Metal Atom Synthesis and Photochemistry of Bis(η-pentamethylcyclopentadienyl)-tungsten Dihydride

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Cocondensation of tungsten vapour with 1,2,3,4,5-pentamethylcyclopentadiene gives bis(η-pentamethylcyclopentadienyl)tungsten dihydride, $(\eta\text{-}C_5Me_5)_2WH_2$; photolysis of the dihydride yields, sequentially, the 'tucked-in' compounds $(\eta\text{-}C_5Me_5)W(\eta\text{-}C_5Me_4CH_2)H$ and $(\eta\text{-}C_5Me_5)W(\eta\text{-}C_5Me_3CH_2CH_2)$.

Pentamethylcyclopentadienyl–metal complexes are currently of considerable interest since the electron releasing properties of the C_5Me_5 ligand, and its steric bulk, modify considerably the chemistry of the metal centre compared with unsubstituted cyclopentadienyl complexes. In particular, the ligand has been used to prepare highly reactive complexes capable of activating saturated hydrocarbons.[1] We were interested to explore the photochemistry of $(\eta\text{-}C_5Me_5)_2WH_2$, since photolysis of the unsubstituted analogue $(\eta\text{-}C_5H_5)_2WH_2$ generates tungstenocene, $(\eta\text{-}C_5H_5)_2W$,[2] which is capable of inserting into mildly activated C–H bonds, *e.g.* those in $SiMe_4$.[3] We anticipated that the more electron rich metal centre in $(\eta\text{-}C_5Me_5)_2W$ might react with saturated hydrocarbons.

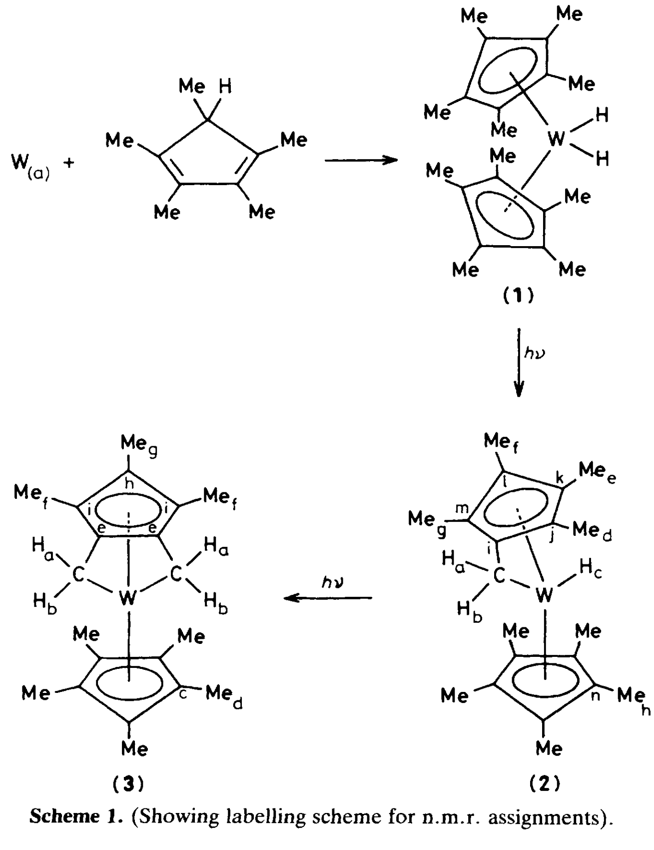
Bis(η-pentamethylcyclopentadienyl)tungsten complexes have not, thus far, been prepared by conventional methods. Recently we described the synthesis of $(\eta\text{-}C_5Me_5)_2MoMe_2$ *via* molybdenum atoms,[4] and $(\eta\text{-}C_5H_5)WH_2$ has also been prepared by metal vapour synthesis.[5] We therefore set out to prepare tungsten complexes containing the C_5Me_5 ligand using this approach.

Tungsten vapour from a positive hearth electron-beam furnace operating at 3500 °C was cocondensed with an excess of 1,2,3,4,5-pentamethylcyclopentadiene at 77 K, in a type of apparatus previously described.[6] Work-up and final chromatography of the resultant product gave air-sensitive yellow crystals of the dihydride $(\eta\text{-}C_5Me_5)WH_2$, (**1**),† in 10% yield based on tungsten vapour. Compound (**1**) is highly soluble in hydrocarbon solvents and sublimes readily (50 °C/10^{-3} mbar). An i.r. band at 1919 cm^{-1} (Nujol mull) and a ^1H n.m.r. resonance at δ −11.27‡ are characteristic of a metal hydride.

Photolysis of (**1**) (500 W medium pressure Hg arc, 48 h) in hydrocarbons gives firstly the 'tucked-in' compound (**2**) (see Scheme 1), isolated by sublimation (50 °C/10^{-3} mbar) as orange crystals. Compound§ (**2**) has been characterised by detailed n.m.r. studies;‡ in particular, the ^1H n.m.r. spectrum of (**2**) shows a W–H peak at δ −12.16 which exhibits coupling to one of the AB protons of the 'tucked-in' methylene group, and also to the protons of a ring methyl group (Me_d) adjacent to the methylene group. This latter coupling indicates that the methyl group must be very close to the hydride ligand: further photolysis of (**2**) (48 h) yields the doubly 'tucked-in' compound (**3**),†§ isolated as dark orange crystals from pentane.

The formation of (**2**) presumably involves the intermediacy of 'decamethyltungstenocene,' $(\eta\text{-}C_5Me_5)_2W$,[2] which undergoes an intramolecular insertion reaction into a ring methyl group. The possible mechanism for its conversion into (**3**) is less clear: given the proximity of the hydride ligand and ring methyl group, it is tempting to suggest a simple concerted loss of dihydrogen, although other mechanisms may be operative (*e.g.* one involving an $\eta^5 \rightarrow \eta^3$ ring shift).

These results demonstrate an alternative pathway for C–H activation involving pentamethylcyclopentadienyl complexes: that is, *intra*molecular insertion into ligand methyl groups as opposed to intermolecular reaction with a hydrocarbon substrate.



Scheme 1. (Showing labelling scheme for n.m.r. assignments).

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† Satisfactory microanalysis has been obtained.

‡ Selected n.m.r. data: recorded at probe temperature on Bruker WH400 or WH360 instruments; all assignments have been confirmed by double resonance and nuclear Overhauser enhancement difference spectra as appropriate. Coupling constants are in Hz; δ is relative to internal solvent.

(**1**) ^1H (C_6D_6): 1.95 [15 H, s, C_5Me_5]; −11.27 [1 H, s, W–H, *J*(W–H) 42.6].

(**2**) ^1H (C_6D_{12}): 3.11 [1 H, t, H_a, $J(H_a–H_b)$ 1.56, $J(H_a–H_c)$ 1.79, $J(W–H_a)$ 6.22]; 2.84 [1 H, d, H_b, $J(H_a–H_b)$ 1.56, $J(W–H_b)$ 7.30]; 2.86 [15 H, s, H_h]; 2.04, 2.89, 2.49 [each 3 H, s, H_e, H_f, H_g]; 2.01 [3 H, d, H_d, $J(H_d–H_c)$ 3.44]; −12.16 [1 H, d of quartets, H_c, $J(H_c–H_d)$ 3.44, $J(H_a–H_c)$ 1.79, $J(W–H_c)$ 91.74]. ^{13}C (C_6D_{12}): 107.36, 96.83, 91.09, 87.45, 85.57 [all s, C_i, C_j, C_k, C_l, C_m]; 92.01 [s, C_n]; 35.32 [t, C_{ab}, *J*(C–H) 151.3, *J*(C–W) 29.5]; 12.82, 11.81, 9.30, 8.37 [all q, C_d, C_e, C_f, C_g]; 11.43 [q, C_h].

(**3**) ^1H (C_6D_6): 2.882 [2 H, d, H_a, $J(H_a–H_b)$ 1.80, $J(W–H_a)$ 6.7]; 1.705 [3 H, s, H_g, $J(W–H_g)$ 2.33]; 1.675 [15 H, s, H_d, $J(W–H_d)$ 1.50]; 1.650 [2 H, d, H_b, $J(H_b–H_a)$ 1.80, $J(W–H_b)$ 6.7]; 1.595 [6 H, s, H_f]. ^{13}C (C_6D_6): 109.71, 101.70 [both s, C_i, C_h]; 94.32 [s, C_c, *J*(C–W) 8.8]; 89.60 [s, C_e, *J*(C–W) 8.4]; 45.85 [t, C_{ab}, *J*(C–H) 152, *J*(C–W) 31.4]; 11.18 [q, C_d]; 9.56, 9.03 [both q, C_f, C_g].

§ A parent ion was observed in the mass spectrum, with the appropriate tungsten isotope pattern.

Similar 'tucked-in' complexes have also been observed in the thermolysis reactions of certain pentamethylcyclopentadienyltitanium alkyl compounds.[7,8] Also, decamethyltitanocene has been shown to exist in equilibrium with a 'tucked-in' form, as in the following sequence.[7]

$$(\eta\text{-}C_5Me_5)_2Ti \rightleftharpoons (\eta\text{-}C_5Me_5)\overline{Ti(\eta\text{-}C_5Me_4C}H_2)H \xrightarrow{-\frac{1}{2}H_2} (\eta\text{-}C_5Me_5)\overline{Ti(\eta\text{-}C_5Me_4C}H_2)$$

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