_2Ph)H]^+$ PF_6^- in *ca.* 40% yield.

We have been studying systems of the general type '*cis*'-[M]LX, where [M] represents a complexed transition metal atom, L is an unsaturated hydrocarbon ligand, and X is a σ-bonded hydrocarbon ligand, in order to gain understanding of their mutual interactions and influence. The complexes $[(\pi\text{-}C_5H_5)_2M(CH_2{=}CHR)H]^+$ PF_6^- (M=Mo, R=H or M=W, R=H or Me) have been shown to react readily with triphenylphosphine causing addition of the M–H system to the olefin giving the alkyl derivatives $[(\pi\text{-}C_5H_5)_2M(CH_2\text{-}CH_2R)PPh_3]^+$ PF_6^- (I).[1] The alkylethylene derivatives $[(\pi\text{-}C_5H_5)_2M(CH_2{=}CH_2)R]^+$ PF_6^- (II; M=Mo, R=Me; M=W, R=Me or CH_2Ph) may be readily prepared by treatment of the neutral ethylene complexes $(\pi\text{-}C_5H_5)_2M\text{-}(CH_2{=}CH_2)$ with the corresponding alkyl halides, MeI or $PhCH_2Br$ followed by addition of the PF_6^- anion.[2] We have studied the reaction between the complexes (II; R=Me) and dimethylphenylphosphine. The molybdenum complex (II; M=Mo) reacts smoothly forming the phosphinemethyl compound $[(\pi\text{-}C_5H_5)_2MoMe(PMe_2Ph)]^+$ PF_6^- (III) in *ca.* 60% yield; τ [$(CD_3)_2CO$; 60 MHz]: 2·3—2·6 (5H, complex m, Ph), 4·91 [10H, d, $J[^{31}P\text{–}\pi\text{-}(C_5H_5)]$ 2·1 Hz, 2 × (π-C_5H_5)], 8·05 [6H, d, $J(^{31}P\text{–}Me)$ 9·3 Hz, Me_2P], 9·99 [3H, d, $J(^{31}P\text{-}Me)$ 7·2 Hz, *Me*Mo].



Scheme

There was no evidence for formation of a phosphinepropyl cation, which might have been expected by analogy with the observed insertion of propene into the W–H bond giving the complex (I; M = W, R = Me). The tungsten complex (II; M = W, R=Me) also reacts readily in refluxing acetone (72 h) with dimethylphenylphosphine and ethylene is displaced during the reaction (g.l.c.). Analytical, i.r., and ^1H n.m.r. data show that the yellow, crystalline product (IV) (*ca.* 40%) is not analogous to (III) but rather contains the quarternary phosphonium ligand $\text{–}CH_2P^+Me_2Ph$; τ[$(CD_3)_2$-CO; 60 and 100 MHz]: 2·0—3·0 (5H, complex m, Ph), 5·33 (10H, s, 2 × π-C_5H_5), 8·09 [6H, d, $J(^{31}P\text{–}Me)$ 12·6 Hz, Me], 8·84 [2H, d, $J(^{31}P\text{–}CH_2)$ 13·5 Hz, CH_2], and 22·11 [1H, d, $J(^{31}P\text{–}H)$ 9·7 Hz, WH]. The i.r. spectrum

(Nujol) shows bands characteristic of a (π-C_5H_5)$_2$W system, and also a band at 1938 cm^{-1} assignable to ν_{W-H}.

The structure proposed for the complex (IV) is shown in the Scheme. Although the complex is oxidised in air it is unusually stable for an alkylhydride derivative and there is no evidence for the reductive elimination which would yield the cation [Me_3PPh]$^+$. However, treatment of the complex (IV) with hydrogen chloride immediately precipitates the dichloride (π-C_5H_5)$_2$$WCl_2$ and the salt [Me_3PPh]$^+$ PF_6^- may be isolated from the reaction mixture in good yield. This observation strongly supports the proposed structure.

The mechanism of formation of the complex (IV) is presently unclear and further studies are in progress. We note, however, that substitution at phosphorus has been previously observed in reaction between tertiary-phosphines and nickelmethyl intermediates.[3] Also, a $-CH_2PMe_3$ ligand has recently been found in the compound [Me_3PNiCl-(CH_2PMe_3)$_2$]$^+$$Cl^-$.[4]

(*Received*, 17*th December*, 1973; *Com.* 1699.)

---

[1] F. W. S. Benfield, B. R. Francis, and M. L. H. Green, *J. Organometallic Chem.*, 1972, **44**, C13.
[2] F. W. S. Benfield, N. J. Cooper, and M. L. H. Green, *J. Organometallic Chem.*, submitted for publication.
[3] M. L. H. Green, M. J. Smith, H. Felkin, and G. Swierczewski, *Chem. Comm.*, 1971, 158.
[4] H. H. Karsch and H. Schmidbaur, *Angew. Chem. Internat. Edn.*, 1973, **12**, 853.