

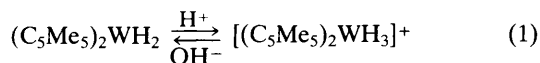
## Direct Protonation of the W–H Bonds of Bis(pentamethylcyclopentadienyl)tungsten Dihydride

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Protonation of  $(C_5Me_5)_2WH_2$  to give  $[(C_5Me_5)_2WH_3]^+$  is proposed to occur by attack at both W–H bonds rather than by direct attack at the  $d^2$  metal centre.

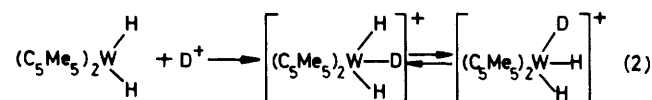
Protonation reactions of  $d^n$  ( $n \geq 2$ ) transition metal complexes are generally believed to occur by direct attack at the metal centre. The dihydride,  $(C_5Me_5)_2WH_2$ ,<sup>1</sup> is readily, and reversibly, protonated by a variety of acids (*e.g.*  $HBF_4 \cdot Et_2O$ ,  $HCl_{aq.}$ , and  $[Me_3NH][BPh_4]$ ) to give the trihydride cation,  $[(C_5Me_5)_2WH_3]^+$  [equation (1)].

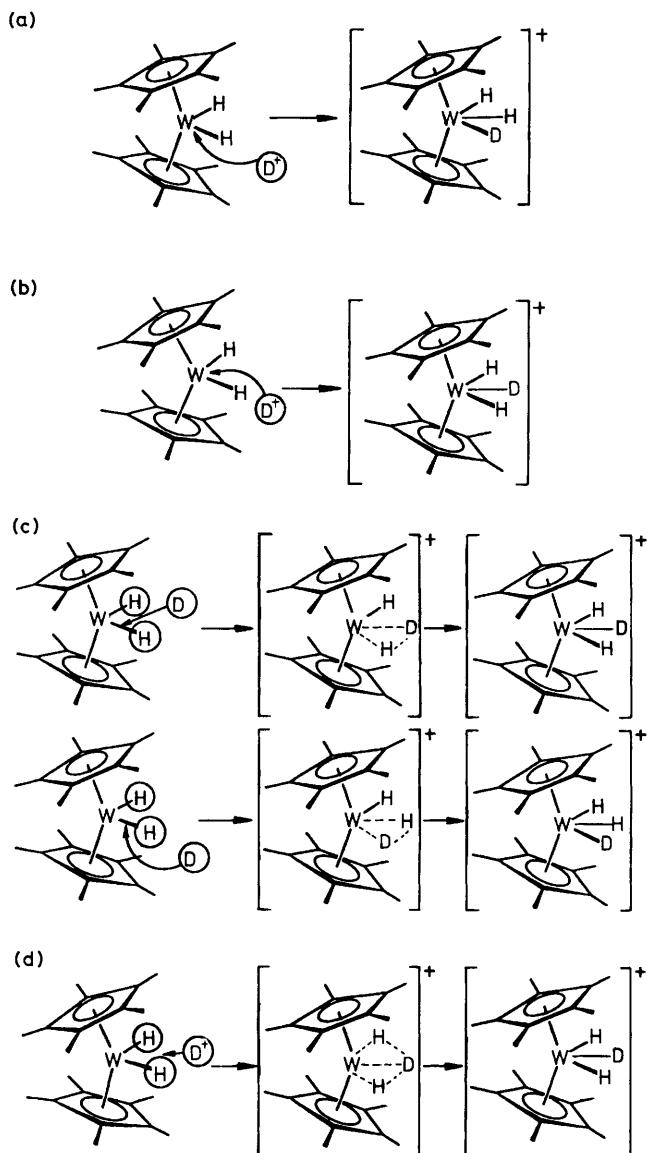


Some rather unexpected features of the stereochemistry of this protonation have been revealed by examination of the addition of  $D^+$  to  $(C_5Me_5)_2WH_2$ . Treatment of a suspension of  $(C_5Me_5)_2WH_2$  in  $D_2O$  with a solution of  $DCl/D_2O$  initially (within 1 min) affords a mixture of isomers of  $[(C_5Me_5)_2W(H)_2(D)]^+$ : that with the deuterium occupying the central position,  $[(C_5Me_5)_2W(H)(D)(H)]^+$  predominates (*ca.* 90%) [equation (2)], with a much smaller fraction of the laterally deuteriated isotopomer,  $[(C_5Me_5)_2W(H)(H)(D)]^+$  (*ca.* 10%). Subsequent exchange of the lateral and central ligands occurs over a period of several hours [equation (2)], accompanied by further incorporation of deuterium from the solvent.

Possible pathways for the protonation of  $(C_5Me_5)_2WH_2$  with  $D^+$  are shown in Scheme 1. On the basis of ground state orbital control arguments, an electrophile would be predicted

to attack initially at the HOMO. A qualitative MO diagram for  $(C_5Me_5)_2WH_2$ , based on the results of theoretical calculations<sup>2</sup> on bent metallocene derivatives and supported by numerous structural and spectroscopic studies,<sup>3</sup> is shown in Figure 1. The  $2a_1$  HOMO is a tungsten-localised lateral orbital that interacts minimally with the two hydride ligands, *i.e.* the orbital containing the tungsten 'lone pair'. Thus, protonation according to orbital control would be expected to proceed by path (a) giving the lateral  $[^2H_1]$ -isotopomer,  $[(C_5Me_5)_2W(H)(H)(D)]^+$ . Observation of the central  $[^2H_1]$ -isotopomer,  $[(C_5Me_5)_2W(H)(D)(H)]^+$ , which arises by attack along the pseudo- $C_2$  axis, indicates a more subtle situation, however. Since there is no occupied, metal-based, central orbital, path (b) may be ruled out as a dominant mechanistic pathway. If the tungsten-hydride bonds are polarized substantially towards  $W-H^{\delta-}$ , the alternative protonation pathways, (c) and (d), should be particularly likely. Thus, protonation may be subject to charge control (*i.e.*  $H^+$  attack at the  $W-H^{\delta-}$  bond) rather than orbital control ( $H^+$  attack at the HOMO).<sup>4</sup> Protonation of a single tungsten-hydrogen bond of  $(C_5Me_5)_2WH_2$  would thus proceed through a species that

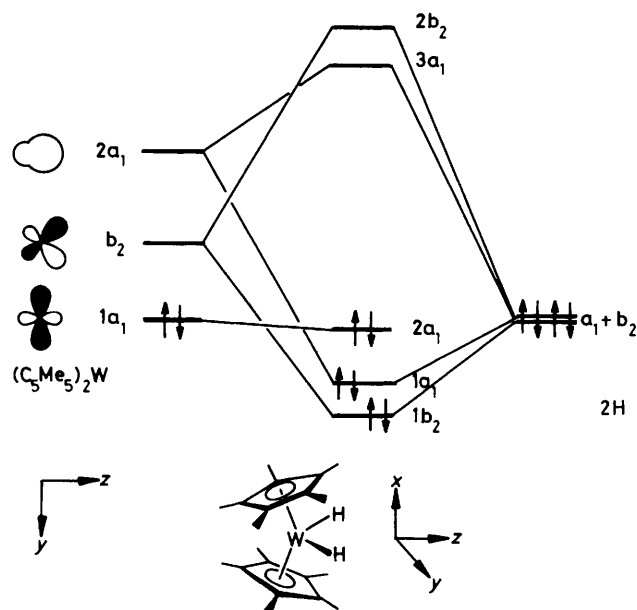




**Scheme 1.** Possible pathways for protonation of  $(C_5Me_5)_2WH_2$ . (a) Electrophilic attack at a lateral, metal-based orbital; (b) electrophilic attack at a central, metal-based orbital; (c) central and lateral electrophilic attack at one of the hydride ligands; (d) central electrophilic attack at both the hydride ligands.

closely resembles (or may, in fact, be) the dihydrogen-hydride cation,  $[(C_5Me_5)_2W(\eta^2-H_2)H]^+$ ,<sup>5</sup> which subsequently collapses to the trihydride cation. An analogous sequence for protonation of the M-H bonds of the  $d^0$  complex  $Re(PR_3)_2H_7$ <sup>6</sup> and  $d^6$  complex  $(\eta^5-C_5H_5)(Me_2PCH_2CH_2PMe_2)RuH$ <sup>7</sup> have recently been discussed.

Protonation of a single W-H bond of  $(C_5Me_5)_2WH_2$  from the 'inside' of the H-W-H angle, rather than from a lateral position could possibly be strongly preferred; however, the factors dictating such a preference are not obvious. Alternatively, it could be argued that the preferential ( $\geq ca. 20:1$ ) central protonation is a consequence of the interaction of the proton with both hydride ligands [pathway (d)], thus proceeding through a species that closely resembles (or may, in fact, be) the trihydrogen cation,  $[(C_5Me_5)_2W(\eta^3-H_3)]^+$ , which subsequently collapses to the trihydride cation. The rather acute ( $ca. 75^\circ$ ) H-W-H angle simultaneously offers both

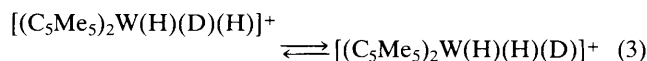


**Figure 1.** A qualitative MO diagram for  $(C_5Me_5)_2WH_2$ .

hydrides to electrophilic attack. A trihydrogen adduct has recently been invoked to account for the unusual n.m.r. behaviour for  $[(\eta^5-C_5H_5)(PMe_3)Ir(\eta^3-H_3)]^+$ .<sup>8</sup> An equivalent molecular orbital picture is that attack occurs at the second highest occupied molecular orbital (SHOMO), that of  $1a_1$  symmetry.

In contrast, treatment of  $(C_5Me_5)_2W(CH_3)_2$  with  $HBF_4 \cdot Et_2O$  leads to oxidation to the radical cation,  $[(C_5Me_5)_2W(CH_3)_2]^+$ , rather than simple protonation.<sup>9</sup> This oxidation sequence may proceed by initial attack of  $H^+$  at the tungsten centre, rather than at the W-CH<sub>3</sub> bond(s), the latter being less favoured relative to attack at W-H.<sup>†</sup>

Kinetic analysis of  $^1H$  n.m.r. data over a period of hours clearly reveals that  $[(C_5Me_5)_2W(H)(H)(D)]^+$  builds up in concentration, and does so faster than the overall conversion of the  $[^2H_1]$  isotopomer  $[(C_5Me_5)_2WH_2D]^+$  to the  $[^2H_2]$ -isotopomer,  $[(C_5Me_5)_2WHD_2]^+$ , and the  $[^2H_3]$ -isotopomer,  $[(C_5Me_5)_2WD_3]^+$ . This observation demonstrates that there must be an additional pathway for the direct intramolecular interconversion of the two  $[^2H_1]$ -isotopomers which does not involve a deprotonation mechanism, *i.e.* reaction (3). A possible direct pathway for the intramolecular exchange would involve pseudorotation out of the equatorial plane of the bent sandwich structure; however, we are not aware of a precedent for such a process. More likely mechanisms include (i) the intermediacy of a dihydrogen adduct which rotates, (ii) the intermediacy of a (closed) trihydrogen adduct<sup>10</sup> which rotates, and (iii) migration of the hydride ligand to the  $C_5Me_5$  ligand to give an  $\eta^4$ -diene intermediate,  $(C_5Me_5)(\eta^4-C_5Me_5H)WHD]^+$ , followed by a 'Tarzan' type swing over the deuterium, and return to the metal centre.



<sup>†</sup> The greater propensity for attack at W-H vs. W-CH<sub>3</sub> may be ascribed to the more favourable three-centre bonding involving the nondirectional s valence orbital of H relative to the highly directional  $sp^3$  orbital of the methyl group.

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