Photoinduced Insertion of Tungsten into Aromatic and Aliphatic Carbon–Hydrogen Bonds by Bis(η-cyclopentadienyl)tungsten Derivatives

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Photolysis of solutions of $[W(\eta-C_5H_5)_2H_2]$ in fluorobenzene, *o*-xylene, anisole, *p*-chlorotoluene, *p*-xylene, mesitylene, *p*-methylanisole, and methyl benzoate gives the compounds $[W(\eta-C_5H_5)_2H(C_6H_4F\text{-}3$ and $\text{-}4)]$, $[W(\eta-C_5H_5)_2H(C_6H_3Me_2\text{-}3,4)]$, $[W(\eta-C_5H_5)_2H(C_6H_4OMe\text{-}4)]$, $[W(\eta-C_5H_5)_2Cl(C_6H_4Me\text{-}4)]$, $[W(\eta-C_5H_5)_2(CH_2C_6H_4Me\text{-}4)_2]$, $[W(\eta-C_5H_5)_2(CH_2C_6H_3Me_2\text{-}3,5)_2]$, $[W(\eta-C_5H_5)_2(CH_2C_6H_4OMe\text{-}4)_2]$, and $[W(\eta-C_5H_5)_2H(C_6H_4CO_2Me\text{-}3$ and $\text{-}4)]$ together with $[W(\eta-C_5H_5)_2H(OCOPh)]$, respectively. Thermal decomposition of $[W(\eta-C_5H_5)_2H(Me)]$ in mesitylene gives $[W(\eta-C_5H_5)_2H(CH_2C_6H_3Me_2\text{-}3,5)]$. Photolysis of this compound in *p*-xylene gives $[W(\eta-C_5H_5)_2(CH_2C_6H_4Me\text{-}4)(CH_2C_6H_3Me_2\text{-}3,5)]$. Photolysis of $[W(\eta-C_5H_5)_2H_2]$ in tetramethylsilane gives *cis*- and *trans*-$[H(\eta-C_5H_5)W(\sigma:\eta^5-C_5H_4)_2W(\eta-C_5H_5)(CH_2SiMe_3)]$. The photoinduced reaction between $[W(\eta-C_5H_5)_2H_2]$ and toluene, a toluene–mesitylene mixture, and methyl propionate are also described. The mechanisms of these photoinduced insertions of tungsten into aromatic and aliphatic C–H bonds are discussed.

In 1967 it was observed that thermolysis of a benzene solution of $[W(\eta-C_5H_5)_2H_2]$ (1) in the presence of isoprene gave the hydridophenyl derivative $[W(\eta-C_5H_5)_2H(Ph)]$ (2).[1] It was proposed that the reaction involved as the reactive intermediate a 16-electron compound tungstenocene $[W(\eta-C_5H_5)_2]$ which could insert into the aromatic C–H bond of benzene giving (2).

In a subsequent search for a convenient source of tungstenocene it was found that photolysis of (1) in benzene gave (2) in up to 70% yield.[2] It was proposed that the photolysis of (1) caused evolution of dihydrogen and the formation of tungstenocene. In view of the mild conditions under which the tungstenocene inserted into the aromatic C–H bond, the reactivity of tungstenocene was equated with that of carbene species which similarly insert into carbon–hydrogen bonds.[3]

Following these observations we set out to explore the reactivity of the presumed tungstenocene species by the method of photolysis of (1) in the presence of a variety of substrates. In preliminary communications we have described the photoinduced insertions of tungsten into both aromatic and aliphatic systems.[4,5] We now describe these and further studies in full.

RESULTS

Chemical Studies.—The photolysis reactions of (1) were all carried out under quite similar conditions. Dilute solutions of (1) in a potential reactant were irradiated with a medium-pressure mercury lamp through Pyrex apparatus at room temperature. The products were characterised by microanalysis and n.m.r., i.r., and mass spectra where appropriate. The data are presented in the Experimental section or the Table and only salient features will be further discussed in the text.

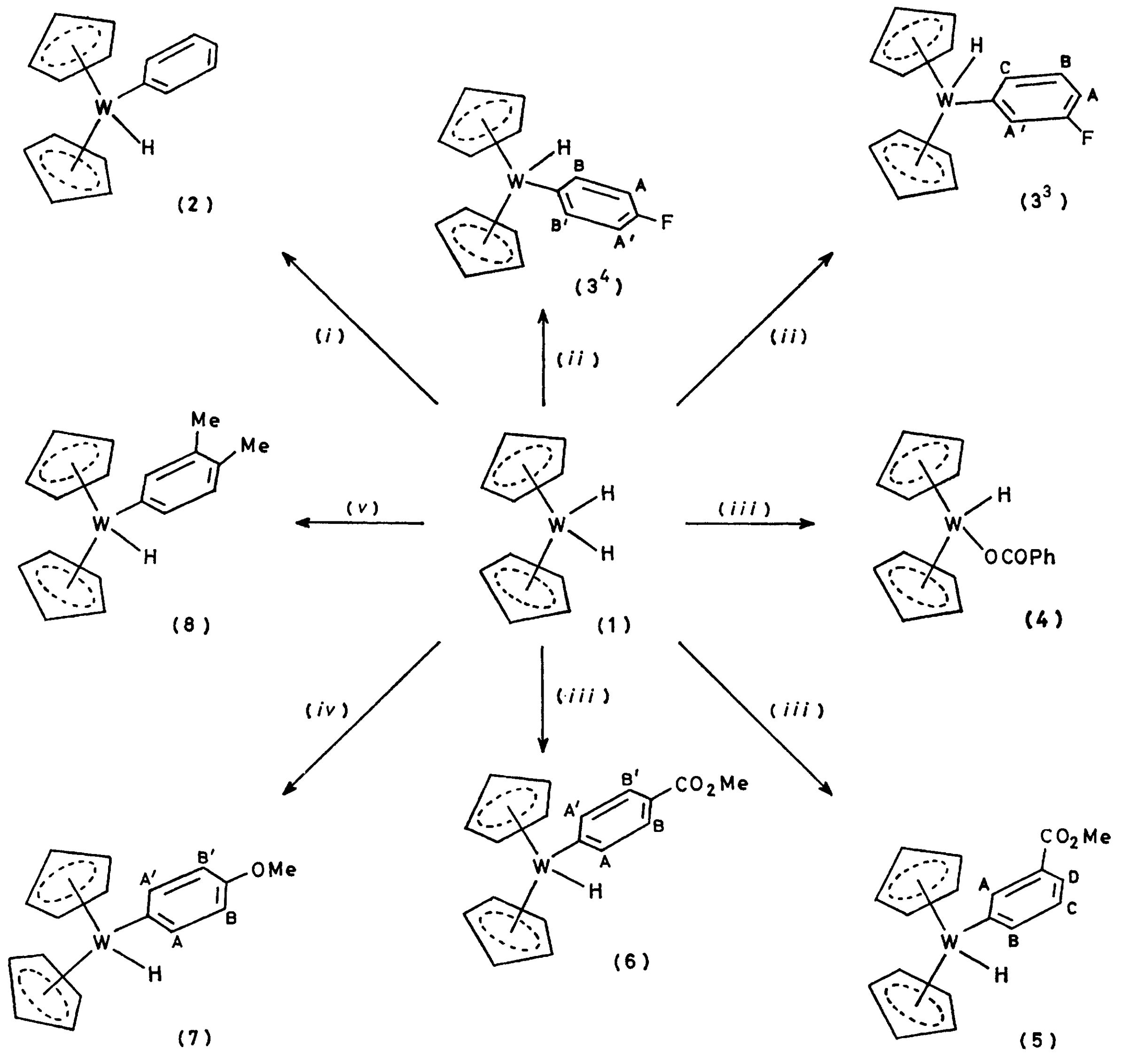
Irradiation of (1) in fluorobenzene gave yellow air-sensitive needle crystals soluble in light petroleum. They had the stoicheiometry $[W(\eta-C_5H_5)_2H(C_6H_4F)]$ (3). The ^1H and ^{19}F n.m.r. spectra showed compound (3) to be a mixture of isomers. In particular, the ^{19}F n.m.r. showed two well separated complex bands which could be unambiguously analysed. The higher-field band was a triplet of triplets corresponding to a C_6H_4F-4 group and the lower-field band showed 16 lines corresponding to coupling of the fluorine with the four different hydrogens of a C_6H_4F-3 group. The data are given in the Table. The intensity ratio of the two ^{19}F resonances was 2 : 3 for the C_6H_4F-3 and -4 isomers respectively. This ratio is the same as that found for the two singlet bands at τ 26.49 and 26.40 assignable to W–H resonances. Attempts to separate the isomers on a long alumina column were only partially successful, as shown by the ^1H n.m.r. spectra of the initial and final portions of the eluate. The n.m.r. spectra showed that the initial fraction of the eluate was rather richer in the C_6H_4F-3 isomer than the final portion.

Irradiation of (1) in methyl benzoate using a 500-W medium-pressure lamp gave, after careful chromatography, orange crystals of stoicheiometry $[W(\eta-C_5H_5)_2H(OCOPh)]$ (4), orange-red crystals of stoicheiometry $[W(\eta-C_5H_5)_2H(C_6H_4CO_2Me)]$ (5), and a yellow oil (6) whose mass spectrum showed it to be isomeric with (5). The ^1H n.m.r. of (6) showed a clear AA′BB′ pattern indicating the isomer $[W(\eta-C_5H_5)_2H(C_6H_4CO_2Me\text{-}4)]$ (6). The ^1H n.m.r. spectrum of compound (5) showed the presence of four different aromatic hydrogens with fine structure, indicating the presence of $[W(\eta-C_5H_5)_2H(C_6H_4CO_2Me\text{-}3)]$ (5). The ratio of these isomers was 1 : 3.

Irradiation of (1) in anisole or *o*-xylene gives the compounds $[W(\eta-C_5H_5)_2H(C_6H_4OMe\text{-}4)]$ (7) and $[W(\eta-C_5H_5)_2H(C_6H_3Me_2\text{-}3,4)]$ (8) respectively. When (1) in chlorotoluene is irradiated two products may be separated by chromatography. The first band gave brown crystals of the compound $[W(\eta-C_5H_5)_2Cl(C_6H_4Me\text{-}4)]$ (9). The second band gave brown-red crystals of the known hydridochloro-derivative $[W(\eta-C_5H_5)_2Cl(H)]$.[6] Irradiation of (1) in mesitylene followed by chromatography gave air-stable orange-red crystals $[W(\eta-C_5H_5)_2(CH_2C_6H_3Me_2\text{-}3,5)_2]$ (10). Similarly, photolysis of (1) in *p*-xylene or 1-methyl-4-methoxybenzene gave air-stable orange crystals of $[W(\eta-C_5H_5)_2(CH_2C_6H_4Me\text{-}4)_2]$ (11) and $[W(\eta-C_5H_5)_2(CH_2C_6H_4OMe\text{-}4)_2]$ (12) respectively.

The low solubility of compounds (10)—(12) made it difficult to obtain good quality ^1H n.m.r. spectra. However, whilst the spectra obtained for (10) entirely support the crystal structure, there are features which require some comment. The bands assignable to two CH_2 groups in compounds (10)—(12) occur as broad doublets. However, analogy with the spectrum of the dibenzyl compound

$[W(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$ [7] would have led one to expect a sharp singlet for the two CH_2 groups. We noted also that the band assigned to the $\eta\text{-}C_5H_5$ hydrogens is very broad, although the width depends on the solvent. We conclude that there is steric overcrowding in these molecules which causes the CH_2 hydrogen to become non-equivalent on the time scale of the experiment. This proposal is supported by the crystal structure of (10) which shows close interaction of the CH_2 hydrogens.[8] The low-temperature spectrum of (10) in carbon disulphide (−90 °C) showed a marked increase in breadth of the peak of the $\eta\text{-}C_5H_5$ hydrogens which is consistent with there being some steric interaction between the two $CH_2C_6H_3Me_2$-3,5 groups and the $\eta\text{-}C_5H_5$ rings.



SCHEME 1 Irradiation for 12 h of *ca.* 10^{-3} mol dm^{-3} solutions of (1) in: (*i*) benzene, 70%; (*ii*) C_6H_5F, 50% (ratio of C_6H_4F-4 to -3-isomer = 3 : 1); (*iii*) $MeCO_2C_6H_5$, 18% (4), 9% (5), 26% (6); (*iv*) $MeOC_6H_5$, 40%; (*v*) 1,2-$Me_2C_6H_4$, 35%

Irradiation of (1) in toluene followed by chromatography gave, as the first band, a yellow air-sensitive oil of stoicheiometry corresponding to $[W(\eta\text{-}C_5H_5)_2H(C_6H_4Me)]$ (13). The n.m.r. spectrum showed the presence of two compounds in the ratio 10 : 1 as deduced from the relative intensity of bands assigned to the $\eta\text{-}C_5H_5$ hydrogens. Comparison of the spectrum with that of an authentic sample of $[W(\eta\text{-}C_5H_5)_2H(C_6H_4Me\text{-}4)]$ showed the latter to be identical with the major component of (13). The second component of (13) could not be separated from the 4-tolyl derivative and was present in only rather small amounts. The partial data in the Table are, however, consistent with this minor component being the 3-tolyl isomer $[W(\eta\text{-}C_5H_5)_2H(C_6H_4Me\text{-}3)]$ (13^3).

A second product eluted from the reaction mixture was obtained as orange crystals which were unchanged on exposure to air for some hours. They were slightly soluble in light petroleum and had a stoicheiometry $[W(\eta\text{-}C_5H_5)_2(C_7H_7)_2]$ (14). The ^1H n.m.r. spectrum indicated the presence of two compounds, presumably isomers, neither of which was the known dibenzyl derivative $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$.[7] The 100-MHz n.m.r. spectrum showed two bands assignable to $\eta\text{-}C_5H_5$ groups in intensity ratio 3 : 2. Also, careful chromatography demonstrated it was possible

Characterisation data for the new compounds

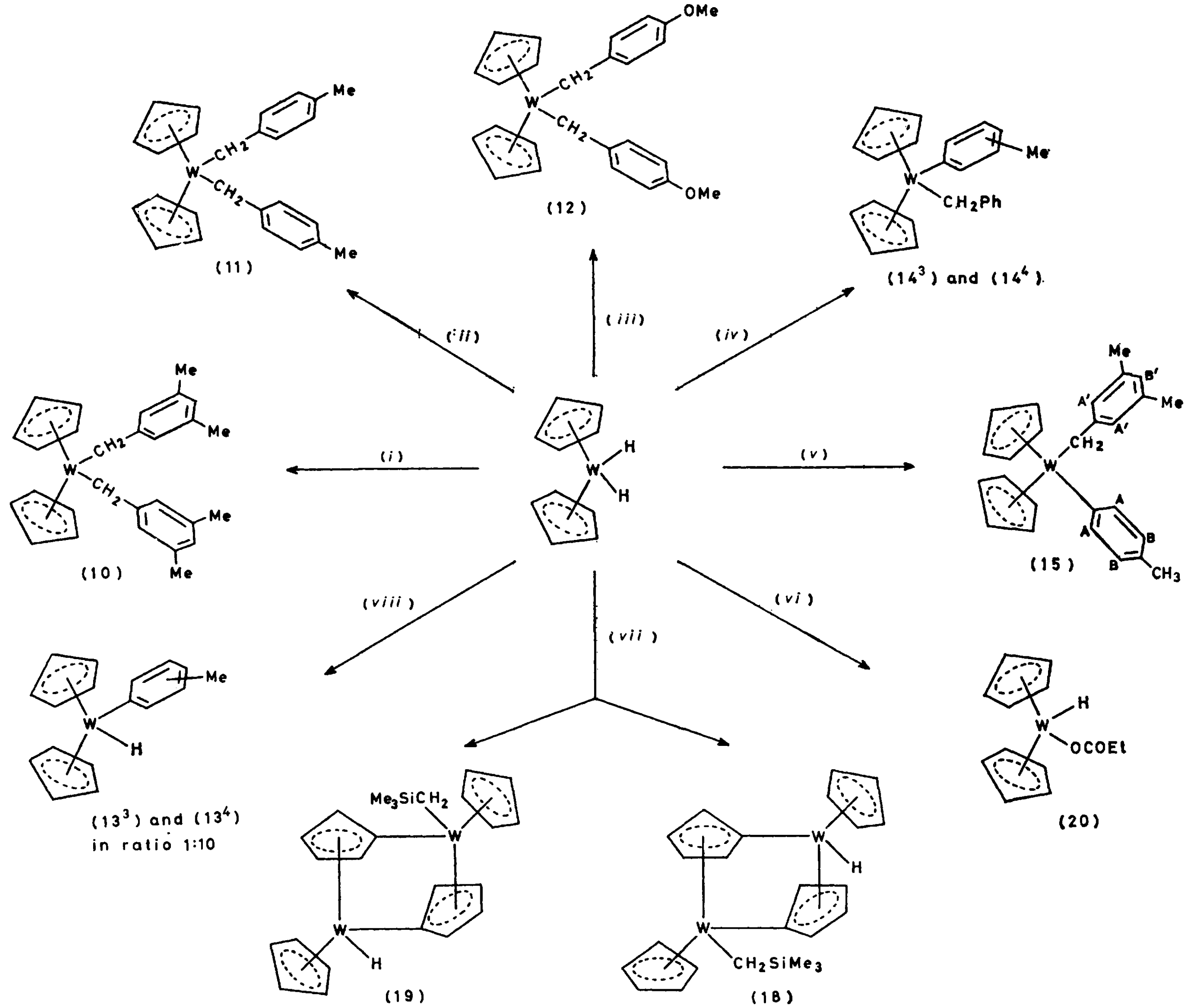
	Compound	Colour	Analyses (%) [a]		I.r. bands (cm^{-1})	N.m.r. data [b]
			C	H		
(3^3)	$[W(\eta\text{-}C_5H_5)_2H(C_6H_4F\text{-}3)]$	Yellow	47.0 (46.8)	(4.0) (3.7)	ν(WH) 1 910br	3.0, **4**, *c*, C_6H_4; 5.37, **10**, *d* (J 0.4), $(\eta\text{-}C_5H_5)_2$; 26.49, **1**, *s*, WH. ^{19}F, 16 lines, lower field band, J(H^A or H$^{A'}$–F) 11.1, J(H^A or H$^{A'}$–F) 9.2, J(H^B–F) 6.8, J(H^C–F) 1.3 [c,d]
(3^4)	$[W(\eta\text{-}C_5H_5)_2H(C_6H_4F\text{-}4)]$	Yellow	See text			3.08, **4**, *c*, C_6H_4; 5.39, **10**, *d* (J 0.4), $\eta\text{-}C_5H_5$; 26.40, **1**, *s*, WH. ^{19}F, 9 lines, *t of t*, J(H^A–F) 10.5, J(H^B–F) 7.3 [d]
(4)	$[W(\eta\text{-}C_5H_5)_2H(OCOPh)]$	Orange	46.5 (46.8)	3.7 (3.7)	ν(WH) 1 938m, ν(CO) 1 627s	2.64, **5**, *c*, Ph; 5.54, **10**, *d* (J 0.6), $(\eta\text{-}C_5H_5)_2$; 21.09, **1**, *s*, WH [d]
(5)	$[W(\eta\text{-}C_5H_5)_2H(C_6H_4CO_2Me\text{-}3)]$	Yellow	48.3 (48.0)	4.0 (4.0)	ν(WH) 1 927, ν(CO) 1 640s	1.61, **1**, *t* (J 1.5), H^A; 2.11, **1**, *t of t* (J 1.5, 7.2), H^B; 2.67, **1**, *t of t* (J 1.8, 7.8), H^C; 3.28, **1**, *t* (J 7.8); H^D; 5.34, **10**, *d* (J 0.6), $(\eta\text{-}C_5H_5)_2$; 6.21, **3**, *s*, Me; 20.9, **1**, *s*, WH [d]
(6)	$[W(\eta\text{-}C_5H_5)_2H(C_6H_4CO_2Me\text{-}4)]$	Yellow			ν(WH) 1 906m, ν(CO) 1 938vs	2.07, **2**, *d* (J 8); 2.71, **2**, *d* (J 8), 2H$^{AA'}$ and 2H$^{BB'}$; 5.35, **10**, *d* (J 0.6), $(\eta\text{-}C_5H_5)_2$; 6.23, **3**, *s*, Me; 20.9, **1**, *s*, WH [d]
(7)	$[W(\eta\text{-}C_5H_5)_2H(C_6H_4OMe\text{-}4)]$	Yellow-orange	50.15 (48.4)	4.3 (4.2)	ν(WH) 1 900	2.42, 2.52, 3.5, 3.6, **4**, *AA′BB′*, C_6H_4; 6.02, **10**, *s*, $(\eta\text{-}C_5H_5)_2$; 6.88, **3**, *s*, Me; 22.0, **1**, *s*, WH [e]
(8)	$[W(\eta\text{-}C_5H_5)_2H(C_6H_3Me_2\text{-}3,4)]$	Golden-yellow	51.5 (51.3)	5.0 (5.0)	ν(WH) 1 900	2.29, 2.44, 3.20, 3.41, **3**, *c*, C_6H_3; 5.82, **10**, *s*, $(\eta\text{-}C_5H_5)_2$; 7.85, **6**, *c*, Me_2; 20.5, **1**, *s*, WH [e]
(9)	$[W(\eta\text{-}C_5H_5)_2Cl(C_6H_4Me\text{-}4)]$	Brown	46.1 (46.4)	3.9 (3.9)		2.17, 3.21, **4**, *AA′BB′*, C_6H_4; 5.70, **10**, *s* $(\eta\text{-}C_5H_5)_2$; 7.93, **3**, *s*, Me [f]
(10)	$[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_3\text{-}Me_2\text{-}3,5)_2]$	Orange-red	60.5 (60.9)	6.1 (5.8)		3.25, **6**, *br s*, 2, C_6H_3; 5.30, **10**, *v br s*, $(\eta\text{-}C_5H_5)_2$; 7.47, **12**, *s*, 4Me; 8.41, **2**, *c*, CH_2; 8.78, **2**, *c*, CH_2 [g]
(11)	$[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_4Me\text{-}4)_2]$	Orange-yellow	60.3 (59.5)	6.4 (5.4)		2.86, **8**, *br m*, $2C_6H_4$; 5.30, 10, *br s*, $(\eta\text{-}C_5H_5)_2$; 7.48, **6**, *s*, 2Me; 8.50, **2**, *c*, CH_2; 8.88, **2**, *c*, CH_2 [f]
(12)	$[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_4OMe\text{-}4)_2]$	Orange	55.8 (56.1)	5.1 (5.0)		2.43, **4**, 2.87, 4, *AA′BB′*, $2C_6H_4$; 5.15, **10**, *s*, $(\eta\text{-}C_5H_5)_2$; 5.88, **6**, *s*, OMe; 7.2—8.6, **4**, *c*, $2CH_2$ [g]
(14)	$[W(\eta\text{-}C_5H_5)_2(CH_2Ph)\text{-}(C_6H_4Me\text{-}3$ and $\text{-}4)]$	Orange-red	58.1 (58.1)	4.9 (4.8)		3.25, **9**, *c*, Ph, C_6H_4; 5.67, **10**, 2, $\eta\text{-}C_5H_5$; [h] 7.95, **5**, *c*, CH_2, CH_3 [g,i]
(15)	$[W(\eta\text{-}C_5H_5)_2(C_6H_4Me\text{-}4)\text{-}(CH_2C_6H_3Me_2\text{-}3,5)]$	Red	 (59.5)	 (5.3)		2.52, **2**, *d* (J 7.2), 2H^A; 3.34, **2**, *d* (J 7.2), 2H^B; 3.36, **2**, *s*, 2H$^{A'}$; 3.52, **1**, *s*, H$^{B'}$; 5.33, **10**, *s*, $2\eta\text{-}C_5H_5$,[d] 5.70, **10**, *s*, $2\eta\text{-}C_5H_5$; 7.45, **2**, *s*, Me of C_6H_4Me; 7.57, **6**, *s*, Me_2 of $CH_2C_6H_3Me_2$; 7.71, **2**, *d* (J 0.5), W–CH_2 [e]
(16)	$[W(\eta\text{-}C_5H_5)_2H(CH_2C_6H_3\text{-}Me_2\text{-}3,5)]$	Orange	52.2 (52.5)	4.6 (5.1)	ν(WH) 1 890m	3.18, **2**, *s*, 2H^A; 3.29, **1**, *s*, H^B; 5.71, **10**, *d* (J 0.7), $2\eta\text{-}C_5H_5$; 7.58, **6**, *s*, $2Me_2$; 7.59, **2**, *s*, CH_2; 20.95, **1**, *s*, WH [e]
(17)	$[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_4Me\text{-}4)\text{-}(CH_2C_6H_3Me_2\text{-}3,5)]$	Red	Mixture with (11) [j]			Mixture of (17) and (11): 2.76, 2.85, 2.91, 2.99; 3.18, **8**, aromatic H; 5.80, **7.5**, *s*, $2\eta\text{-}C_5H_5$ of (17); 5.83, **2.5**, *s*, $2\eta\text{-}C_5H_5$ of (11); 7.68, 7.96, 7.98, **13**, aliphatic H [e,k]
(18)	*cis*-$[H(\eta\text{-}C_5H_5)W(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2W(\eta\text{-}C_5H_5)\text{-}(CH_2SiMe_3)]$	Orange	40.3 (40.3)	4.3 (4.2)	ν(WH) 1 898m	4.32, **1**, *c*, H [l]; 4.67, **1**, *c*, H [l]; 5.22, **1**, *c*, H [l]; 5.41, **5**, *d* (J 0.6), $\eta\text{-}C_5H_5$; 5.45, **1**, *c*, H [l]; 5.47, **5**, *s*, $\eta\text{-}C_5H_5$; 5.68, **1**, *c*, H [l]; 6.18, **1**, *c*, H[l]; 6.23, **1**, *c*, H [l]; 6.47, **1**, *c*, H [l]; 9.63, **9**, *s*, $SiMe_3$; 10.66, **1**, *d* (J 14), H [m]; 10.71, **1**, *d* (J 14), H [m]; 21.64, **1**, *s*, WH [e] (270 MHz)
(19)	*trans*-$[H(\eta\text{-}C_5H_5)W(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2W(\eta\text{-}C_5H_5)\text{-}(CH_2SiMe_3)]$	Orange	40.5 (40.3)	4.3 (4.2)	ν(WH) 1 884m	4.65, **1**, *c*, H [l]; 4.74, **1**, *c*, H [l]; 5.17, **1**, *c*, H [l]; 5.41, **1**, *c*, H [l]; 5.52, **5**, *d* (J 0.7), $\eta\text{-}C_5H_5$; 5.58, **5**, $\eta\text{-}C_5H_5$; 5.95, **1**, *c*, H [l]; 6.14, **1**, *c*, H [l]; 6.27, **1**, *c*, H [l]; 6.45, **1**, *c*, H [l]; 9.60, **9**, *s*, $SiMe_3$; 10.48, **1**, *d* (J 14), H [m]; 10.87, **1**, *d* (J 14), H [m]; 21.65, **1**, *s*, WH [e] (270 MHz)
(20)	$[W(\eta\text{-}C_5H_5)_2H(OCOEt)]$	Red	40.5 (40.2)	3.9 (3.9)	ν(WH) 1 901m	5.14, **10**, *d* (J 0.7), $(\eta\text{-}C_5H_5)_2$; 8.23, **2**, *q* (J 9), CH_2; 9.23, **3**, *t* (J 9), Me; 21.77, **1**, WH [d]

[a] Calculated values are given in parentheses. [b] Given as: chemical shift (τ), **relative intensity**, *multiplicity* (J in Hz), assignment· Lettering of hydrogens as in the Schemes. [c] The chemical-shift separation between the centres of the fluorine resonances of the C_6H_4F-3- and -4 isomers was 5.8 p.p.m., relative intensity 2 : 3. [d] In $C(CD_3)_2O$. [e] In C_6D_6. [f] In $CDCl_3$. [g] In CS_2. [h] Two peaks showing the presence of two different $W(\eta\text{-}C_5H_5)_2$ systems. [i] Consistent with two different Me groups and a broad CH_2 resonance. [j] See mass spectrum and text. [k] See text: the spectrum analyses as a 3 : 1 mixture of (17) and (11) respectively. [l] The eight hydrogens of two different $\sigma:\eta^5\text{-}C_5H_4$ groups, each occurring as ABCD systems. [m] The diasterotopic hydrogens of the W–CH_2–Si group.

to change the ratio of the two bands assignable to the $\eta\text{-}C_5H_5$ groups when the components of the initial eluate were compared to those of the final portion of the eluate. The close proximity of the two $\eta\text{-}C_5H_5$ resonances suggests that the two isomers of (14) have similar structure. Further, when the intensity ratio of the $\eta\text{-}C_5H_5$ resonances corresponded to 1 : 1 the ratio of the intensity of the aromatic compared to the aliphatic hydrogens corresponded more nearly to 9 : 5 than to 8.5 : 5.5 or 8 : 6. On the basis of this evidence we tentatively assign the structures of the isomers as $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)(C_6H_5Me\text{-}4)]$ (14^4) and $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)(C_6H_4Me\text{-}3)]$ (14^3), rather than to suppose that one or both of these components are isomers of the ditolyl derivative $[W(\eta\text{-}C_5H_5)_2(C_6H_4Me)_2]$. Strong circumstantial evidence supporting this conclusion is the observation that there is no case where photolysis of (1) in aromatic solvents has led to formation of diaryl derivatives.

Irradiation of (1) in mesitylene–toluene (2 : 1) gave after chromatography four components. The first band yielded red crystals, soluble in light petroleum and moderately sensitive to oxidation in air. The mass spectrum showed a highest peak corresponding to the ion $[W(\eta\text{-}C_5H_5)_2\text{-}$

$(C_6H_4Me)(CH_2C_6H_3Me_2)]^+$. The fragmentation pattern has peaks corresponding to the loss of the groups C_6H_4Me and $CH_2C_6H_3Me_2$. The ^1H n.m.r. spectrum suggested that the compound was the isomer $[W(\eta\text{-}C_5H_5)_2(C_6H_4Me\text{-}4)(CH_2C_6H_3Me_2\text{-}3,5)]$ (15). The second component of the reaction mixture was orange-red crystals of the compound (10). The third band was present in only trace quantities. The mass spectrum showed it to contain a dimeric species. The fourth component was unchanged compound (1).



SCHEME 2 Irradiation of (1) in *ca.* 10^{-3} mol dm^{-3} solutions at room temperature (r.t.) in: (*i*) $1,3,5\text{-}Me_3C_6H_3$, 60%; (*ii*) $1,4\text{-}Me_2C_6H_4$, 60%; (*iii*) $1\text{-}Me\text{-}4\text{-}MeOC_6H_4$, 55%; (*iv*) MeC_6H_5, 18% (ratio of C_6H_4Me-4 to -3 isomers = 3 : 2); (*v*) toluene–mesitylene (1 : 2), 9%; (*vi*) $MeCO_2Et$, 33%; (*vii*) $SiMe_4$, 31% (*trans* : *cis* = 0.8 : 1); (*viii*) toluene, 26% (ratio of C_6H_4Me-4 to -3 isomers = 10 : 1)

Photolysis of (1) in mesitylene for 6 h only, followed by removal of the solvent, gave a dark red solid. The ^1H n.m.r. spectrum of this unpurified material shows there to be at least four components present since there were four bands assignable to hydrogens attached to tungsten. A careful examination of the chemical-shift data showed that the major component was unchanged (1). The next most intense high-field band, at τ 20.9, has a chemical shift corresponding to the compound $[W(\eta\text{-}C_5H_5)_2H(CH_2C_6H_3Me_2\text{-}3,5)]$ (16). There were also bands in the region τ 0—10 consistent with the presence of (16). Chromatography of The crude mixture yielded also the compound (10), as would be expected. We conclude that (16) is present in a partially photolysed solution of (1) in mesitylene.

It has been shown that thermolysis of the hydridomethyl $[W(\eta\text{-}C_5H_5)_2H(Me)]$ in benzene or *p*-xylene gave the hydridophenyl $[W(\eta\text{-}C_5H_5)_2H(Ph)]$ and 4-methylbenzyl $[W(\eta\text{-}C_5H_5)_2H(CH_2C_6H_4Me\text{-}4)]$ derivatives respectively.[9] In order to gain insight into the mechanism of formation of compound (10) it was decided to prepare and study the photolysis of the derivative $[W(\eta\text{-}C_5H_5)_2H(CH_2C_6H_3Me_2\text{-}3,5)]$ (16). It was found that compound (16) could be readily prepared by thermolysis of the hydridomethyl $[W(\eta\text{-}C_5H_5)_2H(Me)]$ in pure mesitylene as air-sensitive orange crystals which were unstable to chromatography on an alumina column.

A solution of (16) in mesitylene was irradiated for 12 h and after chromatography compound (10) was isolated in good yield. Moreover, irradiation of (16) in *p*-xylene gave, after chromatography, two bands. The first band yielded orange-red crystals which were soluble in light petroleum and whose solutions were air sensitive. The ^1H n.m.r. spectrum showed the presence of two compounds one of which was clearly the bis(4-methylbenzyl) derivative (11). The spectrum of the other component, which could be obtained by subtraction of the known spectrum of the compound (11) from that of the spectrum of the mixture, was entirely consistent with the structure $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_4Me\text{-}4)(CH_2C_6H_3Me_2\text{-}3,5)]$ (17). This formulation is strongly supported by the mass spectrum of the mixture which shows a highest parent-ion peak at *m/e* 538 corresponding to the parent ion of (17). The next highest band occurs at *m/e* 524 corresponding to the parent ion $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_4Me\text{-}4)_2]^+$. There was no evidence for the presence of (10) in the mass spectrum. Also, the mass spectrum shows fragments corresponding to $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_3Me_2\text{-}3,5)]^+$ at *m/e* 433 and $[W(\eta\text{-}C_5H_5)_2(C_6H_4Me\text{-}4)]^+$ at *m/e* 419. Moreover, the relative intensity of the band at *m/e* 419 compared to that at 524 was markedly greater than in the mass spectrum of pure (11). This is consistent with the formation of the ion at *m/e* 419 from both (11) and (17) rather than from (11) alone.

As a further study of the reactivity of the tungstenocene species the photolysis of (1) in tetramethylsilane was investigated. Careful chromatography of the reaction mixture gave four components, the first and second of which yielded orange hexagonal crystals. The third component was compound (1) and the fourth was a trace quantity of a red oil which was not further studied.

The two orange crystalline compounds were thermally stable up to *ca.* 150 °C and they could be sublimed. The mass spectra suggest they were isomers, with parent ions at *m/e* 714. The more soluble isomer was shown by determination of the crystal structure and by the detailed ^1H n.m.r. data in the Table to be *cis*-$[H(\eta\text{-}C_5H_5)W(\sigma\text{:}\eta^5\text{-}C_5H_4)_2W(\eta\text{-}C_5H_5)(CH_2SiMe_3)]$ (18), whilst the crystal structure and ^1H n.m.r. data show the less-soluble isomer to be the *trans* isomer (19). The structures of (18) and (19) are shown in Scheme 2.[10] Treatment of (18) with concentrated H_2SO_4 releases $SiMe_4$ (g.l.c.).

The benzoatohydride (4) was treated with an excess of benzoic acid but there was no formation of the known dibenzoate $[W(\eta\text{-}C_5H_5)_2(OCOPh)_2]$. Irradiation of the benzoatohydride (4) in a solution of methyl benzoate containing benzoic acid gave the dibenzoate in good yield.

Photolysis of (1) in methyl propionate gave, after chromatography, (1) and red crystals which were sparingly soluble in light petroleum. The solution was readily oxidised in air. The data showed the compound to be $[W(\eta\text{-}C_5H_5)_2H(OCOEt)]$ (20).

DISCUSSION

Here we consider both the work reported above and the thermally induced insertions of tungsten into aromatic and aliphatic C–H bonds which have been described in a separate paper.[9]

As mentioned in the introduction, our initial hypothesis was that photolysis of (1) caused evolution of dihydrogen and formation of tungstenocene $[W(\eta\text{-}C_5H_5)_2]$. Direct evidence for the presence of monomeric tungstenocene is unavailable at present, but there is a considerable body of circumstantial evidence which may be summarised as follows. Tungstenocene has been postulated as the reactive intermediate in the photolysis of $[W(\eta\text{-}C_5H_5)_2(CO)]$.[11] In this work attention was further drawn to the carbene-like nature of the proposed tungstenocene. Thomas and Brintzinger[12] invoked tungstenocene as the active intermediate in the reduction of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ by sodium amalgam. Molybdenocene has been postulated as the intermediate in the thermal reactions of $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ and sodium amalgam with olefins[13] and acetylenes[11,13,14] and in photoinduced reactions of $[Mo(\eta\text{-}C_5H_5)_2H_2]$ giving the red dimer $[\{Mo(\eta\text{-}C_5H_5)(\mu\text{-}\sigma\text{:}\eta^5\text{-}C_5H_4)\}_2]$ and $[Mo(\eta\text{-}C_5H_5)_2(PR_3)]$.[14] We note also that tungstenocene and molybdenocene are heavier congeners of the stable monomer chromocene. The work described in this paper shows that there are very close similarities between the products of the photoinduced reactions of (1) with benzene and fluorobenzene and the products of thermolysis of $[W(\eta\text{-}C_5H_5)_2H(Me)]$[9] in the presence of these same substrates. Thus the distribution of the 3- and 4-fluorophenyl isomers (3^3) and (3^4) is similar in both reactions. This suggests that the reactive intermediate is the same, *i.e.* tungstenocene. We consider this body of evidence as sufficient reason to continue with the proposal that tungstenocene is the initial product of photolysis of (1) or thermolysis of $[W(\eta\text{-}C_5H_5)_2H(Me)]$ but we briefly consider alternatives to tungstenocene later in the discussion.

The formation of tungstenocene by thermal elimination of methane from $[W(\eta\text{-}C_5H_5)_2H(Me)]$ may be regarded as a simple example of the well known reductive elimination of an alkane from a metal hydridoalkyl, as discussed elsewhere.[9]

Although the thermally induced reductive elimination of dihydrogen from metal hydrides is well established, *e.g.* for $[Nb(\eta\text{-}C_5H_5)_2H_3]$,[15] there are only a few other examples of photoinduced evolution of dihydrogen from metal dihydrides, *e.g.* for $[Ir(CO)(PPh_3)_2H_2]$.[16] A matrix-isolation study of the photolysis of (1) is presently in progress.

Tungstenocene is a d^4 16-electron molecule and has a vacant co-ordination site. The η-cyclopentadienyl ligand is sterically rather compact given the consideration that it contributes five electrons to the metal centre. Therefore, the co-ordination site on tungstenocene is sterically unencumbered and accessible to the close approach of quite bulky molecules.

The photoelectron spectra of bis(η-cyclopentadienyl)-molybdenum and -tungsten compounds, *e.g.* $[W(\eta\text{-}C_5H_5)_2R_2]$ where M = Mo or W and R = H or Me, show that the ionisation potentials of the essentially d^2 electrons occur in the region 5.5—6.5 eV.* Relatively few classes of transition-metal compounds are known with lower ionisation energies so that these bis(η-cyclopentadienyl)-molybdenum and -tungsten compounds may be regarded as 'electron-rich' molecules.[17] Since

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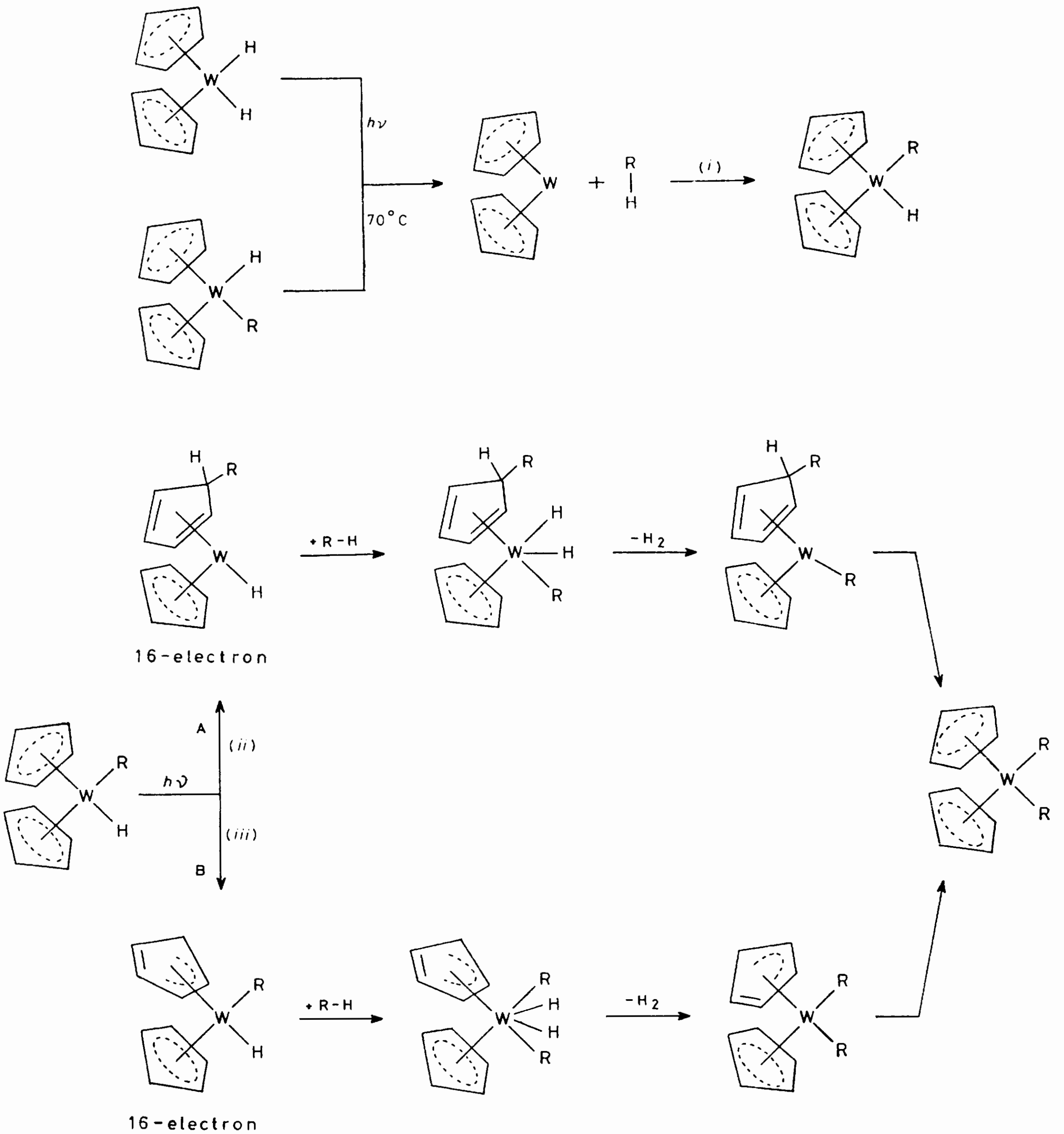
* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

hydrogen and carbon are more electronegative than molybdenum and tungsten it follows that molybdenocene and tungstenocene would be even more electron rich than the d^2 compounds.



SCHEME 3 Mechanism for the photoinduced reactions of (1): (*i*) insertion into sp^2- or sp^3-C–H bond; (*ii*) reversible alkyl migrations (route A); (*iii*) reversible $\eta^5 \rightleftarrows \eta^3$-ring shift (also postulated elsewhere [21])

We propose that the insertion of tungstenocene into aromatic or aliphatic C–H bonds proceeds by a homolytic three-centred interaction akin to the addition of dihydrogen to a metal centre. It is possible that the insertion into aromatic C–H bonds proceeds *via* prior formation of a metal–π-arene complex but there seems little likelihood that there could be any significant initial complex formation between tungstenocene and tetramethylsilane.

We have shown that the photolysis of (1) in mesitylene or *p*-xylene gives the dialkyl derivatives (10) and (11) respectively, whilst thermolysis of $[W(\eta\text{-}C_5H_5)_2H(Me)]$ in mesitylene or *p*-xylene gives (16) and $[W(\eta\text{-}C_5H_5)_2H(CH_2C_6H_4Me\text{-}4)]$ [9] respectively. Clearly the formation of the dialkyl derivative (**10**) may proceed by initial insertion of tungstenocene into mesitylene giving (**16**) but the reaction with the second mesitylene molecule must arise by reaction with a tungsten centre other than that of tungstenocene. Whilst thermolysis of (**16**) in mesitylene does not give rise to (**10**) we have shown that photolysis of (**16**) in *p*-xylene gives compound (**17**) so that we have established that monoalkylhydrides can be intermediates in the photoinduced formation of the dialkyl compounds. At present, we envisage two possible mechanisms for the photoinduced formation of dialkyl derivatives from monoalkyls. They are shown in Scheme **3**. Route A proceeds *via* reversible migration of the alkyl from the metal to the η-cyclopentadienyl ring. Some precedent for this comes from the observed reversible migration of ethyl group in the following sequence.[18] Route B proceeds *via* a reversible η^3 to η^5 ring shift. Circumstantial evidence for this arises from the characterisation by Brintzinger of the first η^3-C_5H_5 ring, in the compound $[W(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(CO)_2]$.[19,20] The η^3 to η^5 shift is demonstrated in the photolysis of the dicarbonyl, causing smooth evolution of a molecule of carbon monoxide and formation of the monocarbonyl $[W(\eta\text{-}C_5H_5)_2(CO)]$.[19,20] The formation of the binuclear isomers (**19**) and (**20**) may be envisaged to occur by reaction between intermediate $[W(\eta\text{-}C_5H_5)_2H(CH_2SiMe_3)]$ and tungstenocene.

$$[Mo(\eta\text{-}C_5H_5)_2Cl(Et)] \xrightarrow{PMe_2Ph} [Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_5Et\text{-}endo)(PMe_2Ph)Cl] \xrightarrow{Tl[PF_6]} [Mo(\eta\text{-}C_5H_5)_2Et(PMe_2Ph)][PF_6] + TlCl$$

The activation of saturated C–H bonds by insertion of a transition metal is of interest in the context of metal-catalysed reactions of hydrocarbons and, for example, in the development of specific catalysts for the functionalisation of alkanes. Apart from the above studies, the intramolecular insertion of a metal into a saturated C–H bond under homogeneous conditions giving isolable hydridoalkyl derivatives has been observed for the system $[M(Me_2PCH_2CH_2PMe_2)_2]$ (M = Fe or Ru).[22] The metal centre in this compound is also likely to be unusually electron rich.

Many clean surfaces of large transition metals, *e.g.* tungsten, will readily activate pure alkanes and in this context we note that the work functions of transition-metal surfaces lie in the region of 4—5 eV. We note also that exchange of hydrogen in methane has been catalysed by platinum salts in deuterium oxide.[23]

On the basis of our studies and related work discussed above we are inclined to the view that activation of saturated C–H bonds under homogeneous conditions by insertion of a metal will be favoured by metal compounds which have highly electron-rich metal centres and 16 electrons or less. They should be sterically unencumbered [24] and have at least two non-bonding *d* electrons available for formation of the M–H and M–C bonds. The ligand environment will have to donate electrons to the metal in order to create the electron-rich condition. It will be necessary or desirable that the ligands attached to the metal do not present portions of themselves to the metal site and thereby quench the activity, for example, by internal oxidative-addition reactions of bound alkyl groups of the ligand.

EXPERIMENTAL

All preparations and manipulations were carried out under dinitrogen or in a vacuum, unless otherwise stated. Solvents were dried and distilled before use. Microanalyses were by the A. Bernhardt Microanalytical Laboratory or by the analytical laboratory of this department. Infrared spectra were determined as mulls on a Perkin-Elmer 457 spectrometer and were calibrated with polystyrene film. Hydrogen-1 n.m.r. spectra were recorded using a JEOL C6OH7, Bruker (90 MHz), or a 270-MHz instrument of the Oxford Enzyme Group. Fluorine-19 n.m.r. spectra were determined on a Bruker (90 MHz) instrument, mass spectra using an A.E.I. M.S.9 spectrometer. Photolysis experiments were carried out in a standard Pyrex-glass apparatus cooled by tap water. The lamps used were 100- or 500-W medium-pressure mercury lamps, supplied by Hanovia. Chromatography was carried out on alumina columns (length 30—80 cm, diameter 2—3 cm) (100—110 mesh, approximately grade 3), which were made up in light petroleum.

The compounds $[M(\eta\text{-}C_5H_5)_2H_2]$, M = Mo or W, were prepared as described.[25]

3- *and* 4-*Fluorophenyl-bis*(η-*cyclopentadienyl*)*hydridotungsten*, (3^3) *and* (3^4).—The compound $[W(\eta\text{-}C_5H_5)_2H_2]$ (**1**) (1.0 g, 3.2 mmol) in distilled fluorobenzene (1 l) was irradiated (100-W lamp for 60 h). The initially yellow solution became red and a small quantity of a dark solid separated. After filtration, the solvent was removed from the filtrate under reduced pressure giving an orange residue. This was chromatographed. Elution with toluene–light petroleum (b.p. 30—40 °C) (3 : 7) gave a yellow band (A). Further elution with toluene–diethyl ether (1 : 1) gave a second yellow band, shown by the i.r. spectrum to contain compound (**1**). Band A, after removal of solvent, gave a yellow-orange oil. This was dissolved in light petroleum (b.p. 60—80 °C) and after concentration and cooling (−40 °C) yellow needles separated. These were collected, washed with cold light petroleum, and dried *in vacuo*, yield 0.65 g (50%). The ^1H and ^{19}F n.m.r. spectra showed the product to be a 3 : 2 mixture of compounds (3^3) and (3^4). Rechromatography on a long alumina column (1 m) and elution with pure light petroleum gave a very broad band which was collected into an initial, middle, and final fraction. The ^1H n.m.r. spectra showed the first fraction to contain *ca.* 10% more of (3^3) than the final fraction.

3- *and* 4-*Methoxycarbonylphenyl-bis*(η-*cyclopentadienyl*)-*hydridotungsten*, (**5**) *and* (**6**), *Benzoatobis*(η-*cyclopentadienyl*)*hydridotungsten*, (**4**).—The dihydride (**1**) (0.8 g, 2.5 mmol) in methyl benzoate (100 cm³) was irradiated (400 W) for 60 h. The initially yellow solution became red and a small quantity of a dark material separated. After filtration the solvent was removed under reduced pressure giving a red oily solid which was chromatographed. Elution with toluene–light petroleum (b.p. 60—80 °C) (3 : 17) gave, in sequence, a yellow band (A), a salmon-pink band (B), and an orange band (C). During this elution the ratio of toluene to light petroleum was gradually increased to 3 : 2. Band (A) was shown (i.r.) to be due to (**1**) (0.08 g). The salmon-pink band was rechromatographed on a longer column (1 m). Elution with toluene–light petroleum separated two components, an initial yellow band (B1) and a second orange band (B2). Band (B1) gave a yellow solid which was recrystallised from light petroleum–diethyl ether as the pure compound (6) (0.3 g, 26%). Band (B2) gave orange-red crystals which were crystallised from warm (70 °C) light petroleum–diethyl ether (b.p. 100—120 °C) as the pure compound (5) (0.1 g, 8.8%). Band (C) gave orange crystals which were crystallised from hot benzene–light petroleum (b.p. 100—120 °C) as the pure compound (4) (0.2 g, 18%).

Bis(*η-cyclopentadienyl*)*hydrido*(4-*methoxyphenyl*)*tungsten* (7).—The reaction was carried out as described above using $[W(\eta\text{-}C_5H_5)_2H_2]$ (0.1 g, 0.32 mmol) and pure dry methoxybenzene (100 cm^3). Irradiation was carried out for 20 h at r.t. The product was obtained from the alumina column as the first band eluted using toluene–light petroleum (b.p. 30—40 °C) (1 : 1) and was recrystallised from this solvent, yield 0.051 g (40%). Further elution of the column with toluene–diethyl ether gave (1) (0.04 g, 40%).

Bis(*η-cyclopentadienyl*)(3,4-*dimethylphenyl*)*hydridotungsten*, (8).—Compound (1) (0.1 g) in *o*-xylene (250 cm^3) was irradiated for 8 h. The product was isolated by chromatography, eluting with toluene–light petroleum (b.p. 30—40 °C) (1 : 1), and recrystallised from the same solvent, yield 0.1 g (70%).

Chlorobis(*η-cyclopentadienyl*)(4-*tolyl*)*tungsten*, (9).—Compound (1) (0.29 g, 0.9 mmol) in *p*-chlorotoluene (250 cm^3) was irradiated for 12 h. The product was isolated by chromatography, eluting with toluene–diethyl ether (8 : 2), as brown crystals. Further elution with toluene–diethyl ether (4 : 6) gave a red-brown band which yielded red crystals. The brown crystals were recrystallised from toluene–light petroleum as the pure compound (9) (0.16 g, 40%). The red crystals were also crystallised from this solvent giving $[W(\eta\text{-}C_5H_5)_2Cl(H)]$ which was identified by comparison of the i.r. spectrum with that of an authentic sample, yield 0.1 g (30%).[6]

Bis(*η-cyclopentadienyl*)*bis*(3,5-*dimethylbenzyl*)*tungsten*, (10).—Compound (1) (0.34 g, 1.7 mmol) in mesitylene (250 cm^3) was irradiated for 12 h. The initial yellow solution became orange and a brown material separated from solution. The product was isolated by chromatography, eluting with toluene–light petroleum followed by toluene–diethyl ether (1 : 1). Two bands were eluted. The first gave orange crystals which were recrystallised from hot toluene as the pure compound (10) (0.22 g, 46%). The second band yielded unchanged (1) (0.13 g, 38%).

Bis(*η-cyclopentadienyl*)*bis*(4-*methylbenzyl*)*tungsten*, (11).—Compound (1) (0.2 g, 0.63 mmol) in *p*-xylene (250 cm^3) was irradiated for 14 h. The products were isolated as described above for compound (10). The first band yielded orange crystals which could be recrystallised from toluene–light petroleum as pure (11) (0.3 g, 63%). The second band gave unchanged (1) (0.09 g, 31%).

Bis(*η-cyclopentadienyl*)*bis*(4-*methoxybenzyl*)*tungsten*, (12).—Compound (1) (0.26 g, 0.82 mmol) in pure dry *p*-methylanisole (250 cm^3) was irradiated under standard conditions for 12 h. The product was isolated by chromatography, eluting with toluene–diethyl ether (8 : 2), and then crystallised from toluene–light petroleum as orange crystals of the pure compound (12) (0.23 g, 49%). Further elution with toluene–diethyl ether (1 : 1) gave compound (1) (0.09 g, 35%).

Photolyses.—(1) *in toluene: synthesis of* (13) *and* (14).—The dihydride (1) (0.9 g, 2.85 mmol) in dry toluene (1 l) was irradiated for 48 h, giving an orange-red solution and some dark material. After removal of the solvent the residual red oil was chromatographed. Elution with toluene–light petroleum (b.p. 60—80 °C) (1 : 5) gave, after removal of solvent from the eluates, first a yellow oil (A) and secondly orange-red crystals (B). The oil (A) was reprecipitated from cold light petroleum (b.p. 30—40 °C) and dried *in vacuo* (0.3 g, 26%). The ^1H n.m.r. spectrum suggested it to be a 1 : 10 mixture of the 3-,4-Me isomers (13). The eluate (B) was recrystallised from warm saturated light petroleum (b.p. 100—120 °C) as the isomers (14) (0.25 g, 18%). Rechromatography of (14) and elution with toluene–light petroleum (b.p. 60—80 °C) (1 : 4) gave a broad yellow band. The ^1H n.m.r. spectrum of the initial and final portions of the band were determined and showed the ratio of the two isomers of (14) had changed by *ca.* 10%.

$[W(\eta\text{-}C_5H_5)_2H(CH_2C_6H_3Me_2\text{-}3,5)]$ (16) *in* p-*xylene: synthesis of* (17). Compound (16) (0.2 g, 0.46 mmol) in *p*-xylene (200 cm^3) was irradiated for 17 h. After removal of the solvent from the orange reaction mixture the resulting red solid was chromatographed. Elution with light petroleum (b.p. 60—80 °C) then toluene–light petroleum (3 : 7) gave an orange band (A) and then a yellow band (B). Band (A), after removal of the solvent, yielded orange crystals which were recrystallised from warm light petroleum, yield 0.12 g. The ^1H n.m.r. spectrum showed the product to be a mixture of (11) and (17).

(16) *in mesitylene*. Compound (16) (0.2 g, 0.46 mmol) in mesitylene (200 cm^3) was irradiated for 17 h giving an orange solution. After removal of the solvent the resulting red solid was chromatographed. Elution with toluene–light petroleum (b.p. 60—80 °C) (7 : 3) yielded a single yellow band. The eluate gave orange-red crystals which the i.r. spectrum showed to be pure (10) (0.15 g, 61%).

$[W(\eta\text{-}C_5H_5)_2H_2]$ *in a toluene–mesitylene mixture*. Compound (1) (0.3 g, 0.95 mmol) in toluene–mesitylene (1 : 2) (200 cm^3) was irradiated (100-W lamp, 24 h). The resulting yellow solution was filtered free from some red material and the solvent was removed from the filtrate giving a red oil. This was chromatographed. Elution with toluene–light petroleum (b.p. 60—80 °C) (1 : 9) gave a yellow band (A). Further elution with toluene–petroleum (1 : 1) yielded a red-orange band (B). Band (A) gave a yellow solid which was recrystallised from warm (70 °C) light petroleum (b.p. 100—120 °C) as red crystals of (15) (0.05 g, 9%). Band (B) yielded a red solid which was recrystallised from warm light petroleum (b.p. 40—60 °C) as orange-red crystals of (10) (0.05 g, 10%).

Further elution of the column with pure toluene resulted in a third band (C) which, after removal of the solvent and recrystallisation from light petroleum, was shown (i.r. spectrum) to be the known compound *trans*-$[\{H(\eta\text{-}C_5H_5)W(\mu\text{-}\sigma\text{:}\eta^5\text{-}C_5H_4)\}_2]$ (0.01 g, 3.3%).[26] Finally, elution with toluene–diethyl ether (1 : 1) gave a yellow band containing (1) (0.05 g, 17%).

cis- *and* trans-*bis*(*μ-σ*:1—5-*η-cyclopentadienediyl*)-[(*η-cyclopentadienyl*)*hydridotungsten*][(*η-cyclopentadienyl*)(*trimethylsilylmethyl*)*tungsten*], (18) *and* (19).—Compound (1) (0.1 g, 0.32 mmol) in tetramethylsilane (200 cm^3) was irradiated (500 W, for 22 h). The initially pale yellow solution darkened and a small quantity of dark red material precipitated. The above procedure was repeated four times and the products were combined. After filtration the solvent was removed from the filtrate giving an orange-red solid. This was chromatographed. Elution with toluene–light petroleum (b.p. 30—40 °C) (1 : 10) gave a yellow band (A). Further elution with toluene–light petroleum (3 : 10) yielded a second yellow band (B). Finally, elution with toluene–light petroleum (3 : 2) gave a third band shown to contain (1).

After removal of solvent from the band (A) the residual orange solid was crystallised from warm light petroleum (b.p. 60—80 °C), yield 0.1 g (22%). The compound was shown to be pure (18). Similar work-up of band (B) gave orange crystals of pure (19) (0.7 g, 15%). Crystals suitable for *X*-ray diffraction were obtained from warm saturated acetonitrile solutions.

Dibenzoatobis(η-cyclopentadienyl)tungsten.—Irradiation of (4) (0.15 g, 0.34 mmol) and benzoic acid (0.2 g, 1.5 mmol) in methyl benzoate (200 cm^3) (500 W, 24 h) gave a red solution. After filtration the solvent was removed under reduced pressure giving a deep red solid which was chromatographed. Elution with diethyl ether yielded an orange band which contained unchanged (4) (0.05 g, 33%). Further elution with acetone gave a purple band from which purple crystals were obtained after removal of the solvent. These were recrystallised from hot benzene–light petroleum (b.p. 60—80 °C), yield 0.08 g (31%).

Bis(η-cyclopentadienyl)hydridopropionatotungsten, (20).—Compound (1) (0.5 g, 1.6 mmol) in dry methyl propionate (200 cm^3) was irradiated (500 W, for 17 h). The resulting red solution was filtered free from a dark solid and the solvent was removed under reduced pressure. The red residue was chromatographed. Elution with toluene–diethyl ether (1 : 1) gave a yellow band containing (1) (0.05 g, 10%). Further elution with acetone yielded a red band which after removal of the solvent gave a red residue. This was recrystallised from hot benzene–petroleum as red crystals of the pure compound (20) (0.2 g, 33%).

Mass-spectral Data.—Data are presented as compound number, *m/e*, for ^{184}W isotope only, assignment, *etc.* *P* represents the parent ion, further assignments being given in terms of loss of a fragment, *e.g.* $P - H$ indicates loss of one hydrogen from the parent ion. W(cp)$_2$ indicates [W(η-C$_5$H$_5$)$_2$]. Characteristic isotope patterns for tungsten-containing species were observed for all reported peaks.

(3): 410, *P*; 409, $P - H$; 389, $P - H_2F$; 314, $P - C_6H_5F$. (4): 437, $P - H$; 314, $P - C_6H_5CO_2H$. (5): 499, $P - H$; 391, $[W(cp)_2(C_6H_5)]^+$; 314, $[W(cp)_2]^+$. (6): 499, $P - H$; 391, $[W(cp)_2(C_6H_5)]^+$; 314, $[W(cp)_2]^+$. (7): 422, *P*. (8): 421, *P*. (9): 440, *P*; 405, $P - Cl$; 349, $P - MeC_6H_4$; 314, $[W(cp)_2]^+$. (10): 552, *P*; 433, $P - CH_2C_6H_3Me_2$; 314, $[W(cp)_2]^+$. (11): 524, *P*; 419, $P - CH_2C_6H_4Me$; 314, $[W(cp)_2]^+$. (12): 556, *P*; 435, $P - CH_2C_6H_4OMe$; 314, $[W(cp)_2]^+$. (14): 496, *P*; 405, $[W(cp)_2(C_7H_7)]^+$; 314, $[W(cp)_2]^+$. (15): 524, *P*, 433, $P - C_6H_4Me$; 314, $[W(cp)_2]^+$. (16): 434, *P*; 314, $P - C_6H_3Me_3$. (11) and (17): 538, $[W(cp)_2(CH_2C_6H_3Me_2)CH_2C_6H_4CH_3)]^+$; 524, $[W(cp)_2(CH_2C_6H_4Me)_2]^+$; 433, $[W(cp)_2(CH_2C_6H_3Me_2)]^+$; 419, $[W(cp)_2(CH_2C_6H_4Me)]^+$; 314, $[W(cp)_2]^+$. (18): 714, *P*; 627, $P - CH_2SiMe_3$; 626, $[P - SiMe_3]^+$; 313, $[P - SiMe_4]^{2+}$; 73, $[SiMe_3]^+$. (19): 714, *P*; 627, $P - CH_2SiMe_3$; 626, $P - SiMe_4$; 313, $[P - SiMe_4]^{2+}$; 88, $[SiMe_4]^+$. (20): 387, $P - H$; 331, $[W(cp)_2(OH)]^+$; 314, $[W(cp)_2]^+$.

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