

Activation of sp^2 and sp^3 Carbon–Hydrogen Bonds *via* Thermolysis of Bis-(η -cyclopentadienyl)hydridomethyltungsten

By N. John Cooper, Malcolm L. H. Green,* and Rahina Mahtab, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

The methylhydride $[W(\eta\text{-C}_5\text{H}_5)_2\text{Me(H)}]$ has been prepared by treatment of the compounds $[W(\eta\text{-C}_5\text{H}_5)_2\text{MeX}]$, where X = I or OCOPh, with $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2]$. Thermal decomposition of $[W(\eta\text{-C}_5\text{H}_5)_2\text{Me(H)}]$ in benzene, fluorobenzene, *p*-xylene, trimethyl phosphite, methanol, or dimethyl(4-tolyl)phosphine evolves methane and the compounds $[W(\eta\text{-C}_5\text{H}_5)_2\text{R(H)}]$, where R = Ph, $\text{C}_6\text{H}_4\text{F-3}$ or -4 , $\text{CH}_2\text{C}_6\text{H}_4\text{Me-4}$, OP(OMe)_2 , OMe, or $\text{PH(C}_6\text{H}_4\text{Me-4)}$ are formed. Treatment of $[W(\eta\text{-C}_5\text{H}_5)_2\{\text{PH(C}_6\text{H}_4\text{Me-4)}\}\text{H}]$ with methyl iodide gives $[W(\eta\text{-C}_5\text{H}_5)_2\{\text{PH(Me)(C}_6\text{H}_4\text{Me-4)}\}\text{H}]^+$. The oxidation of $[W(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2]$ with iodine yields paramagnetic $[W(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2]^+$ which may be reduced to the parent dimethyl compound.

THE photoinduced insertion of tungsten into both sp^2 and sp^3 carbon–hydrogen bonds has been demonstrated for compounds derived from bis(η -cyclopentadienyl)di-hydridotungsten.^{1–3} We had previously shown that tungsten species derived from the thermolysis of the compound $[W(\eta\text{-C}_5\text{H}_5)_2(\text{CHRCH}_2\text{R})\text{H}]$, R = CO_2Me , could insert into the C–H bond in benzene.⁴ However, in this thermolysis a number of other reactions occurred, for example β elimination of hydrogen giving $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$, so that a complex reaction mixture was obtained. In a search for a more convenient thermal source of reactive bis(η -cyclopentadienyl)tungsten systems we set out to synthesise and study the hitherto unknown hydridomethyl compound $[W(\eta\text{-C}_5\text{H}_5)_2\text{Me(H)}]$. This compound was chosen since there is evidence that simple *cis*-orientated hydridoalkyl derivatives of transition metals are thermally unstable and we hoped that the above hydridomethyl compound would decompose readily with formation of the 16-electron tungstenocene $[W(\eta\text{-C}_5\text{H}_5)_2]$ as the intermediate. This intermediate is thought to be one of the reactive tungsten species with the ability to activate, by insertion, sp^3 carbon–hydrogen bonds.^{2,3} Here we report the synthesis of $[W(\eta\text{-C}_5\text{H}_5)_2\text{Me(H)}]$, its properties and reactions.

RESULTS

Treatment of the iodomethyl compound $[W(\eta\text{-C}_5\text{H}_5)_2\text{Me(I)}]$ (1) in toluene with $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2]$ gives the hydridomethyl compound $[W(\eta\text{-C}_5\text{H}_5)_2\text{Me(H)}]$ (2) in good yield. However, the synthesis of (1) is rather lengthy⁵ and we have found an improved route to (2) starting from the dichloride $[W(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$. This is first converted into the dimethyl derivative $[W(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2]$ by the reported procedure.⁶ Treatment of the dimethyl compound with 1 mol equivalent of benzoic acid causes smooth evolution of methane and the methylbenzoate $[W(\eta\text{-C}_5\text{H}_5)_2(\text{OCOPh-Me})]$ (3) may be isolated in 90% yield. Treatment of (3) with $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2]$ causes smooth conversion of (3) into (2).

The yellow-orange crystalline (2) is very sensitive to oxygen. It is soluble in acetone, toluene, and light petroleum. The solutions appear to be stable at room temperature for prolonged periods. However, on warming to 60–80 °C there is steady evolution of methane. The pure solid (2) also decomposes at *ca.* 70 °C with evolution of methane. Thus (2) is a rare example of a methylhydride which has moderate thermal stability at room temperature.

Thermolysis of (2) in benzene at 70 °C causes evolution of methane and the known phenylhydride $[W(\eta\text{-C}_5\text{H}_5)_2\text{-Ph(H)}]$ may be isolated from the reaction mixture in good yield. Similarly, thermolysis of (2) in monofluorobenzene gives rise to the known⁷ isomers $[W(\eta\text{-C}_5\text{H}_5)_2(\text{C}_6\text{H}_4\text{F-4})\text{H}]$ (4) and $[W(\eta\text{-C}_5\text{H}_5)_2(\text{C}_6\text{H}_4\text{F-3})\text{H}]$ (5) in the ratio *ca.* 2 : 3.

When solutions of (2) in *p*-xylene are heated at 70 °C, methane is evolved and the alkylhydride derivative $[W(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_4\text{Me-4})\text{H}]$ (6) is formed. Prolonged heating (80 °C) of solutions of (6) in excess of *p*-xylene did not give rise to any of the known dialkyl derivative, namely $[W(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_4\text{Me-4})_2]$.² Compound (6) is rapidly oxidised in air.

Thermolysis of (2) in methanol gives the known⁸ methoxyhydride $[W(\eta\text{-C}_5\text{H}_5)_2(\text{OMe})\text{H}]$ and, unlike the photolysis of $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ in methanol, there is no evidence for the formation of the methoxymethyl derivative $[W(\eta\text{-C}_5\text{H}_5)_2(\text{OMe})\text{Me}]$.⁸

Compound (2) was thermally decomposed in solutions of trimethyl phosphite. Chromatography on alumina gave yellow crystals as the major product (*ca.* 25%). The mass spectrum and analytical data corresponded to the stoichiometry $[W(\eta\text{-C}_5\text{H}_5)_2\{\text{OP(OMe)}_2\}\text{H}]$ (8). The ¹H n.m.r. spectrum of (8) is consistent with and does not distinguish between isomers which have the structures W-OP(OMe)_2 or W-P(=O)(OMe)_2 for the OP(OMe)_2 ligand. We note that the methyl ester P(OMe)_3 can be induced to rearrange to MeP(=O)(OMe)_2 .⁹ The ³¹P n.m.r. spectrum shows only a strong single band and there was no evidence for satellites arising from any coupling between the ¹⁸³W and ³¹P nuclei. The i.r. spectrum of (8) shows no strong absorption in the region 1250–1300 cm^{-1} which is normally characteristic for the P=O stretching mode. We, therefore, concluded that (8) has the structure shown in the Scheme. During our initial studies of the reaction mixture from (2) and P(OMe)_3 we found that the mass spectrum of a sample of (8) obtained from the first part of the chromatography band gave a peak at *m/e* 438 which is 14 mass units higher than the observed parent ion in the mass spectrum of pure (8). The impurity may be the initially expected product, namely $[W(\eta\text{-C}_5\text{H}_5)_2\{\text{CH}_2\text{OP(OMe)}_2\}\text{H}]$.

Treatment of (8) in toluene with carbon tetrachloride gives red-brown crystals of the compound $[W(\eta\text{-C}_5\text{H}_5)_2\{\text{OP(OMe)}_2\}\text{Cl}]$ (9). The i.r. spectrum of this compound also showed no band assignable to a P=O stretching mode.

Thermal decomposition of (2) in pure dimethyl(4-tolyl)phosphine gave as the major product yellow crystals of (10). The mass spectrum showed the highest mass peak at *m/e* 438 corresponding to $[W(\eta\text{-C}_5\text{H}_5)_2\{\text{PH(C}_6\text{H}_4\text{Me-4)}\}\text{-}]$

Analytical and spectroscopic data

Compound	Colour	Analysis (%) ^a		Selected i.r. data (cm ⁻¹)	¹ H N.m.r. data ^b
(2) [W(η-C ₅ H ₅) ₂ Me(H)]	Yellow-orange	39.8 (40.0)	4.3 (4.2)	ν(W-H) 1 868vs	5.73, 10 , <i>d</i> (<i>J</i> 0.5), (η-C ₅ H ₅) ₂ ; 9.88, 3 , <i>d</i> (<i>J</i> 1.0) [<i>J</i> (¹⁸³ W-H) 5.2], Me; 20.51, 1 , <i>s</i> , W-H ^c
(3) [W(η-C ₅ H ₅) ₂ (OCOPh)Me]	Red-brown	47.7 (48.0)	4.1 (4.0)	ν(C=O) 1 630	2.45, 5 , <i>c</i> , Ph; 4.95, 10 , <i>s</i> , (η-C ₅ H ₅) ₂ ; 8.10, 3 , <i>s</i> , Me ^c
(6) [W(η-C ₅ H ₅) ₂ (CH ₂ C ₆ H ₄ Me-4)H]	Yellow-orange	50.2 (51.5)	4.9 (4.8)	ν(W-H) 1 900s	2.85, 4 , <i>c</i> , C ₆ H ₄ ; 5.68, 10 , <i>d</i> (<i>J</i> 0.5), (η-C ₅ H ₅) ₂ ; 7.51, 3 , <i>s</i> , Me; 9.48, 2 , <i>s</i> , CH ₂ [satellites partially resolved, <i>J</i> (¹⁸³ W-H) 6.7]; 21.54, 1 , <i>br s</i> , W-H ^c
(10) [W(η-C ₅ H ₅) ₂ {PH(C ₆ H ₄ Me-4)H}]	Yellow	46.6 (47.4)	4.3 (4.5)	ν(P-H) 2 280, ν(W-H) 1 895m	2.98, 4 , <i>c</i> , C ₆ H ₄ ; 5.30, 10 , <i>dd</i> [<i>J</i> (P-H) 2.0; <i>J</i> (H-H) 0.7], (η-C ₅ H ₅) ₂ ; 7.78, 3 , <i>s</i> , Me; 21.53, 1 , <i>d</i> [<i>J</i> (P-H) 21], W-H ^c
(11) [W(η-C ₅ H ₅) ₂ {PH(Me)(C ₆ H ₄ Me-4)H}][PF ₆]	Yellow	36.5 (36.2)	3.9 (3.7)	ν(W-H) 1 925w	2.47, <i>c</i> , 4 , C ₆ H ₄ ; 3.46, 1 , <i>dq</i> [<i>J</i> (P-H) 378; <i>J</i> (H-Me) 6.7], P-H; 4.75, 10 , <i>dd</i> [<i>J</i> (P-H) 2.8; <i>J</i> (H-H) 6.7], (η-C ₅ H ₅) ₂ ; 7.60, 3 , <i>s</i> , Me; 8.50, 3 , <i>dd</i> [<i>J</i> (P-H) 12, <i>J</i> (H-H) 6.7], Me-P; 22.0, 1 , <i>d</i> [<i>J</i> (P-H) 12], W-H ^d
(8) [W(η-C ₅ H ₅) ₂ {OP(OMe) ₂ }H]	Yellow	33.8 (34.0)	3.9 (4.0)	ν(W-H) 1 905s	5.5, 10 , <i>dd</i> [<i>J</i> (P-H) 1.7, <i>J</i> (H-H) 0.6], (η-C ₅ H ₅) ₂ ; 6.28, 6 , <i>d</i> [<i>J</i> (P-H) 9.3], (OMe) ₂ ; 21.2, 1 , <i>d</i> [<i>J</i> (P-H) 36.0], W-H ^c
(9) [W(η-C ₅ H ₅) ₂ {OP(OMe) ₂ }Cl]	Red	31.5 (31.4)	3.5 (3.5)		5.33, 10 , <i>d</i> [<i>J</i> (P-H) 1.7], (η-C ₅ H ₅) ₂ ; 7.06, 6 , <i>d</i> [<i>J</i> (P-H) 9.3], (OMe) ₂ ^e

^a Calculated values are given in parentheses. ^b Given as: chemical shift (τ), relative intensity, multiplicity (*J* in Hz), assignment, etc. ^c In C₆D₆. ^d In (CD₃)₂CO. ^e In CD₂Cl₂.

H]⁺. The i.r. spectrum of (10) showed bands at 1 895 and 2 280 cm⁻¹ assignable to ν(W-H) and ν(P-H) respectively. The ¹H n.m.r. spectrum showed among other resonances a doublet at τ 21.53 (*J* = 21 Hz) assignable to a W-H which was unaffected by irradiation of the resonances arising from the aromatic tolyl hydrogens. Also, irradiation of the band at τ 21.53 caused no observable change in the bands assigned to the tolyl hydrogens of (10). We conclude that the doublet structure for the hydride arises from coupling with the ³¹P nucleus whilst the broad nature reflects unresolved coupling with the ten (η-C₅H₅) hydrogens. The band assigned to the ten equivalent (η-C₅H₅) hydrogens occurs as a doublet centred at τ 5.30. The multiplet structure may be assigned to coupling with the hydride (*J* = 0.7 Hz) and the ³¹P nucleus (*J* = 2.0 Hz).

The ³¹P n.m.r. spectrum showed a broad doublet at +92.09 p.p.m. with the value *J* = 182 Hz which is typical for neutral tertiary P-H systems. The breadth of the resonance reflects unresolved coupling with the hydride and the ten η-C₅H₅ hydrogens. Broad-band proton decoupling collapses the resonance at +92.09 p.p.m. to a very sharp singlet with satellites whose intensity is consistent with their assignment as satellites arising from coupling between the ³¹P and ¹⁸³W nuclei (*J* = 110 Hz).

Treatment of (10) with an equivalent of methyl iodide gives a water-soluble yellow precipitate which can be precipitated from aqueous solution as a yellow crystalline hexafluorophosphate salt (11). The data given in the Table suggest that (11) contains the cation [W(η-C₅H₅)₂{PH(Me)(C₆H₄Me-4)H}]⁺. For example, the ¹H n.m.r. spectrum shows a doublet of quartets centred at τ 3.46 assignable to the P hydrogen with *J*(H-Me) = 6.7 and *J*(³¹P-H) = 378 Hz. The magnitude of the latter coupling constant is characteristic for phosphonium salts.¹⁰ The resonance assigned to the P-methyl hydrogens occurs as a doublet centred at τ 8.50 [*J*(³¹P-H) = 12 and *J*(H-H) = 6.7 Hz]. The doublet at τ 22.0 (*J* = 12 Hz) is assigned to the hydride coupled to the ³¹P nucleus. The hydrogen-decoupled ³¹P n.m.r. spectrum of (11) in CD₃OD

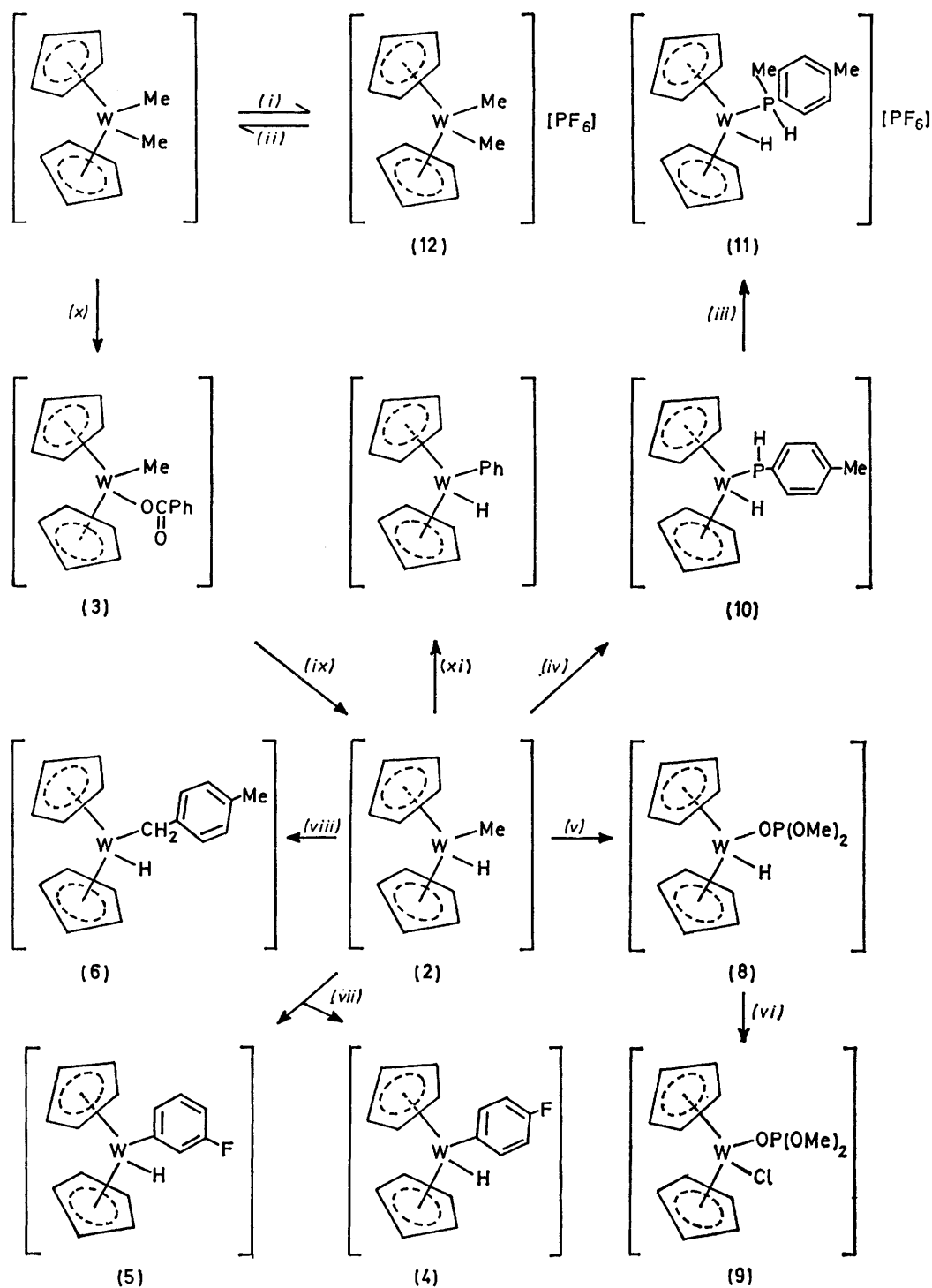
showed a large singlet and a small 1 : 1 : 1 triplet. We conclude that there had been a small degree of exchange between the P hydrogen and the solvent deuterium and that the triplet arises from the presence of the cation [W(η-C₅H₅)₂{PD(Me)(C₆H₄Me-4)H}]⁺.

During a search for an improved route to the iodomethyl compound [W(η-C₅H₅)₂Me(I)] we studied the reaction of [W(η-C₅H₅)₂Me₂] with hydrogen iodide and iodine. Treatment of [W(η-C₅H₅)₂Me₂] with 1 equivalent of hydrogen iodide gave immediate and vigorous reaction. The products isolated, in ca. 1 : 1 ratio, were the di-iodo-compound [W(η-C₅H₅)₂I₂] and the unchanged dimethyl. Since the iodomethyl compound does not itself disproportionate we conclude that initially formed (1) reacts very much faster with hydrogen iodide than the dimethyl compound.

Treatment of [W(η-C₅H₅)₂Me₂] with equimolar proportions of iodine gave, after conversion into the hexafluorophosphate salt, orange crystals of the compound [W(η-C₅H₅)₂Me₂][PF₆] (12). This was moderately soluble in nitrobenzene, and very soluble in nitromethane and liquid sulphur dioxide. Solutions in methanol or acetone underwent rapid decomposition. Compound (12) was paramagnetic with a susceptibility of 2.34 × 10⁻⁶ c.g.s. units corresponding to an effective magnetic moment of 1.76 B.M.* The e.s.r. spectrum of the solid showed a broad band, ⟨*g*⟩ = 2.054 4. A solution of (12) in nitromethane underwent a quasireversible one-electron reduction-oxidation cycle. Although the peak-to-peak separation of the anodic and cathodic waves varies greatly with the scan speed an approximate value of -0.03 V may be estimated for the standard electrode potential of the couple relative to the saturated calomel electrode. Reduction of a solution of (12) in dichloromethane with sodium amalgam gave the parent dimethyl compound in high yield, although treatment of (12) in tetrahydrofuran with Na[BH₄] gave mainly the dihydride [W(η-C₅H₅)₂H₂].

We conclude that the dimethyl compound will undergo

* Throughout this paper: 1 B.M. ≈ 9.27 × 10⁻²⁴ A m²; 1 Torr = (101 325/760) Pa.



SCHEME (i) I_2 then $[PF_6]^-$ (aq), r.t., 75%; (ii) Na-Hg in toluene, 70%; (iii) MeI in toluene at r.t., then $[PF_6]^-$ (aq), 70%; (iv) $PMe_2(C_6H_4Me-4)$ at 70 °C for 14 h, 29%; (v) $P(OMe)_3$ at 65 °C for 15 h, 25%; (vi) CCl_4 in toluene, 65%; (vii) C_6H_5F at 70 °C for 15 h; (viii) *p*-xylene at 76 °C for 14 h, 25%; (ix) $Na[AlH_2(OCH_2CH_2OMe)_2]$ in toluene at r.t. for 48 h, 84%; (x) $PhCO_2H$ in toluene at 60 °C, 90%; (xi) C_6H_6 at 72 °C for 19 h, 87% yield

one-electron oxidation to the cation (12) and that this reaction may be reversed under suitable conditions.

DISCUSSION

The hydridomethyl compound (2) is one of relatively few well characterised, simple, *cis*-orientated hydrido-

methyl compounds and it completes the series $[W(\eta-C_5H_5)_2R_2]$, where $R_2 = Me_2, MeH,$ or H_2 . The only other related series are the compounds $[Os(CO)_4R_2]$. In both series it is noticeable that the hydridomethyl compounds are considerably less thermally stable than the other members,¹¹ *e.g.* for $[W(\eta-C_5H_5)_2R_2]$, decomposi-

tion commences at *ca.* 160, 60, and 130 °C for $R_2 = Me_2$, MeH, and H_2 respectively. Thermal decomposition of solid $[W(\eta-C_5H_5)_2Me_2]$ evolves mainly methane and some ethane and ethylene.

Norton and co-workers^{11,12} have studied the mechanisms of thermal decomposition of the osmium compounds and conclude that the dihydrido- and hydridomethyl compounds decompose *via* a binuclear mechanism whilst the dimethyl decomposes by homolytic fission giving methyl radicals.

We have found that decomposition of (2) in inert solvents, *i.e.* cyclohexane, gives the binuclear compounds *cis*- and *trans*- $[Me(\eta-C_5H_5)W\{\mu-(\sigma:\eta^5-C_5H_4)\}_2-W(\eta-C_5H_5)H]$ which do not themselves react thermally with benzene or *p*-xylene.¹³ Since the thermal decomposition of (2) in benzene or *p*-xylene gives as the major products the compounds $[W(\eta-C_5H_5)_2Ph(H)]$ and (6) respectively we conclude that the thermal decomposition of (2) probably proceeds by initial, mononuclear, reductive elimination of methane and formation of tungstenocene. The mononuclear elimination of alkane is a common step in the homogeneous catalytic hydrogenation of olefins by mononuclear metal catalysts. The proposed intermediate tungstenocene then reacts either with benzene or *p*-xylene by insertion into the C–H bond.⁷ The binuclear compounds arise from reaction of tungstenocene with undecomposed (2); a general mechanism for the formation of these and related binuclear compounds has been devised.¹³

The ready reductive elimination of methane from (2) would be presumed to proceed in the manner envisaged for the reductive elimination of dihydrogen, *i.e.* formation of the C–H bond with simultaneous breaking of the W–H and W–C bonds. The greater thermal stability of the dimethyl compound $[W(\eta-C_5H_5)_2Me_2]$ may arise from the steric inhibition to close approach of the two methyl carbons arising from interhydrogen repulsion. Another significant factor could be reduced orbital overlap in the transition state as a result of the more directional nature of the carbon sp^3 orbitals as compared with hydrogen s orbitals. Steric inhibition to ethane elimination has been proposed to occur in some gold–methyl compounds.¹⁴

It appears that the thermal decomposition of *cis*-dimethyl derivatives is often complex and typical products include methane and ethylene as well as ethane.^{12,14,15} If a simple reductive-elimination route of MMe_2 systems to ethane is a relatively high-energy process then other mechanisms such as homolysis forming radicals or α elimination giving carbene intermediates may occur. We note that the general mechanism such as $MMe_2 \rightarrow MH(=CH_2)Me \rightarrow MEt(H) \rightarrow MH_2 + C_2H_4$ or $M + EtH$, where the methane could arise by reductive elimination from the $MH(=CH_2)Me$ intermediate, could account for the different products which are observed. Evidence for an intramolecular mechanism for the thermal decomposition of $[Ta(CH_2Ph)_5]$, possibly by α elimination, has been presented.¹⁶

We suggest that it is the dimethyl compound $[W(\eta-C_5H_5)_2Me_2]$ which is ‘unexpectedly’ stable rather than the hydridomethyl that is anomalously unstable.

The mechanisms of formation of (8) and (10) are clearly much more complicated and at this stage we do not wish to speculate about them. A comparative account of the reaction of bis(cyclopentadienyl)tungsten derivatives with C–H bonds under thermal and photochemical conditions will be given elsewhere.⁷

Finally, we note that the dimethyl cation (12) is a rare example of a cationic paramagnetic transition-metal alkyl derivative. Oxidation of MMe_2 systems has been shown to cause elimination of ethane in nickel dialkyls.¹⁷ Indeed, reductive elimination of alkane may be induced by the presence of σ - or π -acid ligands.^{17,18}

The stability of (12) which permits its isolation presumably reflects in part the fortuitous kinetic stability characteristic of bis(η -cyclopentadienyl) systems.

EXPERIMENTAL

All reactions and manipulations were carried out under dinitrogen or *in vacuo*. All solvents were dried and distilled. Hydrogen-1 n.m.r. spectra were determined using a Bruker (90 MHz) or JEOL (60 MHz) instrument. Microanalyses were by A. Bernhardt or by the microanalytical department of this laboratory. Infrared spectra were recorded as mulls on a Perkin-Elmer 457 instrument and were calibrated with polystyrene film. Mass spectra were determined using a A.E.I. M.S.9 spectrometer.

Benzoatobis(η -cyclopentadienyl)methyltungsten, (3).—The compound $[W(\eta-C_5H_5)_2Me_2]$ ⁶ (0.52 g, 1.52 mmol) in light petroleum (b.p. 100–120 °C, 25 cm³) was treated with benzoic acid (0.19 g, 1.51 mmol) and the mixture was warmed to 60 °C. Methane was evolved and the solution turned red. After 1 h the solution was filtered and slowly concentrated under reduced pressure. Red-brown crystals separated which were filtered off, washed with light petroleum (2 × 15 cm³), and finally recrystallised from light petroleum–diethyl ether (2 : 1), yield 0.61 g (90%).

Bis(η -cyclopentadienyl)hydridomethyltungsten, (2).—(a) *From bis(η -cyclopentadienyl)iodo(methyl)tungsten.* The compound $[W(\eta-C_5H_5)_2Me(I)]$ ⁵ (1.1 g, 2.2 mmol) in benzene (100 cm³) was treated with $Na[AlH_2(OCH_2CH_2OMe)_2]$ (3 g of a 70% solution in benzene, 14.9 mmol). The dark green solution was stirred for 48 h during which time it became pale yellow. The mixture was filtered to remove a slight white precipitate and water (1 cm³) was added dropwise with stirring. After hydrogen evolution had ceased another 20 cm³ of water was added and the mixture shaken vigorously (20 min). The clear yellow benzene layer was separated and washed with water (10 cm³). The solvent was removed under reduced pressure giving a yellow solid. This was extracted with light petroleum (5 × 100 cm³) and the yellow extract was filtered and concentrated under reduced pressure until it appeared to be saturated. It was then cooled slowly to –75 °C over 5 h and kept at this temperature for 12 h. Yellow needles separated, which were collected, washed with cold light petroleum, and dried *in vacuo*, yield 0.65 g (80%).

(b) *From compound (3).* The compound $[W(\eta-C_5H_5)_2(OCOPh)Me]$ (7 g, 15.56 mmol) in benzene (150 cm³) was

treated with $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2]$ (17 cm³ of a 70% solution in benzene, 60 mmol). The dark red solution was stirred for 48 h giving an orange solution. This was filtered and the filtrate was treated cautiously with water (50 cm³) as described in (a). The pure product was isolated as described above, yield 4.36 g (85%).

Bis(η-cyclopentadienyl)hydridophenyltungsten.—The hydridomethyl compound $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}(\text{H})]$ (0.19 g, 0.6 mmol) in benzene (200 cm³) was warmed to 73 °C for 19 h in an evacuated vessel. Examination of the volatile products after this time showed methane to be present (g.l.c.; estimated yield ca. 80%). The solvent was removed from the reaction mixture giving an orange oil. This was extracted with light petroleum at 80 °C giving an orange solution. The extract was filtered, concentrated under reduced pressure until it appeared to be saturated, and allowed to cool to room temperature (r.t.) over 3 h. Further cooling to -50 °C for 2 h gave long orange needles. These were collected, washed with light petroleum, and dried *in vacuo*, yield 0.197 g (87%). The pure product was identified by its i.r. and ¹H n.m.r. spectra.

Bis(η-cyclopentadienyl)hydrido(4-methylbenzyl)tungsten, (6).—The compound $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}(\text{H})]$ (0.25 g, 0.75 mmol) in *p*-xylene (200 cm³) was heated to 76 °C for 14 h. The solution was filtered from a red-brown suspension and the solvent was removed from the filtrate under reduced pressure. The yellow-orange residue was extracted with light petroleum (b.p. 40–60 °C, 150 cm³) at 40 °C. The extract was filtered and concentrated giving yellow crystals. These were recrystallised from light petroleum (b.p. 40–60 °C), yield 0.08 g (25%).

(3- and 4-Fluorophenyl)-*bis(η-cyclopentadienyl)hydridotungsten*, (5) and (4).—The compound $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}(\text{H})]$ (0.2 g, 0.6 mmol) in monofluorobenzene (200 cm³) was heated at 70 °C for 15 h. The solution was then filtered from a red suspension and the solvent was removed from the filtrate under reduced pressure. The residue was placed on an alumina column made up in light petroleum (b.p. 30–40 °C). Elution with light petroleum-toluene gave a yellow band which was collected. The solvent was removed under reduced pressure giving a yellow solid. This was extracted with light petroleum (b.p. 30–40 °C) (150 cm³) and the extract was slowly concentrated and then cooled to -78 °C giving yellow crystals, yield 45%. Comparison of the ¹H n.m.r. spectra with those of authentic samples⁷ showed the products to be a mixture of *meta* and *para* isomers of the title compounds in the ratio 2:3 respectively.

Bis(η-cyclopentadienyl)hydridomethoxotungsten.—The compound $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}(\text{H})]$ (0.2 g, 0.60 mmol) in methanol (200 cm³) was heated at 70 °C for 14 h. The solution was filtered and the solvent was evaporated from the filtrate giving yellow-orange crystals. These were recrystallised from hot (80 °C) light petroleum (b.p. 100–120 °C) as orange needles, yield 0.22 g (70%). The product was identified by comparison of the i.r. and ¹H n.m.r. spectra with those of authentic samples.⁸

Bis(η-cyclopentadienyl)hydrido(4-tolylphosphido)tungsten, (10).—The compound $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}(\text{H})]$ (0.2 g, 0.60 mmol) in dimethyl(4-tolyl)phosphine (50 cm³) was heated at 70 °C for 14 h. The solvent was removed by distillation under reduced pressure (40 °C at 10⁻³ Torr). The resulting oily residue was washed with light petroleum to remove excess of tertiary phosphine. The residue was dissolved in acetone and placed on an alumina column (Grade III, 100–

120 mesh) made up in light petroleum (b.p. 30–40 °C). Elution with methanol gave first a band which was shown to contain a small quantity of an orange oil which was not further studied. The second band eluted with methanol was collected and removal of the solvent gave an orange oil. This could be recrystallised from acetone-water as orange crystals, yield 0.07 g (29%).

Bis(η-cyclopentadienyl)hydrido[methyl(4-tolyl)phosphine]-tungsten Hexafluorophosphate, (11).—The compound $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{PH}(\text{C}_6\text{H}_4\text{Me-4})\}\text{H}]$ (0.02 g, 0.34 mmol) in toluene (20 cm³) was treated with methyl iodide (0.02 cm³, 0.34 mmol). Immediate reaction occurred precipitating a yellow solid which was collected and dissolved in water. The aqueous extract was treated with aqueous ammonium hexafluorophosphate giving a yellow precipitate. This was collected and recrystallised from aqueous acetone (5:1) as yellow crystals, yield 0.15 g (70%).

Bis(η-cyclopentadienyl)(dimethoxyphosphoryl)hydridotungsten, (8).—The compound $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}(\text{H})]$ (0.23 g, 0.6 mmol) in trimethyl phosphite (200 cm³) was heated at 65 °C for 15 h. The solvent was removed under reduced pressure giving an orange oil which was washed with light petroleum (4 × 25 cm³). The residue was dissolved in a minimum quantity of toluene and placed on an alumina column made up in light petroleum (b.p. 30–40 °C). Elution with toluene gave a yellow band. It is necessary to repeat the chromatography twice, and with care, to obtain the pure product. The yellow eluate was collected and the solvent was removed under reduced pressure giving a yellow solid. This was recrystallised from light petroleum (b.p. 30–40 °C)-toluene (10:1) as yellow crystals which were found to be the dihydride $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$. Further elution with acetone gave a second orange band, which contained only a small quantity of an orange oil and was not further studied. Finally, elution with acetone-methanol (5:1) gave a third, orange, band. Removal of the solvent gave an orange-red oily residue. This was dissolved in toluene and addition of diethyl ether and cooling gave yellow crystals (0.06 g, 25%).

Chlorobis(η-cyclopentadienyl)(dimethoxyphosphoryl)-tungsten, (9).—The compound $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{OP}(\text{OMe})_2\}\text{H}]$ (0.15 g, 0.35 mmol) in toluene (30 cm³) was treated with excess of carbon tetrachloride (5 cm³). After a few minutes the initially yellow solution began to turn orange. After 20 min the solvent was removed and red crystals separated. These were collected, extracted with dichloromethane, and crystallised from dichloromethane-diethyl ether, yield 0.11 g (65%).

Bis(η-cyclopentadienyl)dimethyltungsten Hexafluorophosphate, (12).—The compound $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2]$ (2.3 g, 6.7 mmol) in toluene (40 cm³) was treated with iodine (0.8 g, 3.15 mmol) in toluene (40 cm³). The solution was shaken vigorously during the addition stage. An immediate reaction occurred giving a light tan solid and the toluene later became colourless. Extraction with water (500 cm³) gave an orange solution and addition of an excess of ammonium hexafluorophosphate precipitated an orange solid which was collected and washed with water. The dried residue was extracted with dichloromethane and the extract was filtered through a Celite bed. Slow evaporation of the filtrate under reduced pressure gave orange microcrystals which were collected, washed with light petroleum (b.p. 30–40 °C), and dried, yield 2.45 g (75%) (Found: C, 29.7; H, 3.0. C₁₂H₁₆F₆PW requires C, 29.4; H, 3.3%).

Reactions of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2][\text{PF}_6]$.—(a) *With sodium*

amalgam. The title compound (0.15 g, 0.31 mmol) in dichloromethane was stirred with sodium amalgam [1 g of 2% Na-Hg (0.87 mmol)] for 7 h. The solvent layer was separated, filtered, and the solvent was removed from the filtrate under reduced pressure. The orange residue was extracted with light petroleum (b.p. 30–40 °C) (40 cm³) and the extract was concentrated and then cooled to –73 °C giving red needles. These were collected, dried, and shown to be pure [W(η -C₅H₅)₂Me₂] by comparison of the i.r. spectrum with that of an authentic sample; yield 70%.

(b) *With sodium tetrahydroborate.* The title compound (0.1 g, 0.2 mmol) in tetrahydrofuran was treated with Na[BH₄] (0.05 g, 1.32 mmol) and the mixture stirred at r.t. for 12 h. There was no observable change in the colour during this time. The mixture was then warmed to 60 °C for 2 h, again no change was observed. The solvent was removed under reduced pressure and the residue was extracted with light petroleum giving a yellow extract. The extract was concentrated until the solution appeared to be saturated and then cooled to –70 °C. Orange-yellow needles separated which were collected and dried. They were shown to be pure [W(η -C₅H₅)₂H₂] (0.06 g, 65%) from the i.r. spectrum.

Mass spectra.—Data are presented as compound, *m/e*, relative intensity, tentative assignment, *etc.*, for the ¹⁸⁴W isotope only. Compound (2): 330, 13, [W(C₅H₅)₂Me(H)]⁺; 314, 100, [W(C₅H₅)₂]⁺; 288, 25, [W(C₅H₅)(C₃H₃)]⁺; 157, 16, [W(C₅H₅)₂]²⁺; 143, 19, [W(C₅H₅)(C₃H)]²⁺. Compound (3): 450, 10, [W(C₅H₅)₂(OCOPh)Me]⁺; 435, 50, [W(C₅H₅)₂(OCOPh)]⁺; 314, 8, [W(C₅H₅)₂]⁺. Compound (6): 420, 2, [W(C₅H₅)₂(CH₂C₆H₄CH₃)H]⁺; 314, 100, [W(C₅H₅)₂]⁺. Compound (8): 429, 9, [W(C₅H₅)₂{OP(OMe)₂}H]⁺; 393, 2, [W(C₅H₅)₂{OP(OMe)}H]⁺; 345, 2, [W(C₅H₅)₂P]⁺; 314, 100, [W(C₅H₅)₂]⁺. Compound (9): 458, 19, [W(C₅H₅)₂{OP(OMe)₂}Cl]⁺; 349, 100, [W(C₅H₅)₂Cl]⁺. Compound (10): 438, 25, [W(C₅H₅)₂{PH(C₆H₄Me)}H]⁺; 314, 100, [W(C₅H₅)₂]⁺.

We thank the Petroleum Research Fund administered by the American Chemical Society for support (to R. M.), and the Climax Molybdenum Company for a generous gift of Chemicals. We also thank the Northern Ireland Department of Education for a grant (to N. J. C.).

[8/1621 Received, 11th September, 1978]

REFERENCES

- 1 C. Gianotti and M. L. H. Green, *J.C.S. Chem. Comm.*, 1972, 1114.
- 2 K. Elmitt, M. L. H. Green, R. A. Forder, C. Jefferson, and K. Prout, *J.C.S. Chem. Comm.*, 1974, 747.
- 3 M. L. H. Green, M. Berry, C. Couldwell, and K. Prout, *Nouveau J. Chimie*, 1977, **1**, 187.
- 4 M. L. H. Green, B. R. Francis, and G. G. Roberts, *Chem. Comm.*, 1971, 1290.
- 5 N. J. Cooper and M. L. H. Green, unpublished work.
- 6 F. W. S. Benfield and M. L. H. Green, *J.C.S. Dalton*, 1974, 1324.
- 7 M. Berry, K. Elmitt, and M. L. H. Green, unpublished work.
- 8 L. Farrugia and M. L. H. Green, *J.C.S. Chem. Comm.*, 1975, 416.
- 9 R. F. Hudson, 'Organophosphorus Chemistry,' Academic Press, New York, 1965.
- 10 C. J. Jameson, *J. Amer. Chem. Soc.*, 1969, **91**, 6232.
- 11 S. J. Okrasinski and J. R. Norton, *J. Amer. Chem. Soc.*, 1977, **99**, 295.
- 12 J. Evans, S. J. Okrasinski, A. J. Pribula, and J. R. Norton, *J. Amer. Chem. Soc.*, 1977, **99**, 5835; J. Evans and J. R. Norton, *ibid.*, 1974, **96**, 7578.
- 13 N. J. Cooper, S. J. Simpson, and M. L. H. Green, unpublished work.
- 14 S. Komiya, T. A. Albright, R. Hoffmann, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1977, **99**, 8440.
- 15 F. S. D'yachkovskii and N. E. Khrushch, *Zhur. obshchei Khim.*, 1971, **41**, 1779; G. M. Whitesides, J. F. Gaasch, and E. R. Sledronsky, *J. Amer. Chem. Soc.*, 1972, **94**, 5258; E. L. Muetterties and P. L. Watson, *ibid.*, 1976, **98**, 4665.
- 16 R. R. Schrock, *J. Organometallic Chem.*, 1976, **122**, 209.
- 17 T. Yamamoto, Y. Nakamura, and A. Yamamoto, *Bull. Chem. Soc. Japan*, 1976, **49**, 191.
- 18 T. Yamamoto and A. Yamamoto, *J. Organometallic Chem.*, 1973, **57**, 127.