Evidence for a Reversible 1,2-Hydrogen Shift (α Elimination) in Some Bis-(η-cyclopentadienyl)tungsten Compounds

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The reaction of $[W(\eta\text{-}C_5H_5)_2(C_2H_4)Me][PF_6]$ with PMe_2Ph gives $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2PMe_2Ph)Me][PF_6]$ (2) which eliminates ethylene when heated to give, in sequence, $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H][PF_6]$ (3) and $[W(\eta\text{-}C_5H_5)_2Me(PMe_2Ph)][PF_6]$ (4). Repeating this sequence with the deuteriated methyl analogues shows that the CD_3 unit in (2) is reformed quantitatively in (4) and supports the proposal that the mechanism of the reaction involves a reversible 1,2-hydrogen shift equilibrium between the intermediates $[W(\eta\text{-}C_5H_5)_2Me]^+$ and $[W(\eta\text{-}C_5H_5)_2(CH_2)H]^+$. The compounds $[W(\eta\text{-}C_5H_5)_2L(Me)]$ (L = SEt_2 or PPh_3) and $[W(\eta\text{-}C_5H_5)_2Me(I)]$ have also been prepared and treated with PMe_2Ph to give (3). Some implications of the 1,2-hydrogen shift (α elimination) are discussed.

THE bis-η-cyclopentadienyl complexes of molybdenum and tungsten form an extensive system of related compounds in which the metal has an 18-electron, or occasionally 17-electron, configuration. These species can be represented by the general formulae $[M(\eta\text{-}C_5H_5)_2X(Y)]$, $[M(\eta\text{-}C_5H_5)_2L(X)]^+$, $[M(\eta\text{-}C_5H_5)_2L]$, $[M(\eta\text{-}C_5H_5)_2X(Y)]^+$, and $[M(\eta\text{-}C_5H_5)_2X(Y)Z]^+$, in which X, Y, and Z represent σ-bonded one-electron ligands and L represents two-electron donor ligands such as olefins, amines, or tertiary phosphines.[1] The stereochemistry of these compounds has been firmly established experimentally by single-crystal *X*-ray diffraction studies[2] and interpreted in terms of molecular-orbital bonding schemes in which the orbitals involved in the bonding of the X, Y, Z, and L ligands to the metal are derived mainly from the d_{xy}, $d_{x^2-y^2}$, and d_{z^2} orbitals.[3,4] These ligands are essentially *cis* orientated with respect to each other and provide an unusual opportunity to investigate the reactions and interactions of a wide range of ligands.

We have previously shown that the ethylene hydrido-compound $[W(\eta\text{-}C_5H_5)_2(C_2H_4)H][PF_6]$ reacts with the tertiary phosphine PMe_2Ph to give the ethyl compound $[W(\eta\text{-}C_5H_5)_2Et(PMe_2Ph)][PF_6]$ in which the ethylene ligand has inserted into the W–H bond, and we were interested to discover whether the ethylene ligand in the isoelectronic $[W(\eta\text{-}C_5H_5)_2(C_2H_4)Me][PF_6]$[5,6] (1) would undergo a similar insertion into the W–Me bond to give the propyl compound $[W(\eta\text{-}C_5H_5)_2Pr(PMe_2Ph)][PF_6]$ when treated with PMe_2Ph. Similar insertion reactions are widely believed to form the key chain-growth step in Ziegler–Natta polymerization of alkenes,[7] but there is no well established example of a stoicheiometric insertion reaction involving a simple alkene which does not carry electron-withdrawing constituents.

The first product to be isolated from the reaction of (1) with PMe_2Ph was neither the propyl derivative expected as the product of the insertion reaction nor $[W(\eta\text{-}C_5H_5)_2Me(PMe_2Ph)][PF_6]$, the simple replacement product, but the surprising phosphonium hydride salt $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H][PF_6]$. This reaction has now been investigated in some detail and our findings in this area are reported in this paper. A preliminary account of this work has appeared.[8]

RESULTS

Treatment of the compound $[W(\eta\text{-}C_5H_5)_2(C_2H_4)Me][PF_6]$ (1) in acetone with dimethylphenylphosphine at room temperature produced a rapid colour change of the solution from yellow to orange. After 12 h, orange plates were isolated from the mixture which the data given in the Table show to be the compound $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2PMe_2Ph)Me][PF_6]$ (2). A noticeable feature of the ^1H n.m.r. spectrum of (2) was that, despite considerable precautions to exclude oxygen during the filling and sealing of the n.m.r. tube *in vacuo*, the spectrum of freshly prepared solutions invariably showed considerable line broadening. When sealed solutions were left to stand overnight the linewidths reduced to normal values, *e.g.* $W_{\frac{1}{2}}$ for the $\eta\text{-}C_5H_5$ resonance was 6 Hz. The line-broadening effect varied considerably for different resonances, *e.g.* the $\eta\text{-}C_5H_5$ absorptions were markedly broader than the PMe_2 absorptions. There was no observable broadening of the solvent resonances. We conclude that, despite our precautions, the line-broadening is due to the presence of trace amounts of paramagnetic impurities which decompose with time to non-interfering species. The sharp line spectrum of (2) showed complex absorptions centred at τ 7.18 and 9.57 assignable to the CH_2P and WCH_2 hydrogens. In support of these assignments, irradiation of the band at τ 7.18 caused the complex band at τ 9.57 to collapse to a doublet [$J(^{31}P\text{–}H)$ 9.6 Hz], whilst irradiation at τ 9.57 caused the multiplet at τ 7.18 to change to a doublet [$J(^{31}P\text{–}H)$ 10.0 Hz]. These values for $J(^{31}P\text{–}H)$ are well within the range quoted for two- and three-bond ^{31}P–H coupling constants.[9] The ^{13}C n.m.r. spectrum of (2) also supports the proposed structure. The crystal structure of (2) has been determined and it is the same as that found from solution studies.[10] The formation of (2) from (1) may be regarded as proceeding *via* nucleophilic attack on the co-ordinated ethylene ligand. Similar reactions are well documented in a variety of systems.[11,12]

A solution of (2) in acetone was warmed to 70 °C for 8 h and the ^1H n.m.r. spectrum was determined at intervals. The spectra conclusively show a steady disappearance of (2) with evolution of ethylene (confirmed by g.l.c.) and the simultaneous appearance of a new compound which was identified as $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H][PF_6]$ (3), which had previously been prepared by heating (1) under reflux with PMe_2Ph in acetone for 2 d. Compound (3) was characterized by the data in the Table and the structure was confirmed by treatment of (3) with an excess of HCl which gives the compounds $[W(\eta\text{-}C_5H_5)_2Cl_2]$ and $[PMe_3Ph]$-

Analytical and hydrogen-1 n.m.r. data

Compound	Colour	Analytical data (%)		Hydrogen-1 n.m.r. data [a]
		C	H	
(2) $[W(\eta-C_5H_5)_2(CH_2CH_2PMe_2Ph)Me][PF_6]$	Orange	39.5 (39.4)	4.4 (4.4) [b]	1.8—2.6, **5**, *c*, Ph; 5.40, **10**, *s*, $(\eta-C_5H_5)_2$; 7.18, **2**, *c*, CH_2P; 7.76, **6**, *d* [J(H–P) 13.8], PMe_2; 9.57, **2**, *c*, WCH_2; 10.25, **3**, *s* [satellites, J(W–H) 5.7], W–Me [c]
(3) $[W(\eta-C_5H_5)_2(CH_2PMe_2Ph)H][PF_6]$	Orange	37.3 (37.2)	4.1 (3.9)	3—5, **5**, *c*, Ph; 5.23, **10**, *s* $(\eta-C_5H_5)_2$; 7.99, **6**, *d* [J(P–H) 12.6], Me_2; 8.74, **2**, *d* [J(P–H) 13.5], CH_2; 22.11, **1**, *d* [J(P–H) 9.7], W–H [d]
(4) $[W(\eta-C_5H_5)_2Me(PMe_2Ph)][PF_6]$	Orange	37.2 (37.2)	4.2 (3.9)	2.0—2.6, **5**, *c*, Ph; 4.88, **10**, *d* [J(P–H) 2.1], $(\eta-C_5H_5)_2$; 7.93, **6**, *d* [J(P–H) 9.6], PMe_2; 9.66, **3**, *d* [J(P–H) 7.8] [satellites J(W–H) 5.6], WMe [d]
(5) $[W(\eta-C_5H_5)_2Me(SEt_2)][PF_6]$	Brick red	32.3 (31.9)	4.2 (4.1) [e]	4.76, **10**, *s*, $(\eta-C_5H_5)_2$; 7.23, **4**, *q* (J 7.2), $(CH_2)_2$; 8.80, **6**, *t* (J = 7.2), Me_2; 9.72, **3**, s, WMe [d]
(6) $[W(\eta-C_5H_5)_2Me(I)]$	Dark green	29.2 (29.0)	2.9 (2.9) [f]	4.46, **10**, *d*, $(\eta-C_5H_5)_2$; 8.88, **3**, *s* [satellites, J(W–H) 5.3], WMe [g]

[a] Given as chemical shift (τ), **relative intensity,** *multiplicity* (J in Hz), assignment, *etc.* [b] W, 28.6 (28.7); F, 17.8 (17.8); P, 9.6 (9.7)%. Calculated values are given in parentheses. [c] In $(CD_3)_2CO$. Carbon-13 n.m.r. in $(CD_3)_2CO$: 113.8, 131.6, 131.1, 129.7, 129.4, Ph; 86.3, *s*, $(\eta-C_5H_5)_2$; 33.4, *d* [J(P–C) 30.52], CH_2P; 5.7, *d* [J(P–C) 54.10], PMe_2; 19.1, *d* [J(P–C) 15.56 Hz], WCH_2; and −27.5 p.p.m., *s*, WMe. [d] In $(CD_3)_2CO$. [e] S, 5.9 (5.7)%. [f] Mass spectrum, given as *m/e*, intensity, assignment for ^{184}W only: 456,97,P^+; 441,100, $[W(C_5H_5)_2I]^+$; 376,5, $[W(C_5H_5)I]^+$; 350,8, $[W(C_3H_3)I]^+$; 314, 39, $[W(C_5H_5)_2]^+$; 288,11, $[W(C_5H_5)(C_3H_3)]^+$; 228,5, $[W(C_5H_5)_2Me(I)]^{2+}$; 220.5, 19, $[W(C_5H_5)_2I]^{2+}$; 157,17, $[W(C_5H_5)_2]^{2+}$. [g] In C_6D_6.

$[PF_6]$ in high yield. The reaction may be assumed to proceed as in (1) and (2).

$$(3) + HCl \longrightarrow [W(\eta-C_5H_5)_2(CH_2PMe_2Ph)H_2][PF_6]Cl \longrightarrow [W(\eta-C_5H_5)_2H(Cl)] + [PMe_3Ph][PF_6] \quad (1)$$

$$[W(\eta-C_5H_5)_2H(Cl)] + HCl \longrightarrow [W(\eta-C_5H_5)_2Cl_2] + H_2 \quad (2)$$

The formation of $[PMe_3Ph][PF_6]$ in this reaction supports the suggestion that (3) contains the $CH_2\overset{+}{P}Me_2Ph$ ligand. The complex can be regarded either as a phosphonium salt with an organometallic substituent or as a complex in which a phosphorus ylide acts as a donor ligand to an organometallic cation. Charge-distribution considerations lead us to prefer the former formulation, although a variety of related compounds containing ligands such as $CH_2\overset{+}{P}Me_3$ have been prepared from the corresponding ylides,[13] and the ylide description may be more appropriate for some of these, *e.g.* $[Ni(CH_2PMe_3)_2Cl(PMe_3)]Cl$.[14]

A freshly prepared solution of (3) in perdeuterioacetone and a solution prepared by *in situ* decomposition of (2) in a sealed tube both underwent further reaction when heated at 70 °C. After *ca.* 12 d, (3) had totally disappeared from the solution and the compound $[W(\eta-C_5H_5)_2Me(PMe_2Ph)][PF_6]$ (4) could be isolated. Compound (4) was characterized by the data in the Table together with the observation that it could be synthesized by an independent route [equation (3)].

$$[WBr(\eta-C_5H_5)_2(PMe_2Ph)][PF_6] + MgBrMe \longrightarrow (4) \quad (3)$$

We note that the rearrangement of (2) to (3) and of (3) to (4) in perdeuterioacetone proceeded without any evidence for incorporation of deuterium in the products (^1H n.m.r.). Compounds (2)—(4) are all air-sensitive crystalline solids, stable indefinitely at room temperature in an inert atmosphere.

The perdeuteriomethyl derivative of (1), $[W(\eta-C_5H_5)_2(C_2H_4)(CD_3)][PF_6]$ (1d), was prepared by replacement-addition[15] of CD_3I to $[W(\eta-C_5H_5)_2(C_2H_4)]$ followed by counter-ion exchange and was characterized by the data in the Table. The ^1H n.m.r. spectrum of the compound showed it to be of at least 98% isotopic purity. The i.r. spectrum of (1d) showed bands at 2 250w, 2 230m, 2 115m, and 2 080m cm^{-1} assignable to C–D stretching modes. Treatment of (1d) in acetone with PMe_2Ph gives $[W(\eta-C_5H_5)_2(CH_2CH_2PMe_2Ph)(CD_3)][PF_6]$ (2d) of at least 97% isotopic purity (^1H n.m.r.). The i.r. spectrum of (2d) shows bands assignable to C–D stretches at 2 200m, 2 110m, and 2 065m cm^{-1}.

Thermal decomposition of (2d) in perdeuterioacetone gave essentially quantitative conversion into $[W(\eta-C_5H_5)_2(CD_2PMe_2Ph)D][PF_6]$ (3d). The ^1H n.m.r. spectrum of the reaction mixture showed that there was no incorporation of deuterium into the liberated ethylene, nor was there any evidence to suggest that the CD_2 or W–D groups were not isotopically pure. Further heating of the solution for a total of 157 h resulted in essentially quantitative conversion into $[W(\eta-C_5H_5)_2(CD_3)(PMe_2Ph)][PF_6]$ (4d), of high isotopic purity (>97%). A sample of (3d) was also prepared by heating (2d) under reflux in acetone for 3 d, and the absence of a W–H stretching absorption from the i.r. spectrum of this material confirmed that the W–D group was of high isotopic purity. The W–D stretching absorption could be observed at 1 390 cm^{-1}, giving a value of 1.395 for the ratio ν(W–H) : ν(W–D) in agreement with that recorded in the literature for other hydridotungsten compounds.[16] This experiment also confirmed that there was no H–D exchange between the compound and the solvent.

At this stage it was unclear whether (2) was an essential intermediate in the formation of (3), or whether other compounds of the type $[W(\eta-C_5H_5)_2L(Me)][PF_6]$, in which L was a labile ligand other than ethylene, would also give rise to (3) when treated with PMe_2Ph. The work of Crabtree *et al.*,[17] in which they showed that the alkyl sulphide ligands in compounds of the type $[W(\eta-C_5H_5)_2(SR_2)X][PF_6]$ were readily displaced by tertiary phosphines, suggested that diethyl sulphide might be a suitable labile ligand for these studies, and we were able to prepare the desired compound from (1) by treatment with SEt_2. The product $[W(\eta-C_5H_5)_2Me(SEt_2)][PF_6]$ (5) could be isolated in 60% yield as brick-red needles which were soluble in acetone and dimethyl sulphoxide. Solutions of the compound decompose in air after a few hours exposure, and the anticipated lability of the SEt_2 ligand was confirmed by the observation of free SEt_2 in the ^1H n.m.r. spectrum of (5) when the compound was examined as a solution in perdeuteriodimethyl sulphoxide.

The lability of the SEt_2 ligand made (5) a versatile starting material for other compounds. Treatment of a solution of (5) in acetone with PPh_3 resulted in the formation of $[W(\eta\text{-}C_5H_5)_2Me(PPh_3)][PF_6]$ (7) in high yield, and neutral $[W(\eta\text{-}C_5H_5)_2Me(I)]$ (6) was readily prepared by treatment of (5) with NaI in acetone.

The reactions of (5) and (7) with PMe_2Ph clearly demonstrated that (2) was not a necessary precursor of (3). A solution of (5) in acetone reacted with PMe_2Ph at 50 °C to give a 70% yield of (3) after 1.5 h, much milder conditions than those used to generate (3) from (2). The reaction between (7) and PMe_2Ph at 70 °C in perdeuterioacetone was monitored by ^1H n.m.r. spectroscopy. During the initial heating the resonances assigned to (7) decreased in intensity while new resonances assignable to (3) appeared. After 38.5 h the solution contained a 1 : 1 mixture of (7) and (3). Continued heating resulted in the complete disappearance of the signals assigned to (7) and the appearance of new absorptions corresponding to those of (4). After 194 h the spectra showed (3) and (4) to be present in a 1 : 1 ratio. Fractional crystallization of the reaction mixture at this stage gave pure samples of (3) and (4) whose identification was confirmed by comparison of their i.r. spectra with those of authentic samples.

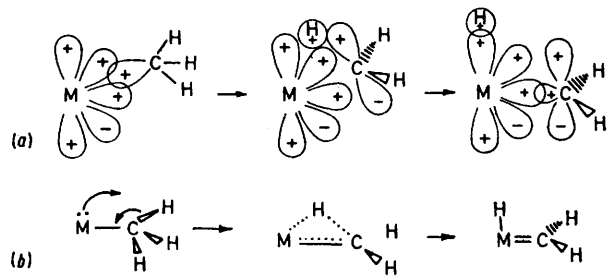
Suspension of powdered $Tl[PF_6]$ in a benzene solution of the iodo(methyl) compound (6) resulted in rapid discharge of the green colour, leaving a yellow-brown powder. This reacted with acetone and other polar solvents. Treatment of the powder with PMe_2Ph in acetone gave the phosphonium hydride complex (3) in good yield. Surprisingly, direct treatment of (5) in acetone with PMe_2Ph also gave (3) in good yield, suggesting that the iodide ligand is relatively labile.

DISCUSSION

The results above show unambiguously that the complex $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2PMe_2Ph)Me][PF_6]$ (2) eliminates ethylene when heated in solution to give $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H][PF_6]$ (3) and that (3) rearranges on prolonged heating to give $[W(\eta\text{-}C_5H_5)_2Me(PMe_2Ph)][PF_6]$ (4). Repeating this sequence with the deuteriated methyl analogues shows that the CD_3 unit in (2) is reformed quantitatively in (4) and strongly supports the proposed mechanism shown in the Scheme. The proposal that these reactions and the others reported in this paper should involve common intermediates follows naturally from the observation that (3) is formed from all of the compounds (2), (5), (6), and (7). That (3) should be accessible from compounds of such diverse structures renders, otherwise reasonable, explanations of individual reactions, such as a cyclic transition state for the elimination of ethylene from (2), as unnecessary and implausible speculation.

Since we originally suggested this mechanism to account for some of these reactions circumstantial evidence in support of the proposed methylene hydride cation (B) has been provided by the isolation and characterization of the isoelectronic tantalum complex $[Ta(\eta\text{-}C_5H_5)_2(CH_2)Me]$ by Schrock and Sharp,[18] who used relatively mild conditions ($CH_2{=}PMe_3$ as base) to deprotonate the cation $[Ta(\eta\text{-}C_5H_5)_2Me_2]^+$. Methylene complexes have also been proposed previously as reaction intermediates,[19] and nucleophilic attack by a phosphine on an electrophilic carbene ligand bonded to a transition metal has been previously reported.[20] The nature of the other proposed intermediate, the 16-electron methyl cation (A), is not clearly defined by the present work. For example, a solvent molecule may well be co-ordinated to the metal atom.

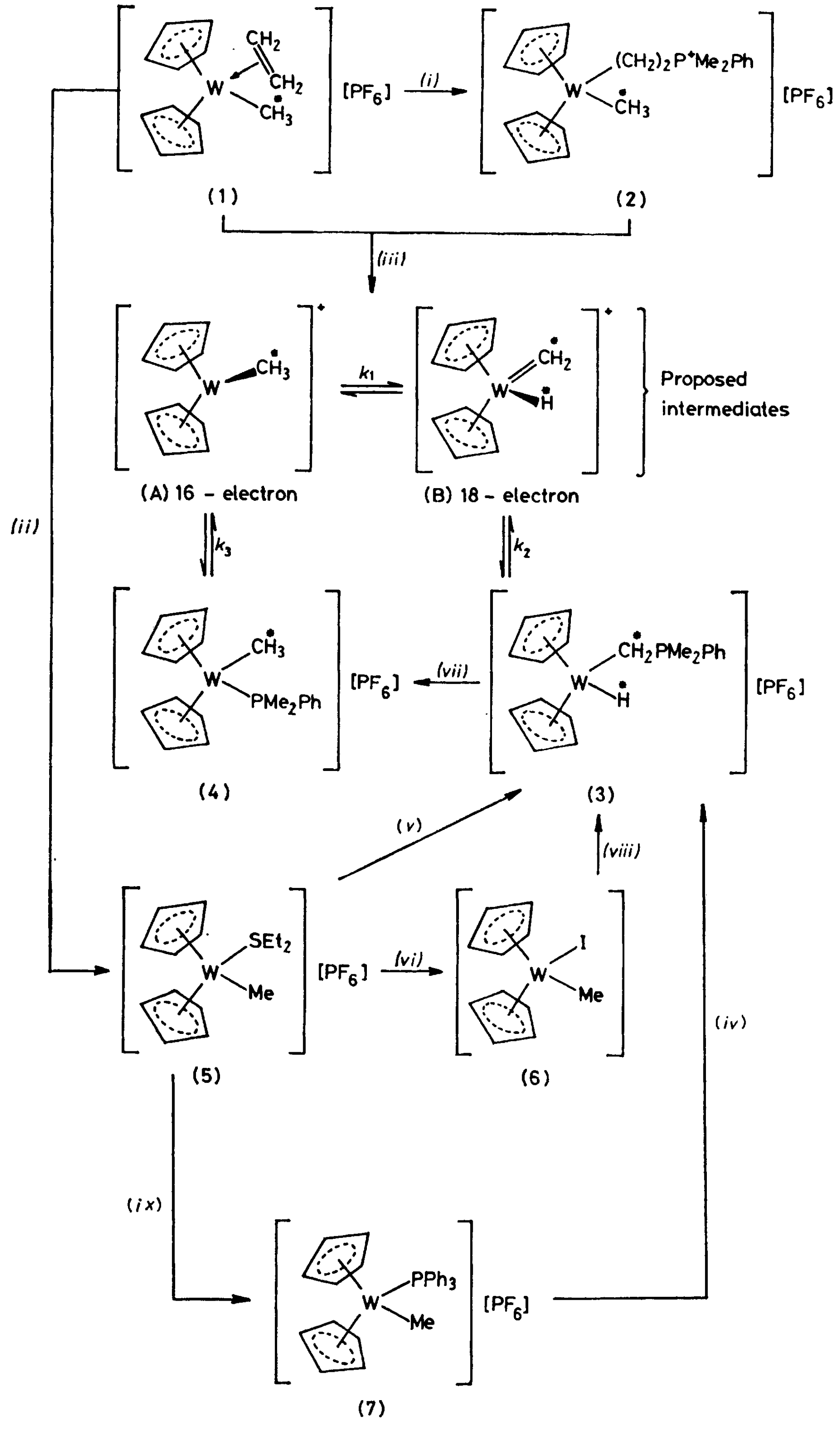
The key feature of the proposed mechanism is the 1,2-hydrogen shift (α elimination) equilibrium between (A) and (B). The reversibility of such a shift is uniquely demonstrated by sequences such as (5) ⟶ (3) ⟶ (4), although similar equilibria have been postulated to account for the distribution of deuterium in the exchange between deuterium and the hydrogen of hydrocarbons, catalysed by transition metals.[21] A ready 1,2-hydrogen shift in alkyl-chromium and -nickel compounds has also been proposed to account for the *in situ* decomposition products formed.[22-25] Since the initial account of this work appeared, similar 1,2-hydrogen shifts have been observed.[26,27] The thermal decomposition of transition-metal dialkyls may also often be best understood in terms of an initial shift of an α-hydrogen to the metal as we have discussed elsewhere.[28]



(*a*) Simple orbital representation of the 1,2-hydrogen shift.
(*b*) An equivalent valence-bond representation

Extensive structural and spectroscopic studies on bent bis(η-cyclopentadienyl) compounds of the early transition metals have led to a detailed description of the bonding.[3,4] It is generally accepted that, apart from the metal–ring bonding orbitals, there remain three orbitals, essentially of *d* character, which are available for bonding further ligands to the bent $M(\eta\text{-}C_5H_5)_2$ framework. Using these orbitals, there is no difficulty in accounting for the $M{-}CH_3 \rightleftharpoons MH{=}CH_2$ equilibrium provided that the metal centre of the initial methyl compound has not more than 16 electrons in total, and not less than two electrons available for formation of the M=C bonds. A simple orbital representation of such a 1,2-hydrogen shift is shown in the Figure.

Since one cannot invoke any special features for the metal site in the $[W(\eta\text{-}C_5H_5)_2Me]^+$ cation there seems little reason why the 1,2-shift equilibrium, within the limitations above, should not be a quite widespread and general phenomenon. The question therefore arises as to why 1,2-hydrogen shifts have not been more frequently observed. A partial answer may be that the shifts have not been recognized as a consequence of the following factors. First, the equilibrium $M{-}CH_3 \rightleftharpoons MH({=}CH_2)$ may normally lie to the left-hand side.



SCHEME An asterisk denotes H or D. (*i*) PMe_2Ph in Me_2CO, r.t., 12 h; (*ii*) SEt_2 in Me_2CO, 50 °C, 1.5 h; (*iii*) PMe_2Ph in Me_2CO, 70 °C, 3 d, to give (3); (*iv*) PMe_2Ph in Me_2CO, 3—4 d, to give (3), 10 d to give (4); (*v*) PMe_2Ph in Me_2CO, 70 °C, 3 d, to give (3); (*vi*) NaI in Me_2CO, 70 °C, 1.25 h; (*vii*) heat in Me_2CO, 194 h, 70 °C; (*viii*) $Tl[PF_6]$ in C_6H_6, r.t., 3 h, then PMe_2Ph in Me_2CO, r.t., 30 min; (*ix*) PPh_3 in Me_2CO, 70 °C, 5 h

Secondly, reactions causing addition of a nucleophile Nu to the methylene carbon to give intermediates of the type $MH(CH_2Nu)$ may often be followed by reductive elimination of CH_3Nu, in which case evidence for the carbene intermediate is lost. Finally, since the migrating hydrogen returns to the original carbon no evidence for the exchange would be provided by deuterium tracer studies, unless there were a trapping agent present as in our studies. Deuteriation might, of course, reveal the shift through kinetic isotope studies.

The major factor contributing to recognition of the 1,2-hydrogen shift in this instance is the fortuitous kinetics of the formation and rearrangement of (3), which permitted its isolation and characterization.

Since our original report of this work we have been looking for reactions in which the 1,2-hydrogen shift might be occurring but be hitherto unrecognized. This has led to new mechanistic interpretations of the vicinal interchange reactions mediated by coenzyme B_{12} dependent enzymes [29] and for the stereospecific oligomerization of olefins by Ziegler–Natta catalysts.[30]

EXPERIMENTAL

All the reactions and manipulations were carried out under nitrogen or *in vacuo*. All solvents were dried and distilled before use. Chromatography was carried out using aluminium oxide (100—120 mesh) supplied by East Anglia Chemicals Ltd. Celite 545 was supplied by Koch–Light Ltd. Microanalyses were by A. Bernhardt or by the microanalytical laboratory of this department. Infrared spectra were recorded as mulls on a Perkin-Elmer 457 instrument and were calibrated with polystyrene film. Hydrogen-1 n.m.r. spectra were determined using Bruker WH-90 (90 MHz) or JEOL (60 MHz) spectrometers. Carbon-13 spectra were recorded on a Bruker WH-90 instrument and calibrated using the solvent as the internal standard. Mass spectra were recorded on an E.E.I. M.S. 9 spectrometer. E.s.r. spectra were obtained on a JEOL JES-PE spectrometer and were calibrated with 1,1-diphenyl-2-phenylhydrazyl. Gas–liquid chromatography (g.l.c.) was carried out on a Pye 104 chromatograph using a 10% KCl–alumina column.

The compounds $[M(\eta\text{-}C_5H_5)_2H_2]$, $[M(\eta\text{-}C_5H_5)_2Cl_2]$ (M = Mo or W), and $[W(\eta\text{-}C_5H_5)_2(C_2H_4)]$ were prepared as described previously.[31]

Bis(η-cyclopentadienyl)[(dimethylphenylphosphonio)methylide)hydridotungsten Hexafluorophosphate, (3).—The compound $[W(\eta\text{-}C_5H_5)_2(C_2H_4)Me][PF_6]$ (1) (0.18 g, 0.36 mmol) in acetone (50 cm^3) was treated with dimethylphenylphosphine (0.4 g, 2.9 mmol) and the mixture was heated under reflux for 3 d. Ethylene was evolved (g.l.c.). The cooled reaction mixture was placed on a short alumina column packed in toluene. An orange band was eluted with acetone. Ethanol was added to the eluate and slow removal of the solvent under reduced pressure gave yellow flat needle crystals which were filtered off and dried *in vacuo*, 0.09 g (40%).

Reaction between (3) *and Hydrogen Chloride*.—Compound (3) (0.11 g, 0.18 mmol) in acetone (30 cm^3) was treated with hydrogen chloride. An immediate reaction gave dark green crystals which were filtered off and dried *in vacuo*. The i.r. spectrum of the crystals showed them to be $[W(\eta\text{-}C_5H_5)_2Cl_2]$. The solvent was removed from the mother liquor under reduced pressure and the residue was extracted with acetone (25 cm^3). Ethanol was added and slow evaporation of the solvent gave white crystals which were collected and dried. They were identified as $[PMe_3Ph][PF_6]$ (0.045 g, 85%) by comparison of their i.r. spectrum with that of an authentic sample.

Bis(η-cyclopentadienyl)[2-(dimethylphenylphosphonio)-ethylide]methyltungsten Hexafluorophosphate, (2).—Compound (1) (1.1 g, 2.2 mmol) in acetone (150 cm^3) was treated with PMe_2Ph (2.0 g, 14.4 mmol). The initially green-yellow solution rapidly became orange. After 12 h at 25 °C the solvent was removed under reduced pressure and the residual red oil washed with light petroleum–diethyl ether (b.p. 30—40 °C, 3 × 20 cm^3). The oil was extracted with acetone and the solution passed down a short column of alumina. Addition of ethanol to the orange acetone eluate and slow concentration under reduced pressure precipitated orange platelets (0.85 g, 60%) which were collected, washed with ethanol, and finally dried *in vacuo*.

Bis(η-cyclopentadienyl)(dimethylphenylphosphine)methyltungsten Hexafluorophosphate, (4).—A suspension of the compound $[WBr(\eta\text{-}C_5H_5)_2(PMe_2Ph)][PF_6]$ [17] (1.1 g, 1.6 mmol) in diethyl ether (80 cm^3) was treated with methylmagnesium bromide in diethyl ether (30 cm^3 of 1.5 mol dm^{-3} solution, 45 mmol). After 2 h the solution was concentrated to 40 cm^3 under reduced pressure and tetrahydrofuran (30 cm^3) was added. After 15 min the initial solids dissolved giving an orange solution. The mixture was cooled (−78 °C) and ethanol added slowly (25 cm^3). After warming to room temperature (r.t.) the solvents were removed under reduced pressure. The residue was extracted with acetone–water (4 : 1) and the extract filtered through an alumina bed. The orange filtrate and acetone washings of the alumina were combined and excess of ammonium hexafluorophosphate (1 g) was added. The solvent was removed under reduced pressure to give an orange solid which was dried *in vacuo*. Extraction of the residue with dichloromethane gave an orange solution which was filtered before removing the solvent under reduced pressure. The oily residue was extracted with acetone and orange crystals precipitated from the solution by addition of diethyl ether. These were recrystallized from acetone–ethanol, as described above, 0.25 g (25%).

Bis(η-cyclopentadienyl)(diethyl sulphide)methyltungsten Hexafluorophosphate, (5).—Compound (1) (3 g, 6.0 mmol) in pure dry acetone (100 cm^3) was treated with diethyl sulphide (3 cm^3, 33 mmol). The initially amber solution was warmed to 70 °C for 4 h to give a purple solution. The solvent was removed under reduced pressure to give a purple-brown oily solid which was extracted with acetone (50 cm^3) and the extract shaken with alumina (10 g) to give a dark red solution. Filtration removed the alumina which was washed with acetone until the washings were colourless. The filtrate and the acetone washings were combined and the solvent was removed under reduced pressure to give a red-brown solid. Rapid recrystallization (1 h) from acetone–ethanol gave brick-red needles, 2.0 g (60%).

Reactions of Compound (5).—(*a*) *With* PMe_2Ph. A solution of (5) (0.07 g, 0.12 mmol) in acetone (40 cm^3) was treated with PMe_2Ph (1.0 g, 7.2 mmol). The orange solution was warmed to 50 °C for 1.5 h during which time the colour lightened. The solvent was removed under reduced pressure and the residual oil washed with light petroleum–diethyl ether (3 × 20 cm^3). The residue was extracted with acetone (40 cm^3) and the solution was shaken with alumina (5 g). After filtration and washing of the alumina with acetone, the combined solutions were concentrated and ethanol (20 cm^3) added to give yellow needles which were collected, washed with ethanol, and dried *in vacuo*. Comparison of the i.r. spectrum of the material with that of an authentic sample showed the product to be pure $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H][PF_6]$, 0.55 g (70%).

(*b*) *With* PPh_3. The reaction was carried out as described in (*a*) at 60 °C for 4—5 h using (5) (0.09 g, 0.16 mmol) and PPh_3 (0.6 g, 4.3 mmol) in acetone (40 cm^3). Addition of diethyl ether (150 cm^3) to the reaction mixture precipitated orange needles, which were shown to be pure $[W(\eta\text{-}C_5H_5)_2Me(PPh_3)][PF_6]$ (7), 0.1 g (85%), by comparison of their i.r. spectrum with that of an authentic sample.

Reaction of (7) *with* PMe_2Ph.—A mixture of (7) (0.05 g) and PMe_2Ph (0.06 g) in perdeuterioacetone (0.5 cm^3) was warmed to 70 °C for 194 h and the ^1H n.m.r. spectrum of the mixture recorded at intervals throughout the heating. The solvent was removed *in vacuo* and the resulting orange oil was washed with light petroleum–diethyl ether (2 × 20 cm^3). The residue was extracted with acetone (10 cm^3) and diethyl ether was slowly added to the extract (*ca.* 30 cm^3). After 12 h, feathery yellow needles separated which were collected, washed with diethyl ether, and dried *in vacuo*. The i.r. spectrum showed the product to be pure $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H][PF_6]$ (0.15 g). The mother liquors were concentrated under reduced pressure to about a quarter of the original volume and diethyl ether was added slowly until the solution became milky. After 12 h orange plates precipitated which were collected, washed with diethyl ether, and dried *in vacuo*. The product was shown to be pure $[W(\eta\text{-}C_5H_5)_2(PMe_2Ph)Me][PF_6]$ (0.015 g) from a comparison of the i.r. spectrum with that of an authentic sample.

Bis(*η-cyclopentadienyl*)*iodo*(*methyl*)*tungsten*, (6).—Compound (5) (12.1 g, 21.5 mmol) in acetone (500 cm^3) was treated with sodium iodide (30 g, 200 mmol, dried *in vacuo* at 70 °C for 1.25 h). The mixture was stirred at 70 °C for 1.5 h to give a green solution from which the solvent was removed under reduced pressure. The resulting green solid was dried *in vacuo* for 30 min and the residue was extracted with benzene (500 cm^3). Light petroleum (b.p. 100—120 °C, 200 cm^3) was added to the filtered solution which was then concentrated under reduced pressure to precipitate dark green needles of the product (7.5 g, 70%), which were collected, washed with light petroleum, and dried *in vacuo*.

Reactions of (6) *with* $Tl[PF_6]$ *and* PMe_2Ph.—Dry finely powdered $Tl[PF_6]$ (0.4 g, 1.15 mmol) was suspended in benzene (30 cm^3) containing (6) (0.1 g, 0.22 mmol). After stirring at r.t. for 3 h the solution became colourless, leaving a tan solid in suspension. Dimethylphenylphosphine (1 g) was added to the tan solid, then acetone (40 cm^3). A red-brown solution developed and after 30 min the mixture was filtered and the residue was extracted with acetone (2 × 15 cm^3). The solvent was removed from the filtrate under reduced pressure giving a brown oil which was washed with light petroleum (2 × 15 cm^3). The residual oil was extracted with acetone (50 cm^3). Toluene (25 cm^3) was added to the orange extract. Concentration under reduced pressure precipitated yellow needles and some red cubic crystals. These were dissolved in acetone and the solution was shaken with alumina and filtered. The filtrate was concentrated (*ca.* 20 cm^3) and diethyl ether (80 cm^3) was slowly added. Yellow needles separated and these were collected and dried *in vacuo*. The product was shown to be pure $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H][PF_6]$, 0.1 g (75%), by comparison of its i.r. spectrum with that of an authentic sample.

Thermal Decomposition of $[W(\eta\text{-}C_5H_5)_2(CH_2CH_2PMe_2Ph)(CD_3)][PF_6]$.—The title compound (0.14 g) in perdeuterioacetone (0.5 cm^3) in a sealed n.m.r. tube was heated at 70 °C for 157 h. The ^1H n.m.r. spectrum was recorded at intervals as discussed under Results, and showed that the title compound was converted sequentially into $[W(\eta\text{-}C_5H_5)_2(CD_2PMe_2Ph)D][PF_6]$ and $[W(\eta\text{-}C_5H_5)_2(CD_3)(PMe_2Ph)][PF_6]$ with evolution of C_2H_4.

A second sample of the title compound (0.16 g) in acetone (20 cm^3) was heated under reflux for 2 d. The solvent was under reduced pressure and the residue extracted with acetone. Addition of ethanol precipitated yellow needle crystals which were shown to be $[W(\eta\text{-}C_5H_5)_2(CD_2PMe_2Ph)D][PF_6]$ by comparison of their i.r. and ^1H n.m.r. spectra with those of the analogue (2). Infrared spectrum (mulls): 3 120m, 3 103 (sh), 3 010vw, 2 935w, 2 855vw, 2 145vw (C–D), 1 579vw, 1 440m, 1 424m, 1 407m, 1 390m, 1 338vw, 1 315w, 1 302m, 1 290m, 1 260vw, 1 190w, 1 125m, 1 106m, 1 077w, 1 064wm, 1 012m, 997m, 959m, 922s, 900m, 875 (sh), 845vs, 773m, 749vs, 703w, 693w, 618w, 602m, 551vs, 505w, 464w, and 408m cm^{-1}.

Thermal Decomposition of (2).—Compound (2) (0.1 g) in perdeuterioacetone (0.6 cm^3) was heated for 2 d at 70 °C and the ^1H n.m.r. spectrum of the solution was determined at intervals throughout the heating. The solvent was removed under reduced pressure and the product crystallized from acetone–ethanol to give orange crystals. These were shown to be identical to a sample of $[W(\eta\text{-}C_5H_5)_2Me(PMe_2Ph)][PF_6]$ by comparison of their i.r. spectra (*ca.* 80% yield).

The thermal decomposition of $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)H][PF_6]$ was carried out in a similar manner to give the same product, *ca.* 80% yield.

Bis(*η-cyclopentadienyl*)*ethylene*(*trideuteriomethyl*)*tungsten Hexafluorophosphate*, (1d).—The compound $[W(\eta\text{-}C_5H_5)_2(C_2H_4)]$ (1.0 g, 2.9 mmol) in toluene (50 cm^3) was treated with CD_3I (0.6 g, 4.1 mmol) and the mixture was left for 12 h. A creamy precipitate settled and was filtered off and dried *in vacuo*. Extraction with ethanol–water (1 : 1, 200 cm^3) gave a yellow solution which was treated with excess of ammonium hexafluorophosphate to give a yellow precipitate. This was collected and recrystallized from acetone–ethanol as yellow needles, 0.75 g (51%). The i.r. spectrum (mulls) showed bands at 3 140s, 3 123 (sh), 2 250w, 2 230, 2 114m, 2 080m, 1 485 (sh), 1 435s, 1 378m, 1 293vw, 1 264vw, 1 188s, 1 128vw, 1 082s, 1 029s, 1 010m, 971m, 947 (sh), 912s, 850vs, 790 (sh), 740w, 721w, 602m, and 663vs cm^{-1}. The ^1H n.m.r. spectrum in acetone was identical to that of (1) except that there was no absorption assignable to the methyl group.

Compounds (2d), (3d), and (4d) were prepared in a similar manner to (2), (3), and (4) respectively.

We thank the Northern Ireland Department of Education for support (to N. J. C.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

[8/1619 *Received*, 11*th September*, 1978]

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