Formation of η-Cyclopentadienylpentahydrido(trimethylphosphine)tungsten from Cyclopentane, Trimethylphosphine, and Tungsten Atoms

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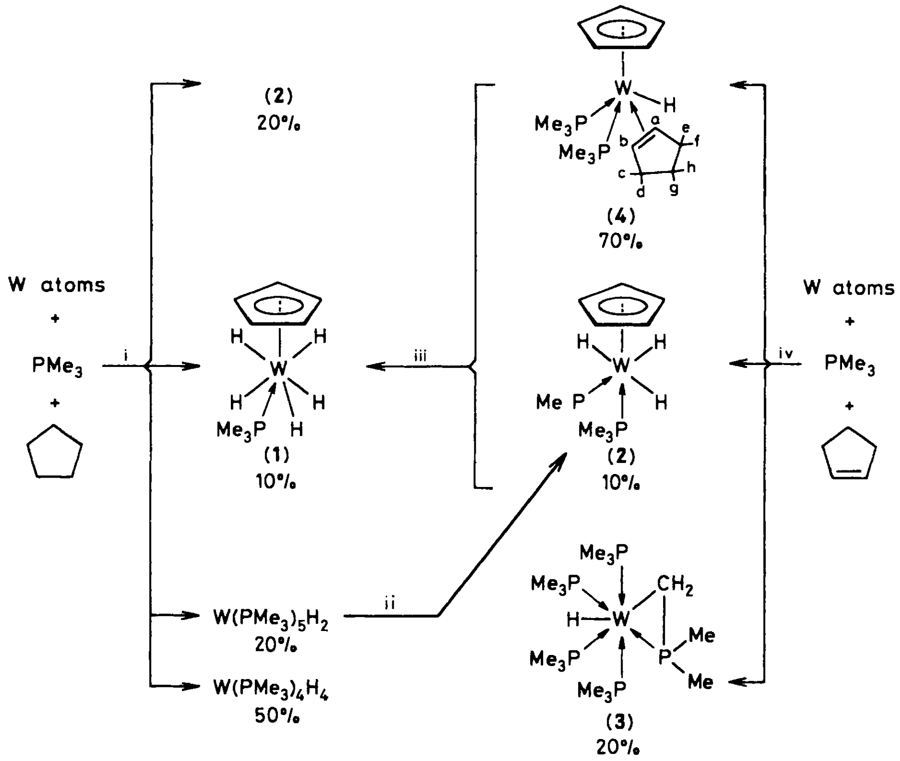
Co-condensation of tungsten atoms with cyclopentane and trimethylphosphine gives *inter alia,* W(η-C_5H_5)(PMe_3)H_5; when cyclopentane is replaced by cyclopentene, W(η-C_5H_5)(PMe_3)$_2H_3$ and W(η-C_5H_5)(PMe_3)$_2$(η-C_5H_8)H are formed which on treatment with dihydrogen form the pentahydride W(η-C_5H_5)(PMe_3)H_5.

Crabtree and Felkin have demonstrated that cyclopentane reacts with iridium and rhenium compounds with formation of (η-C_5H_5)-metal compounds.[1,2] For example, Re(PPh_3)$_2H_7$ in the presence of 3,3-dimethylbut-1-ene in the role of a hydrogen acceptor gives the η-cyclopentadienyl compound Re(η-C_5H_5)(PPh_3)$_2H_2$. These reactions have been shown to be homogeneous.[3,4] Recently, we have found that rhenium atoms react with alkanes in the presence of an excess of benzene forming μ-alkylidene dimers.[5] Reaction between alkanes and atoms of Cu, Fe, and Al have been demonstrated spectroscopically.[6] Here we report on a remarkable reaction between tungsten atoms and cyclopentane.

Tungsten atoms (*ca.* 1.5 g) were co-condensed with cyclopentane and trimethylphosphine (50 cm^3, 5:1). After removal of volatiles, the n.m.r. spectrum of the crude product showed the presence of four compounds. A major component showed three doublets, at δ 4.83, 1.47, and −3.95, assignable to the compound W(η-C_5H_5)(PMe_3)H_5 (**1**). The other bands



Scheme 1. i, co-condensation at −196 °C; ii, cyclopentadiene in benzene at 60 °C; iii, dihydrogen at 50 atm., 60 °C; iv, co-condensation at −196 °C. Relative yields estimated from n.m.r. data.

in the n.m.r. spectrum were assignable by comparison with authentic samples, to the compounds $W(\eta\text{-}C_5H_5)(PMe_3)_2H_3$, (2), $W(PMe_3)_4H_4$,[7] and $W(PMe_3)_5H_2$.[7] Since co-condensation of tungsten atoms with pure PMe_3 gives only $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, (3),[8] the hydrido ligands in (1) and the other products may be presumed to arise from the cyclopentane.

Co-condensation of tungsten atoms with a mixture of cyclopentene and PMe_3 (5:1) gave the compounds $W(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_8)(PMe_3)_2H$, (4), (2), and (3) together with only a trace (<1%) of (1). There was no evidence for the presence of $W(PMe_3)_5H_2$ or $W(PMe_3)_4H_4$.

Treatment of this reaction mixture with dihydrogen at 50 atm. and 60 °C for 3 days gives, after crystallisation, spectroscopically pure (n.m.r.), white crystals of (1). The formulation of (1) is based on the mass spectrum (*m/z* 326, $M^+\{^{184}W\}$ −4H), and detailed n.m.r. studies;† for example, the selectively methyl decoupled ^{31}P n.m.r. spectrum showed a sextet assignable to coupling of the single ^{31}P nucleus to the five W-hydrogens.

The formulation of (2) is based on microanalysis, the mass spectrum (*m/z* 400, $M^+\{^{184}W\}$ −4H), and the n.m.r. data† of a pure sample obtained by the reaction of $W(PMe_3)_5H_2$ with cyclopentadiene. Characterization of (4) is also based upon the mass spectrum (*m/z* 470, $M^+\{^{184}W\}$) and n.m.r. data.†

The structures proposed for the compounds (1), (2), and (4) are shown in Scheme 1. The equivalence at room temperature of the W-hydrogens in (1) and (2) show the compounds to be fluxional, as is normally found for polyhydride compounds.

In conclusion, it seems reasonable to propose that the formation of (1) from cyclopentane proceeds *via* the addition of all five hydrogens from one face of the C_5-ring onto the tungsten in a stepwise intramolecular process. This proposal is supported by the almost complete absence of (1) in the synthesis where cyclopentane is replaced by cyclopentene.

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† *N.m.r. data* (C_6D_6, *J* in Hz). (**1**): ^1H: 4.83 [5H, d, *J*(P–H) 2.1, C_5H_5], 1.47 [9H, d, *J*(P–H) 9.7, PMe_3], −3.95 [5H, d, *J*(P–H) 42.4, *J*(W–H) 42.5, 5W-H]. $^{31}P\{^1H\}$: −22.2 [*J*(P–W) 48.7]; $^{31}P\{Me\}$ −22.2 (sextet). (**2**): ^1H: 4.23 [5H, 4 lines, C_5H_5], 1.44 [18H, d, *J*(P–H) 8.2, $2PMe_3$], −5.27 [3H, t, *J*(P–H) 35, 3W-H]. $^{31}P\{^1H\}$: −26.8 [s, *J*(P–W) 233.8, $2PMe_3$]; $^{31}P\{Me\}$ −26.8 (quartet). (**4**): ^1H: 3.94 [5H, (virtually coupled triplet), *J*′(P–H) 1.9, C_5H_5], 3.14 (2H, br., H_a and H_b), 2.60 (1H, 6 lines, H_g or H_h), 2.16 (4H, br., H_c,H_d,H_e,H_f), 1.05 (18H, br. s, $2PMe_3$), −7.35 [1H, t, *J*(P–H) 14.8, *J*(W–H) 40, W-H]. $^{31}P\{^1H\}$: −36(br.). (Assignments made in conjunction with double resonance experiments.)