acetate = 70/30) to afford 220 mg (74%) of **10**: IR (CCl_4) 3030, 3000–2900, 1765, 1740, 1460, 1440, 1330, 1235, 1200, 1150, 1080, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.71 (m, 2 H, CH=CH), 3.72 (s, 3 H, OMe), 3.70 (s, 3 H, OMe), 3.51 (s, 1 H, *CH*(COOMe)$_2$), 3.20 (s, 3 H, OMe), 2.36–2.24 (m, 1 H), 2.1–1.97 (m, 1 H), 1.75–1.27 (m, 3 H), 1.24 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3).

Anal. Calcd for $C_{16}H_{26}O_5$: C, 64.41; H, 8.78. Found: C, 63.88; H, 8.59.

Oxidation of 2 to 11. To a solution of 983 mg (3.3 mmol) of $Na_2Cr_2O_7 \cdot 2H_2O$ in sulfuric acid (0.7 mL)–water (3.6 mL)–ether (10 mL) was added 563 mg (0.9 mmol) of complex **2**. The mixture was stirred at ambient temperature for 2 h and then extracted with ether. The combined organic layers were washed with water and dried ($MgSO_4$). The solvent was removed on a rotary evaporator in vacuo, and the residue was purified by flash column chromatography (silica, pentane/ether = 80/20) affording 83 mg (25%) of **11** as a colorless liquid: $[\alpha]^{20}_D$ +39.6° ($CHCl_3$); IR (CCl_4) 3040, 2980, 2940, 2880, 1675, 1645, 1545, 1385, 1370, 1210, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.80 (br s, 1 H, CH=C), 2.58 (m, 2 H), 2.45–2.35 (m, 2 H), 2.01 (m, 1 H), 1.94 (br s, 3 H, CH_3C=C), 1.91 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3).

Catalytic Hydrogenation of 11. Neomenthol (12) and Neoisomenthol (13). Ketone **11** (70 mg, 0.37 mmol) and Platinum black[21] (7 mg, 0.036 mmol) were stirred in acetic acid (0.7 mL) under an atmospheric pressure of hydrogen at ambient temperature for 8 h. The reaction mixture was filtered, and the precipitate was washed with ether (5 mL). Water (2 mL) and saturated NaCl solution (2 mL) were added, and the mixture was stirred in a separatory funnel. After collection of the organic layer the aqueous phase was further extracted with ether (2 × 5 mL). The combined organic layers were washed with water (2 mL) and 2 M $NaHCO_3$ (2 × 2 mL) and dried ($MgSO_4$). Rotary evaporation of the solvent in vacuo afforded 54 mg (92%) of menthol isomers. According to ^1H NMR the main components (>90%) were neomenthol (**12**)[22] and neoisomenthol (**13**)[23] in a ratio of 3:1. Small amounts of menthol[24] (5–10%) could be detected in the ^1H NMR spectrum. Distinguishable signals in the ^1H NMR ($CDCl_3$): neomenthol, δ 4.12 (CHO); neoisomenthol, δ 4.03 (CHO); menthol, δ 3.45 (CHO).

Reduction of 7 with $LiAlH_4$. α-Terpineol (14) and 15. To a solution of **7** (100 mg, 0.15 mmol) in anhydrous THF (2 mL) under nitrogen at −78 °C was added 27 mg (0.7 mmol) of $LiAlH_4$. Ethene was bubbled through the solution, which was stirred for 2 h at −78 °C and then for 1 h at −30 °C. The mixture was allowed to slowly warm up to 0 °C (1–2 h) and then quenched with water and 2 M NaOH. The precipitate was removed by filtration and washed several times with ether. The organic phase of the filtrate was collected, and the aqueous phase was extracted with ether. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo on a rotary evaporator to afford 45 mg (98%) of a 3:1 mixture of **14** and **15** according to ^1H NMR. The products were separated and purified by HPLC (hexane/ethyl acetate = 90/10). The main product was shown to be **14**, whose ^1H NMR spectrum and specific rotation are consistent with that of an authentic sample of (+)-α-terpineol: $[\alpha]^{20}_D$ +96.9° (EtOH) (lit.[15] $[\alpha]^{20}_D$ +98.4° (EtOH)).

15:[25] ^1H NMR ($CDCl_3$) δ 5.85–5.65 (m, 2 H, CH=CH), 2.3–2.05 (m, 2 H, allylic CH), 1.8–1.35 (m, 4 H, CH_2CH_2), 1.30 (br s, 1 H, OH), 1.21 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 0.98 (d, 3 H, CH_3).

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Registry No. **1**, 4497-92-1; **2**, 82740-38-3; **3**, 82740-39-4; **4**, 96395-36-7; **5**, 96411-95-9; **6**, 96411-96-0; **7**, 96411-97-1; **8**, 58865-12-6; **8**-d_1, 96395-37-8; **9**, 82795-79-7; **9**-d_1, 96395-38-9; **10**, 96395-39-0; **11**, 96395-40-3; **12**, 2216-52-6; **13**, 64282-88-8; **14**, 7785-53-7; **15**, 23727-04-0.

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A Kinetic Study of the 1,2-Hydrogen Shift in a Bis(η-cyclopentadienyl)tungsten System

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The rate of the thermal isomerization of $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+$ (A) to $[W(\eta\text{-}C_5H_5)_2(CH_3)(PMe_2Ph)]^+$ (B) in acetone solution with hexafluorophosphate as counterion has been measured under a variety of conditions. The rate is found to be first order in *A* ($k_{70°C}$ = (3.2 ± 0.08) × 10^{-6} s^{-1}), strongly temperature dependent (E_A = 144.7 ± 3.6 kJ mol^{-1}), essentially independent of free phosphine concentration, and enhanced by deuteration of the "active" methyl group (k_H/k_D(70 °C) = 0.80 ± 0.02). Hydrogen migration is involved in the rate-determining transition state of the reaction, and simple reversible phosphine dissociation to a cationic metal carbene intermediate is too simple a mechanism to account for all the results. Two alternative mechanisms are proposed, one involves the formation of an agostic methyl intermediate, $[W(\eta\text{-}C_5H_5)_2(CH_2)(\mu\text{-}H)]^+$, and the other an equilibrium between a carbene hydride, $[W(\eta\text{-}C_5H_5)_2(CH_2)(H)]^+$, and a methyl cation, $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$.

Introduction

The 1,2-hydrogen shift (α-elimination) has lately become recognized as an important mechanistic possibility in organo-transition-metal chemistry and in at least one case[1] has been observed directly. Recent work by several authors, reviewed by Brookhart and Green,[2] has demonstrated that such a hydrogen transfer from ligand to metal in transition-metal hydrocarbyl complexes may often

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0276-7333/85/2304-1302$01.50/0

Table I

sample no.	concn of $[Cp_2W(X)CX_2PMe_2Ph]^+$, mol dm^{-3}	X	concn of PMe_2Ph,[a] mol dm^{-3}	temp, °C (±0.25 °C)	10^5 k_{obsd},[b] s^{-1}
1	0.050	H		63.7	0.1186
2	0.047	D		63.7	0.1479
3	0.156	H		78.2	1.025
4	0.085	H		79.8	1.336
5	0.167	H		84.1	2.439
6	0.104	D		84.1	2.970
7	0.091	H		90.8	5.704
8	0.097	H	0.019	90.8	5.341
9	0.112	H	0.187	90.8	5.254
10	0.118	H	0.301	90.8	5.219
11	0.153	D		90.8	9.642

[a] Higher concentrations of PMe_2Ph could not be used owing to insolubility. [b] Observed first-order rate constant, ±2.5%.

proceed via an intermediate where the hydrogen is bridging the metal–carbon bond and that in some cases this may be the ground state of the system.[3] They have coined the term "agostic" to describe this covalent interaction between a carbon–hydrogen group and a metal center.

1,2-Hydrogen shift equilibria have previously been invoked to explain several reactions of bis(η-cyclopentadienyl)alkyltungsten systems.[4] In particular the preparation of $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PR_3)]^+$ (R_3 = Me_3, Me_2Ph, $MePh_2$) from precursors of the form $[W(\eta\text{-}C_5H_5)_2(L)(CH_3)]^+$ (L = C_2H_4, SEt_2, PPh_3) and its thermal conversion to $[W(\mu\text{-}C_5H_5)_2(CH_3)(PR_3)]^+$ have received intensive study. We have undertaken kinetic studies of this last reaction (R_3 = Me_2Ph) in order to gain further insight into its mechanism and in particular to test for the presence of an "agostic"[2] intermediate.

Experimental Section

$[W(\eta\text{-}C_5H_5)_2(X)(CX_2PMe_2Ph)]^+[PF_6]^-$ (X = H or D) was prepared by a method which avoided the intermediacy of $[W(\eta\text{-}C_5H_5)_2(CH_3)(CH_2CH_2PMe_2Ph)]^+[PF_6]^-$ as this assured greater isomeric purity. The method employed was analogous to that used by Canestrari and Green to obtain $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PR_3)]^+[PF_6]^-$ (R_3 = Me_3, $MePh_2$),[4b] that is

$$W(\eta\text{-}C_5H_5)_2(I)(CH_3) \xrightarrow[\text{(ii) } H_2O/NH_4PF_6]{\text{(i) } PMe_2Ph/Me_2CO} A$$

$W(\eta\text{-}C_5H_5)_2(I)(CH_3)$ (2.28 g, 5 mmol) was dissolved in acetone (dried by distillation under dinitrogen off 4-Å molecular sieves, 100 mL) and treated with PMe_2Ph (3.2 g, 23 mmol). The mixture was refluxed for 5 h, then allowed to cool, and left to stir overnight. After this time the initial dark green color of the solution had changed to orange. The solvent was removed by distillation under reduced pressure and the oily residue washed three times with toluene to remove unreacted starting materials. The residue was dissolved in acetone (20 mL) and water added (100 mL). The acetone was then distilled off under reduced pressure to leave an orange-brown aqueous solution. This was filtered off and the residue extracted twice more with the same technique. To the combined filtrates was added excess aqueous ammonium hexafluorophosphate to produce an immediate precipitate. This was allowed to settle, then collected by filtration, and washed three further times with water. Recrystallization, from a mixture of acetone and ethanol, gave orange-brown needles of $[W(\eta\text{-}C_5H_5)(H)(CH_2PMe_2Ph)]^+[PF_6]^-$, yield 2.00 g (3.23 mmol, 65%).

The following technique was used to determine the rate of the thermally induced conversion of A to B. The tungsten-containing compound was dried at 50 °C and a pressure of 10^{-2} mbar for 6 h immediately before use. A sample was then weighed out accurately in a Vacuum Atmospheres He-43-2 drybox under an atmosphere of dinitrogen. A measured quantity of acetone-d_6, purified by repeated distillation from 4-Å molecular sieves, was distilled onto the sample under reduced pressure, as was dimethylphenylphosphine when required. The solution was then filtered into an NMR tube, and this sealed off at a pressure of 10^{-1} mbar, with the solution at −196 °C.

After the mixture was warmed to room temperature, the ^1H NMR spectrum of the sample was recorded by using a JEOL JNMPMX-60MHz spectrometer. The sample was then heated to the desired temperature in an insulated oil bath, which was isothermal to within 0.5 °C.

The ^1H NMR spectrum of the sample was monitored at room temperature at intervals. Because the rate of reaction is negligible at room temperature, the integration of the spectrum could be used as a measure of the relative concentration of each component. The resonances of the cyclopentadienyl protons were most conveniently used, as the bands are sharp and well separated.

Integration of the spectrum could also be used to check the relative concentration of the added tertiary phosphine.

Apart from the conversion of A to B there was no evidence from ^1H NMR data, or by inspection, for side reactions or decomposition.

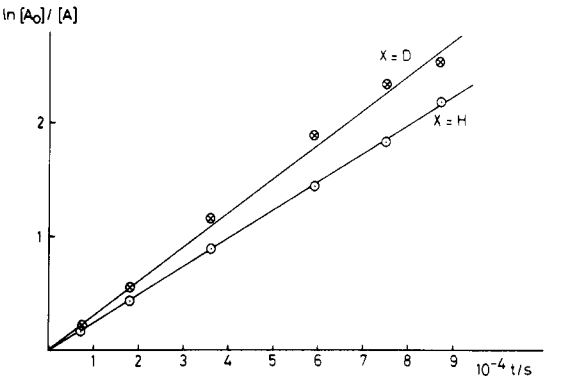

Figure 1. Plot of ln $[A_0]/[A]$ vs. t for $[W(\eta\text{-}C_5H_5)_2(X)(CX_2PMe_2Ph)]^+$ at 84.1 °C where X = H (sample no. 5) and X = D (sample no. 6).

Results

The rate of thermal conversion of $[W(\eta\text{-}C_5H_5)_2(X)(CX_2PMe_2Ph)]^+$ (A) to $[W(\eta\text{-}C_5H_5)_2(CX_3)(PMe_2Ph)]^+$ (B) (X = H or D) was studied in perdeuterioacetone solution with hexafluorophosphate as counterion under a variety of conditions of temperature and added phosphine concentration. Observation was maintained over 3–4 half-lives. Plots of the logarithm of $[A_0]/[A]$ as determined by ^1H NMR spectroscopy against time were linear, establishing first-order behavior of the reaction under all conditions studied. Typical results where X = H and D at T = 84.1 °C are shown in Figure 1. The observed first-order rate constant, k_{obsd}, was the gradient of each plot.

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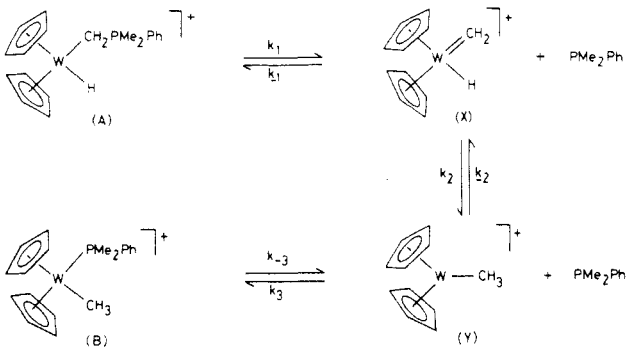
Scheme I



These results are summarized in Table I.

An Arrhenius plot of log k_{obsd} vs. $1/T$ yielded an activation energy for the process of 144.1 ± 3.6 kJ mol^{-1}. The Eyring equation

$$k_{obsd} = (RT/Nh)e^{-\Delta H^{\ddagger}/RT}e^{\Delta S^{\ddagger}/R}$$

was similarly used to obtain values for the enthalpy and entropy of activation by plotting log k_{obsd}/T vs. $1/T$ (see Figure 2). This graph gave $\Delta H^{\ddagger}$ = 141.7 ± 3.5 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 61.7 ± 1.5 J mol^{-1} K^{-1}.

The kinetic isotope effect at the three temperatures studied was $k_{obsd}(H)/k_{obsd}(D)$ = 0.86 (90.8 °C), 0.82 (84.1 °C), and 0.80 (63.7 °C).

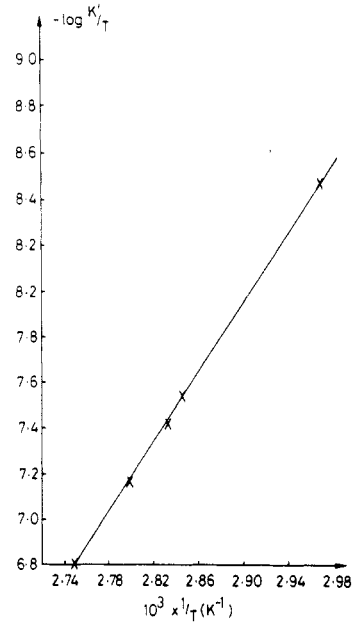


Figure 2. Eyring plot of $-\log k'/T$ vs. $1/T$.

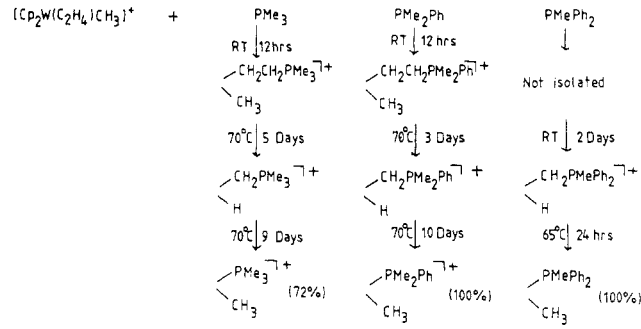


Figure 3. Products of the reaction of $[W(\eta\text{-}C_5H_5)_2(C_2H_4)(CH_3)]^+$ with various tertiary phosphines.[4a-c]

Discussion

Reaction of $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)(CH_3)]^+$ with phosphines gives a number of isolable products, the relative proportions of which are a function of time and of the attacking phosphine. The results are summarized in Figure 3. Other starting materials such as $[W(\eta\text{-}C_5H_5)_2(CH_3)I]$ also give rise to the same products suggesting that all reactions give rise to a common intermediate "$[W(\eta\text{-}C_5H_5)_2CH_3]^+$", which may react with phosphine to produce either the hydride product $[W(\eta\text{-}C_5H_5)_2(CH_2PR_3)H]^+$ or the methyl product $[W(\eta\text{-}C_5H_5)_2(CH_3)(PR_3)]^+$, the eventual ratio of these two being thermodynamically controlled. A bimolecular intermediate is excluded by the following experiment.[4b]

$$[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)CH_3]^+ \xrightarrow[Me_2CO]{PMe_2Ph} \text{only } [W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H]^+$$
$$+ [W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)CD_3]^+ \text{ and } [W(\eta\text{-}C_5H_5)_2(CD_2PMe_2Ph)D]^+$$

Phosphine exchange reactions of the hydride and methyl products have also been studied; for example, PMe_2Ph will react with $[W(\eta\text{-}C_5H_5)_2(CH_3)(PPh_3)]^+$ to give a 50:50 mixture of $[W(\eta\text{-}C_5H_5)_2(CH_3)(PMe_2Ph)]^+$ and $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H]^+$ after 8 days.[4e]

The mechanism for the interconversion of A and B shown in Scheme I has been suggested previously.[4a,b]

Assuming the steady-state approximation for the concentrations of the intermediates leads to the rate expression

$$-\frac{d[A]}{dt} = \frac{k_1k_2k_3[A] - k_{-1}k_{-2}k_{-3}[B]}{k_{-1}k_{-2} + k_2k_3 + k_{-1}k_3[PR_3]}$$

At equilibrium the concentration of A is near zero so that k_{-3} = 0. k_{-1} is assumed to be nonzero because of the formation of A from a variety of methyl starting products $[W(\eta\text{-}C_5H_5)_2(CH_3)L]^{n+}$ and from phosphine exchange reactions. Hence

$$-\frac{d[A]}{dt} = \frac{k_1k_2k_3[A]}{k_{-1}k_{-2} + k_2k_3 + k_{-1}k_3[PR_3]}$$

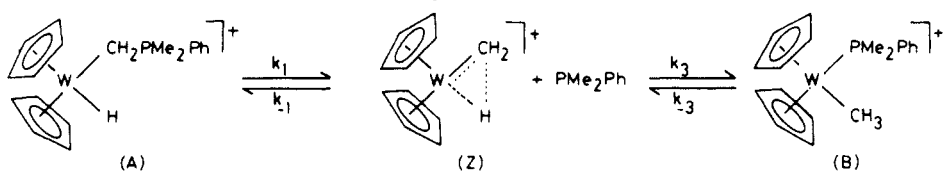
If the concentration of free phosphine is constant, then

$$\log_e [A] = kt + c \qquad [1]$$

where $k = k_1k_2k_3/(k_{-1}k_{-2} + k_2k_3 + k_{-1}k_3[PR_3])$ and c = integration constant. In the light of the observations that (i) thermal decomposition of $[W(\eta\text{-}C_5H_5)_2(D)(CD_2PMe_2Ph)]^+$ leads only to $[W(\eta\text{-}C_5H_5)_2(CD_3)(PMe_2Ph)]^+$ and (ii) thermolysis of a mixture of $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+$ and $[W(\eta\text{-}C_5H_5)_2(D)(CD_2PMe_2Ph)]^+$ leads only to $[W(\eta\text{-}C_5H_5)_2(CH_3)(PMe_2Ph)]^+$ and $[W(\eta\text{-}C_5H_5)_2(CD_3)(PMe_2Ph)]^+$, only one other mechanism readily suggests itself: one that involves the "agostic" intermediate $[W(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(CH_2)]^+$ (Scheme II).

In this case assuming the steady-state approximation for the concentration of the intermediate, and knowing k_{-3}

Scheme II



= 0, leads to

$$-\frac{d[A]}{dt} = \frac{k_1k_3[A]}{-k_{-1} + k_3}$$

so that

$$\log_e [A] = k't + c'$$

where $k' = k_1k_3/(k_{-1} + k_3)$ and c' = integration constant. Both these two mechanisms are obviously in accord with the observed first order kinetics. They differ in that the rate constant of [1] involves the concentration of free phosphine whereas that of [2] does not. However the rate expressions are effectively equivalent if the equilibrium between the intermediates of Scheme I (X and Y) is sufficiently rapid:

$$k = \frac{k_1k_2k_3}{k_{-1}k_{-2} + k_2k_3 + k_{-1}k_3[PR_3]}$$

If k_{-2} and k_2 are large, then $k_{-1}k_{-2} + k_2k_3 >> k_{-1}k_3[PR_3]$ and

$$k = \frac{k_1k_2k_3}{k_{-1}k_{-2} + k_2k_3}$$

Let $K = k_2/k_{-2}$:

$$k = \frac{k_1k_3K}{k_{-1} + k_3K}$$

The absence of the predicted inverse dependence of the rate constant on phosphine [The variation observed is within experimental error at nonzero phosphine concentrations. There is a 5% acceleration at zero phosphine concentration.] rules out a slow equilibrium between X and Y in Scheme I but cannot distinguish between a fast equilibrium between X and Y in Schemes I and II.

The values of the activation parameters suggest that the rate-determining step of the reaction is a dissociative one. In both mechanisms this may be identified with the dissociation of phosphine from A to yield an intermediate (X or Z). The value of $\Delta H^\ddagger$ may be compared with that of the phosphorus–carbon bond in PMe_3 which is 273.2 kJ mol^{-1},[5] and the value of $\Delta S^\ddagger$ is well within the range expected for a step leading from one to two molecular fragments.

The reaction is unusual, in exhibiting an inverse kinetic isotope effect, which decreases with increasing temperature, as would be expected from the Arrhenius equation. It is possible that this inverse isotope effect is a primary one involving a transition state in which the tungsten–hydrogen bond is weakened and a carbon–hydrogen bond is partially formed, tungsten–hydrogen stretching frequencies being appreciably lower than carbon–hydrogen ones. Such a inverse primary effect has been found for the addition of $Mn(CO)_5H$ to α-methylstyrene.[6] The high activation enthalpy and large positive activation entropy found for the reaction studied here imply that the transition state is more like the product X or Z than the precursor A. In the mechanism proposed in Scheme II k_1 would be expected to increase on deuteration consistent with the inverse isotope effect found. The rate constant for the mechanism in Scheme I is given by $(k_1k_3K/(k_{-1} + k_3K))$; the effect of deuteration will be to increase K, the equilibrium constant between the two proposed intermediates X and Y. Deuteration should favor Y, the methyl compound, as opposed to X, the hydride compound, as the former has the more energetic hydrogen stretch. The situation is not clear-cut as K also appears on the denominator of the expression for k', but overall k' would be expected to increase on deuteration. We should also consider the possibility that the inverse effect might well be a secondary one. These have been found associated with rehybridization (e.g., from sp^2 to sp^3 at carbon) of atoms bearing hydrogen, in the formation of the transition state of the rate-determining step of the reaction. Now, the rehybridization necessary for the process A → X (sp^3 to sp^2) would produce a normal isotope effect, the opposite to that observed.

Thus, although Scheme II with the agostic intermediate gives a more direct interpretation of the inverse isotope effect, Scheme I is also consistent with the observations.

Conclusion

The rate and isotope studies have shown that the α-elimination or 1,2-hydrogen shift reaction

$$[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+ \rightarrow \cdot[W(\eta\text{-}C_5H_5)_2(PMe_2Ph)CH_3]^+$$

is a first-order reaction, with no dependence on added phosphine concentration over the concentration range studied, and hydrogen migration is involved in the rate-determining transition state. Mechanistic considerations show these facts to be consistent with either dissociation of the phosphine to an agostic methyl intermediate or to a carbene hydride in rapid equilibrium with a methyl compound. In both cases the inverse isotope effect is accounted for by partial C–H bond formation in the transition state. The data rule out simple dissociation to a carbene hydride intermediate or a slow equilibrium between this and a methyl intermediate.

Acknowledgment is made to the SERC for a grant (to C.P. Morley) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support. We should also like to thank Dr. R. G. Bergmann for helpful comments.

Registry No. A·PF_6, 53232-00-1; B·PF_6, 71531-98-1; W(η-C_5H_5)$_2$(I)(CH_3), 71531-99-2; PMe_2Ph, 672-66-2.

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