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BINUCLEAR TUNGSTENOCENE CHEMISTRY: HYDRIDO AND HALO DERIVATIVES

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Summary

The new compounds $\{(\eta\text{-}C_5H_5WX)[\mu\text{-}(\sigma, \eta\text{-}C_5H_4)]\}_2$, where X = Cl, Br or I are described. The known hydride X = H, protonates and rearranges giving the new cation $\{(\eta\text{-}C_5H_5)WH\}_2(\mu\text{-}H)[\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4)]^+$.

Tungstenocene is formed by photolysis of $W(\eta\text{-}C_5H_5)_2H_2$ (I). The resulting tungstenocene is very reactive and will insert into a variety of carbon—hydrogen bonds. Although the bond strength of aromatic C—H bonds is greater than for aliphatic C—H bonds, we and others have found that transition metal centres, e.g. of tungstenocene, more readily insert into aromatic C—H giving aryl-hydrido derivatives. This may be due both to thermal instability of the alkyl hydride compounds and also the rate of reaction of tungstenocene with aromatic systems is likely to be greater than for alkanes due to the ability of the unsaturated hydrocarbons to form initial π-bonds with the metal center.

When I is irradiated in cyclohexane or diethyl ether then, despite the huge molar excess of saturated C—H bonds, the main product is the dimer $\{(\eta\text{-}C_5H_5W C_5H_5WH)[\mu\text{-}(\sigma, \eta\text{-}C_5H_4)]\}_2$ (II) [1].

Here we describe further chemistry of the compound II.

Results and discussion

Treatment of II with dilute hydrochloric acid causes slow solution of the crystals and addition of ammonium hexafluorophosphate to the resulting pale brown solution gives the compound $\{(\eta\text{-}C_5H_5WH_2)(\mu\text{-}H)[\mu\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4)]\}PF_6$ (III). This could be recrystallised from acetonitrile. The crystal structure of III has been determined and is found to be isostructal with the molybdenum analogue (see Scheme 1). The spectroscopic data in Table 1 shows that the same structure is found for the cation in both solid and solutions.

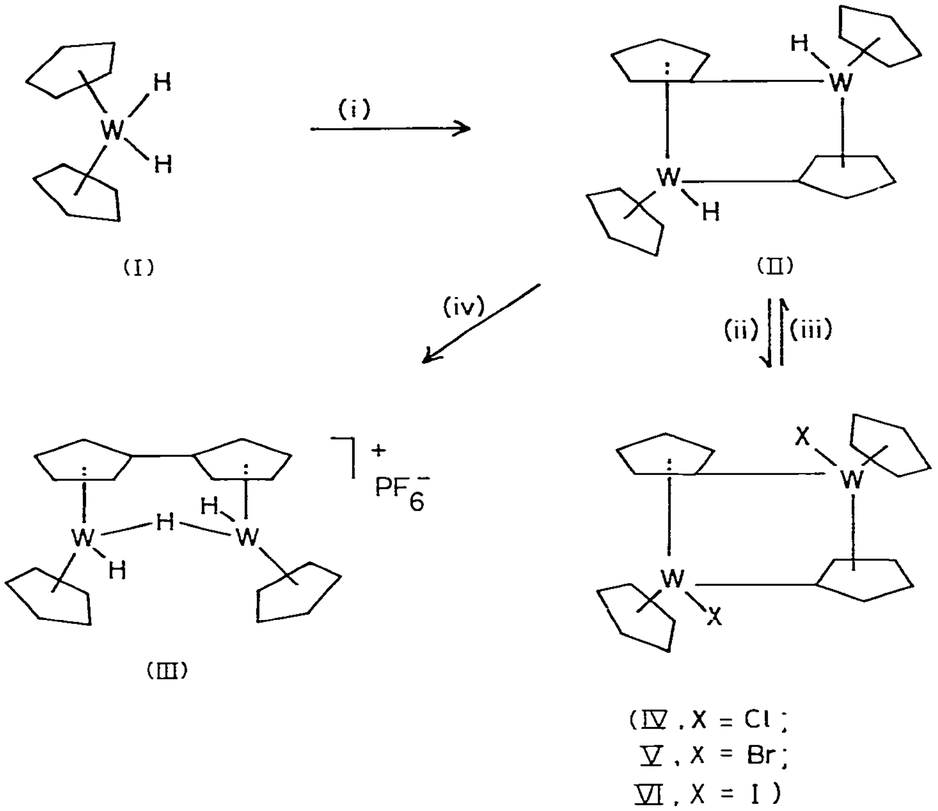
The spectroscopic data for III, given in Table 1, is closely analogous to that of the molybdenum analogue and includes in the IR spectrum bands assignable to

TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA

Compound	Colour	Analyses Found (calcd.) (%)			^{1}H NMR [a] or mass spectra [b]
		C	H	Halogen	
$\{[(\eta\text{-}C_5H_5)WH]_2(\mu\text{-}H)[\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4)]\}PF_6$ (III)	dark brown	31.6 (31.0)	2.7 (2.5)		5.0 (10), s, 2, C_5H_5; 4.90 and 5.3 (4 and 4), each component has a triplet appearance $\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4$; 26.0 (3), "triplet" ($J(^{183}W^0/H)$ 45), WH_3 (in CD_3CN)
$\{(\eta\text{-}C_5H_5WCl)[\mu\text{-}(\sigma, \eta\text{-}C_5H_4)]\}_2$ (IV)	brown/green	35.7 (35.45)	2.5 (2.6)	10.4 (10.2)	Mass spectrum: 696 P^+; 626 $[P - 2\ Cl]^+$
$\{(\eta\text{-}C_5H_5WBr)[\mu\text{-}(\sigma, \eta\text{-}C_5H_4)]\}_2$ (V)	yellow-green	30.5 (30.55)	2.3 (2.3)	21.85 (20.35)	Mass spectrum: 784 P^+; 705 $[P - Br]^+$
$\{(\eta\text{-}C_5H_5WI[\mu\text{-}(\sigma, \mu\text{-}C_5H_4)]\}$ (VI)	green	27.1 (27.3)	2.8 (2.0)	29.8 (28.85)	Mass spectrum: 880 P^+; 754 $[P - I]^+$; 625 $[P - 2\ I]^+$; 312 $[P - 2\ I]^{2+}$

[a] Data presented as: chemical shift (τ), relative intensity (in parentheses), multiplicity (J in Hz) assignment. [b] Data given as: peak:corresponding to two ^{183}W isotopes, assignment (P^+ includes parent ion peak). In all cases the appropriate band envelopes corresponding to the presence of the tungsten isomers were observed.



Scheme 1. (i) Photolysis in cyclohexane or diethylether at room temperature for 52 h, 18%. (ii) X = Cl, CCl_4 in toluene for 1 h, 85%; X = Br, $CHBr_3$ in toluene for 2 h, 85%; X = I, I_2 or MeI in toluene at room temperature for 39 min, 83%. (iii) X = Cl, $NaH_2Al(OCH_2CH_2OMe)_2$ in toluene at room temperature for 5 h, 86%. (iv) 1 *M* HCl_{aq} for 1 h, then NH_4PF_6, ca. 90%.

terminal and bridging hydrogen systems at 1950 and 1285 cm^{-1}, respectively. Interestingly, the ^1H NMR spectrum of III shows only one band assignable to hydrogens attached to a transition metal, as well as only an A_2B_2 group for the two η-C_5H_4 groups. In a rigid structure of the kind shown for III in Scheme 1 two η-C_5H_4 groups should occur as ABCD systems since the tungsten atoms are chiral. Attempts to deprotonate III by treatment with bases such as sodium hydroxide, trimethylamine and sodium hydride did not give a tractable product. This observation contrasts with the readily and reversible deprotonation of the molybdenum analogue of III giving the green dimer $\{(\eta\text{-}C_5H_5MoH)[\mu\text{-}(\sigma,\eta\text{-}C_5H_4)]\}_2$ [1]. This observation supports the thesis that the neutral molecule $\{(\eta\text{-}C_5H_5WH)_2[\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4)]\}$ is not a favoured isomer of tungstenocene dimer. Assuming that, as seems reasonable, the solution structure for III is the same as found for the crystalline state then we can account for the apparent equivalence of the hydride ligands by the postulate of a fluxional process which proceeds in a stepwise manner, as discussed elsewhere for the analogous molybdenum system [1].

Treatment of II with carbon tetrachloride gives a pale brown microcrystalline compound, IV. The compound is slightly soluble in liquid sulphur dioxide but the solutions slowly decompose. A green form of the compound is also prepared by the same method. We note that $M(\eta\text{-}C_5H_5)_2Cl_2$, where M = Mo, W and Nb, also have both green and brown forms which are thought to differ in only their crystal packing.

Analysis and the mass spectrum show that IV has the stoicheiometry corresponding to $\{(\eta\text{-}C_5H_5WCl)[\mu\text{-}(\sigma, \eta\text{-}C_5H_4)]\}_2$. Reduction of IV with $NaH_2Al(OCH_2CH_2OMe)_2$ gives II in high yield and for this reason we propose that IV has two $\mu\text{-}(\sigma, \eta\text{-}C_5H_4)$ groups rather than the isomer with a $\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4)$ group.

Treatment of II with bromoform gives the dibromo analogue of IV i.e. $\{(\eta\text{-}C_5H_5WBr)[\mu\text{-}(\sigma, \eta\text{-}C_5H_4)]\}_2$ (V), which the data in Table 1 suggests to be entirely analogous in structure to IV.

Compound II also reacts with stoicheiometric iodine or methyl iodide giving the diiodo analogue of $\{(\eta\text{-}C_5H_5WI)[\mu\text{-}(\sigma, \eta\text{-}C_5H_4)]\}_2$ (VI). Treatment of VI with a tetrahydrofuran solution of bis-toluenetitanium gives II in 72% yield. The mechanism of this reaction remains unknown.

Comparison of the reactivity of compounds II and III with that of the molybdenum compound shows there are marked differences. Whilst II is thermally stable towards rearrangement (up to 300°C) the molybdenum analogue of II rapidly rearranges at 60°C to the green isomer $[(\eta\text{-}C_5H_5MoH)_2(\mu\text{-}\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4)]$.

Protonation of II and the molybdenum analogue yields in both cases isostructural trihydrido cations. However for molybdenum the protonation is readily reversible but this is not the case for the tungsten cation III. These differences may be understood if the compound $(\eta\text{-}C_5H_5WH)_2$ $(\mu\text{-}(\eta\text{-}C_5H_4\text{-}\eta\text{-}C_5H_4)$ was unstable with respect to rearrangement to II i.e. the reverse of what is observed for the molybdenum analogues. How the electronic and steric forces would interplay to bring about this reverse in equilibria remains unclear.

Experimental

All operations were performed under vacuum or in an inert atmosphere. Mass spectra were measured using an AEI MS9 instrument. ^1H NMR spectra were determined on a Bruker 90 MH2 spectrometer. Solvents were dried and distilled before use. The compound $W(\eta\text{-}C_5H_5)_2H_2$ was prepared as described [3]. We thank Mr. R.D. Bayliss for his experimenta assistance.

Bis(η-cyclopentadienylhydridotungsten)(μ-hydrido)(μ-σ,η-bicyclopentadienyl) hexafluorophosphate (III)

Compound II (150 mg, 0.24 mmol) was added to 1 *M* hydrochloric acid (50 cm^3) with stirring. After 30 minutes the solid had dissolved giving a pale brown solution. Addition of ammonium hexafluorophosphate solution gave a pale brown precipitate which was separated and washed with water, and then dried. It was recrystallised from aqueous acetonitrile, yield 179 mg, 90%.

Bis[μ-(σ,η-cyclopentadienyl)] bis(chloro-η-cyclopentadienyltungsten) (IV).

Compound II (159 mg, 0.24 mmol) in toluene (50 cm^3) was treated with carbon tetrachloride (2 cm^3) at room temperature. Immediately a green or brown precipitate appeared which was collected, washed with toluene and dried in vacuo, yield 140 mg, 84%. The compound is insoluble in all common organic solvents and dissolves with reaction in dimethyl sulphoxide and liquid sulphur dioxide, 85%.

Bis[μ-(σ,η-cyclopentadienyl)] bis(bromo-η-cyclopentadienyltungsten) (V)

Compound II (160 mg, 0.24 mmol) in toluene (50 cm^3) was treated with bromoform (2 cm^3) at room temperature. After 15 min the resulting green precipitate was separated and washed with toluene and dried under vacuum, yield 160 mg, 85%. The compound was insoluble in most solvents and decomposed by dimethyl sulphoxide and liquid sulphur dioxide.

Bis[μ-(σ,η-cyclopentadienyl)] bis(iodo-η-cyclopentadienyltungsten) (VI)

Compound II (160 mg, 0.25 mmol) in toluene (50 cm^3) was treated with either iodine (122 mg, 0.48 mmol) or methyl iodide (35.5 mg, 9.25 mmol) at room temperature. Rapid reaction occurred giving a green solid which was separated, washed with toluene and light petroleum ether (30—40%) and dried in vacuo, yield 89 or 93%, respectively. The compound was not soluble in any solvents in which it did not decompose.

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