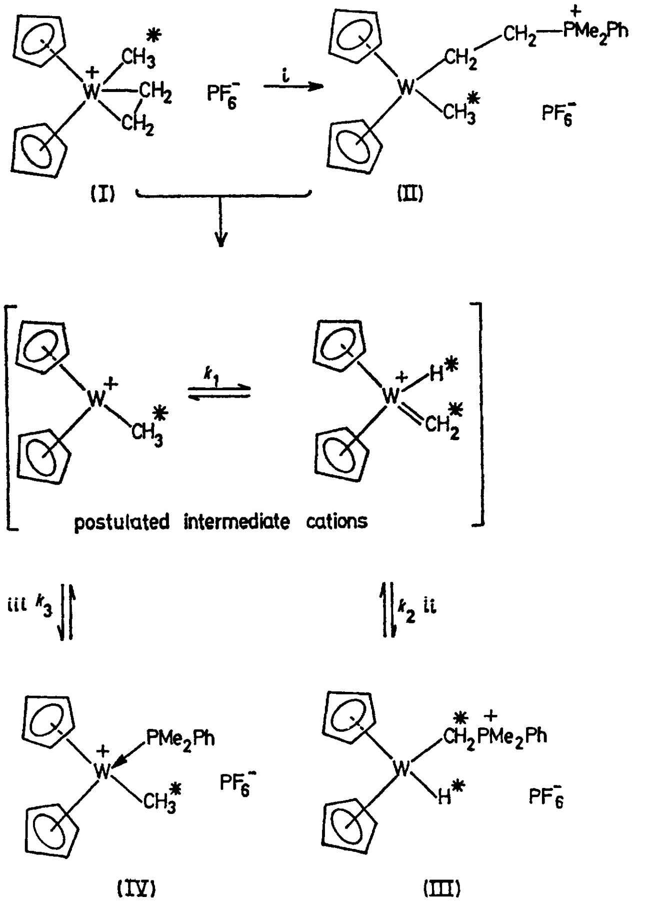
Evidence for Reversible α-Elimination of Hydrogen from a Tungsten–Methyl Compound Giving a Tungsten–Methylene–Hydride Derivative

By N. JOHN COOPER and MALCOLM L. H. GREEN*
(Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR)

Summary The reversible reaction $[W(\eta\text{-}C_5H_5)_2(PR_3)CD_3]^+ \rightleftharpoons [W(\eta\text{-}C_5H_5)_2(CD_2PR_3)D]^+$ and related reactions are described; it is proposed that they proceed *via* a reversible equilibrium $W\text{–}CH_3 \rightleftharpoons W(=CH_2)H$.

TREATMENT of the compound $[W(\eta\text{-}C_5H_5)_2(C_2H_4)Me]^+PF_6^-$ (I)[1] with dimethylphenylphosphine gives, as the first product, orange crystals of $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2PMe_2Ph)\text{-}Me]^+PF_6^-$ (II). The crystal structure of (II) has been determined[2] and is represented in the Scheme. Solutions of (II) in acetone at 70° react over 6 h giving the phosphonium-hydride $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H]^+PF_6^-$ (III) and ethylene is evolved. The formation of (III) has been previously noted.[3] Prolonged heating of (III) in acetone at 70° (14 days) results in yet a further rearrangement giving the methyl derivative $[W(\eta\text{-}C_5H_5)_2(PMe_2Ph)CH_3]^+PF_6^-$ (IV). This unique reaction sequence (I)—(IV) is shown in the Scheme.



SCHEME

* Denotes H or D.

i, PMe_2Ph in acetone, room temp. for 12 h; ii, (II) or (I) with PMe_2Ph, in acetone at 70° for 6 h; iii, (III) in acetone at 70° for 14 days.

When the trideuteriomethyl analogue of (I), namely $[W(\eta\text{-}C_5H_5)_2(C_2H_4)CD_3]^+PF_6^-$ is treated with PMe_2Ph then all the deuterium is retained in the final product $[W(\eta\text{-}C_5H_5)_2(PMe_2Ph)CD_3]^+PF_6^-$; the path of the deuterium is shown in the Scheme.

The observations above are explained by the mechanism given in the Scheme, where we assume $k_1 \gg k_2 \gg k_3$, so the the compounds (II), (III), and (IV) are isolated in the order of their increasing thermodynamic stability, *i.e.*, the system is subject to fortuitious kinetic control.

The mechanism is supported by two independent experiments. The diethyl sulphide compounds $[W(\eta\text{-}C_5H_5)_2(SEt_2)Me]^+PF_6^-$, prepared from (I) and Et_2S, reacts readily with PMe_2Ph (1·5 h at 50°) giving the compound (II) in 70% yield. More directly, treatment of the compound $[W(\eta\text{-}C_5H_5)_2(PPh_3)Me]^+PF_6^-$[1] with PMe_2Ph in acetone at 70° for 8 days gives (II) and (IV) in about equal yields (*ca.* 40%). These reactions provide strong evidence for an equilibrium between the proposed intermediates $[W(\eta\text{-}C_5H_5)_2Me]^+$ and $[W(\eta\text{-}C_5H_5)_2(=CH_2)H]^+$.

The proposal that (III) is formed by nucleophilic attack of PMe_2Ph on the intermediate methylenehydride is also supported by the observation of addition of PMe_2H to the corresponding methylene carbon in $(CO)_5Cr[CPh(OMe)]$.[4]

Reversible elimination of hydrogen from carbon which is in the β-position relative to a transition metal has been widely established to be important in catalytic reactions, such as olefin isomerisation. Hitherto, it has been assumed that the analogous elimination of α-hydrogen was not likely, although there is one example of the abstraction of an α-hydrogen as a hydride.[5] The above observations now strongly suggest that reversible elimination of α-hydrogen may also occur.

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[1] F. W. S. Benfield, N. J. Cooper, and M. L. H. Green, *J. Organometallic Chem.*, 1974, in the press.

[2] R. A. Forder and G. D. Gale, personal communication.

[3] N. J. Cooper and M. L. H. Green, *J.C.S. Chem. Comm.*, 1974, 208.

[4] F. R. Kreissl, C. G. Kreiter, and E. O. Fischer, *Angew. Chem. Internat. Edn.*, 1972, **11**, 643.

[5] A. Sanders, L. Cohen, W. P. Giering, D. Kennedy, and C. V. Magatti, *J. Amer. Chem. Soc.*, 1973, **95**, 5430.