

Lability of Tertiary Phosphine Groups of Tertiary Phosphidomethyl Derivatives of Tungsten

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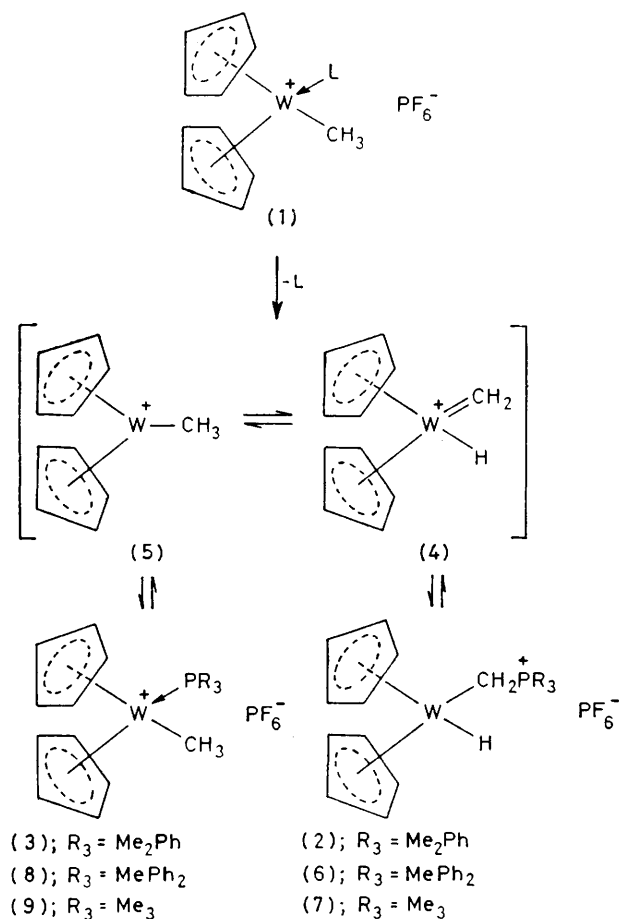
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Summary The rate of the thermal rearrangement of the compounds $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{CH}_2\text{PR}_3)]\text{PF}_6$ to $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}(\text{PR}_3)]\text{PF}_6$ increases in the order $\text{R}_3 = \text{Ph}_2\text{Me} > \text{PhMe}_2 > \text{Me}_3$, and when $\text{R}_3 = \text{Me}_3$ the two compounds are found to be in equilibrium in solution; when $\text{R}_3 = \text{Ph}_2\text{Me}$ the PMePh_2 group exchanges with added PMe_3 giving $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{CH}_2\text{PMe}_3)]\text{PF}_6$.

PREVIOUSLY we have shown that treatment of the compound $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{MeL}]\text{PF}_6$ (**1**), where $\text{L} = \text{C}_2\text{H}_4$, Et_2S , or Ph_3P , with dimethylphenylphosphine gives the dimethylphenylphosphidomethyl derivative $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{CH}_2\text{PMe}_2\text{-Ph})]\text{PF}_6$ (**2**).¹ Thermolysis of (**2**) at 70 °C in acetone results in slow, quantitative conversion into the methyl compound (**3**). It was proposed that the key intermediate in this reaction was the hydrido carbene (**4**) formed by a reversible 1,2-hydrogen shift (α -elimination) from the methyl cation (**5**) (Scheme 1).¹ Here we describe experiments designed to evaluate this mechanism more broadly. Treatment of (**1**, $\text{L} = \text{C}_2\text{H}_4$ or I^-) with PMePh_2 or PMe_3 gives the tertiary phosphidomethyl complexes (**6**) and (**7**), respectively, which

are analogous to (**2**). Thermolysis of (**6**) and (**7**) in acetone causes rearrangement giving the corresponding methyl derivatives (**8**) and (**9**), respectively. The rate at which (**2**), (**6**), and (**7**) rearrange to the corresponding methyl compounds decreases substantially with increasing alkylation of the tertiary phosphido group. For example, rearrangement of (**6**) to (**8**) at 65 °C occurs essentially quantitatively within 24 h whilst rearrangement of (**7**) to (**9**) at 70 °C gives only 28% of (**9**) after 14 days. A pure sample of (**9**) was prepared by treatment of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{PMe}_3)]\text{PF}_6$ with methylmagnesium bromide. Thermolysis of pure (**9**) in acetone at 70 °C results in slow formation of an equilibrium mixture of (**9**) and (**7**). The final equilibrium concentration ratio of (**9**) and (**7**) approaches that obtained from the thermolysis of (**7**) (**9**:**7**, 28:72). It is clear that solutions of (**7**) and (**9**) are thermally equilibrating.

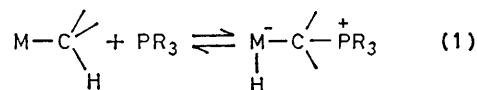
Treatment of (**6**) with an excess of PMe_2Ph or PMe_3 in acetone at 70 °C results in steady formation of (**2**) and (**7**), respectively. The reactions were monitored by ¹H n.m.r. spectroscopy, and clearly there is a smooth and essentially quantitative conversion of (**6**) into (**2**) (and **7**; 41%).



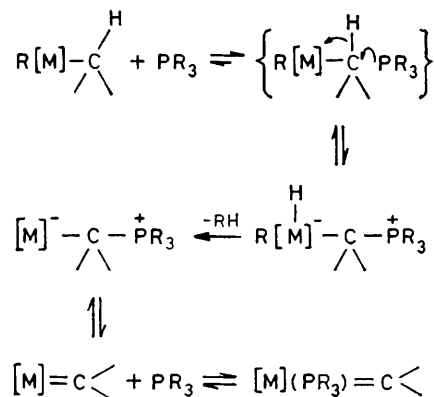
SCHEME 1

The above reactions may be readily understood in the light of the mechanism shown in Scheme 1. For example, the conversion of (6) into (7) is consistent with the relatively easy dissociation to the PMePh_2 group and the trapping of the resulting hydridocarbene intermediate (4) by PMe_3 giving the less labile compound (7). The reversible dissociation of an R_3P group from the system MCH_2PR_3 is

reminiscent of the lability of other α -methyl substituents, for example, in the compounds $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{CH}_2\text{X}$ ($\text{X} = \text{Cl}$ or OMe), for which carbene intermediates have been proposed and are believed to arise *via* induced dissociation of the X ligands.² The reversible addition of tertiary phosphines to the carbene intermediate (4) may be viewed as a means of assisting the 1,2-hydrogen shift equilibrium between (4) and (5), *e.g.* equation (1). This reaction, in



effect a 1,2-hydride ion shift, may be a key step in the formation of carbenes from d^0 transition metal alkyls *via* alkane elimination reactions, associated with the presence of tertiary phosphine ligands,³ *e.g.* Scheme 2.



SCHEME 2

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