

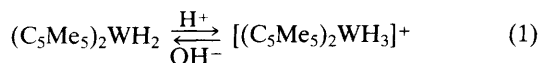
Direct Protonation of the W–H Bonds of Bis(pentamethylcyclopentadienyl)tungsten Dihydride

Gerard Parkin and John E. Bercaw*

A. A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, U.S.A.

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.

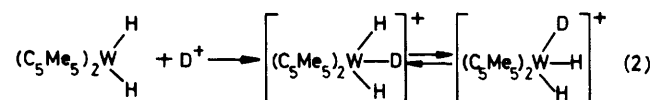
Protonation reactions of d^n ($n \geq 2$) transition metal complexes are generally believed to occur by direct attack at the metal centre. The dihydride, $(C_5Me_5)_2WH_2$,¹ is readily, and reversibly, protonated by a variety of acids (*e.g.* $HBF_4 \cdot Et_2O$, $HCl_{aq.}$, and $[Me_3NH][BPh_4]$) to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

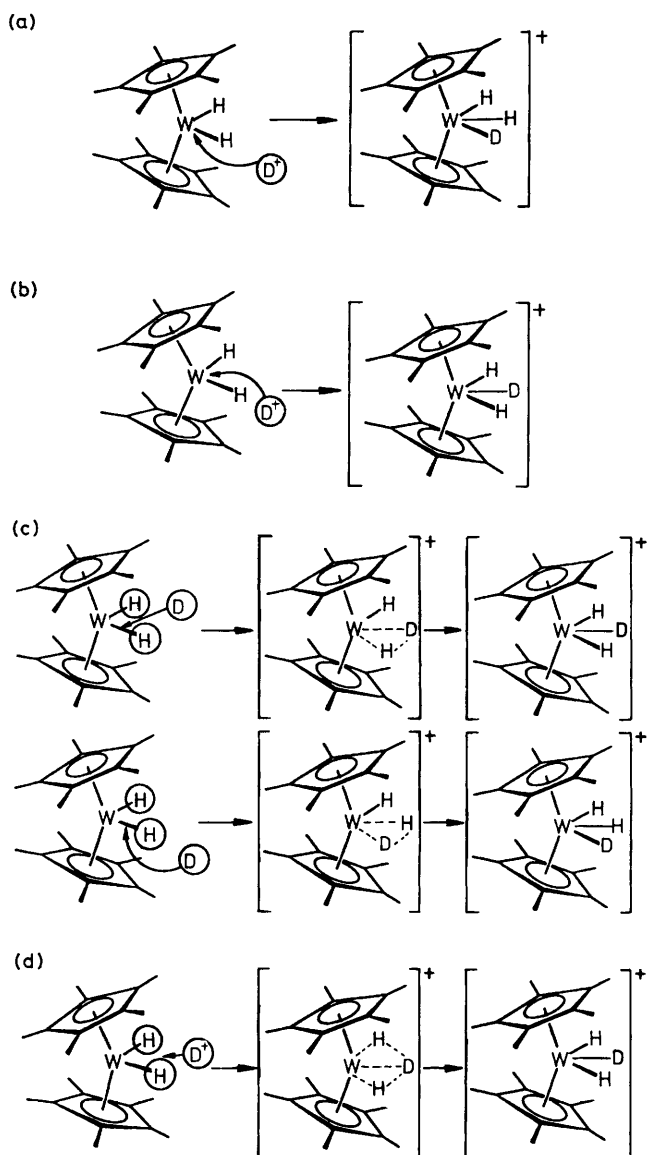


Some rather unexpected features of the stereochemistry of this protonation have been revealed by examination of the addition of D^+ to $(C_5Me_5)_2WH_2$. Treatment of a suspension of $(C_5Me_5)_2WH_2$ in D_2O with a solution of DCl/D_2O initially (within 1 min) affords a mixture of isomers of $[(C_5Me_5)_2W(H)(D)]^+$: 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 calculations² on bent metallocene derivatives and supported by numerous structural and spectroscopic studies,³ 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).⁴ 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, $[(C_5Me_5)_2W(\eta^2-H_2)H]^+$,⁵ which subsequently collapses to the trihydride cation. An analogous sequence for protonation of the M-H bonds of the d^0 complex $Re(PR_3)_2H_7$ ⁶ and d^6 complex $(\eta^5-C_5H_5)(Me_2PCH_2CH_2PMe_2)RuH$ ⁷ 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°) H-W-H angle simultaneously offers both

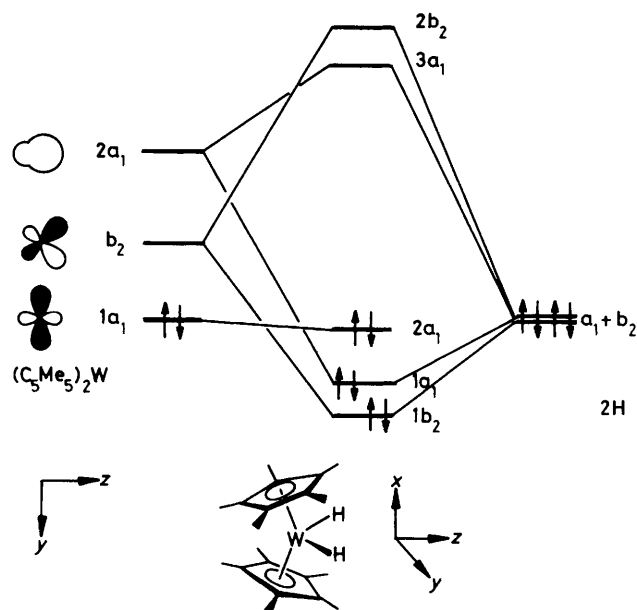
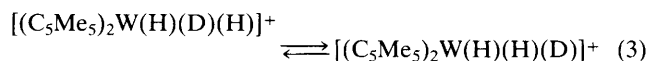


Figure 1. A qualitative MO diagram for $(C_5Me_5)_2WH_2$.

hydrides to electrophilic attack. A trihydrogen adduct has recently been invoked to account for the unusual n.m.r. behaviour for $[(\eta^5-C_5H_5)(PMe_3)Ir(\eta^3-H_3)]^+$.⁸ 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.⁹ This oxidation sequence may proceed by initial attack of H^+ at the tungsten centre, rather than at the W-CH₃ bond(s), the latter being less favoured relative to attack at W-H.[†]

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 adduct¹⁰ which rotates, and (iii) migration of the hydride ligand to the C_5Me_5 ligand to give an η^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.



[†] The greater propensity for attack at W-H vs. W-CH₃ 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.

We thank Professor Bruce Bursten for helpful discussions. This work was supported by the National Science Foundation (Grant No. CHE-8600875) and by Shell Companies Foundation, which are gratefully acknowledged. G. P. acknowledges support through a NATO Postdoctoral Fellowship administered through the S.E.R.C. (U.K.).

Received, 7th June 1988; Com. 8/02277A

References

- 1 F. G. N. Cloke, J. C. Green, M. L. H. Green, and C. P. Morley, *J. Chem. Soc., Chem. Commun.*, 1985, 945; G. Parkin and J. E. Bercaw, *Polyhedron*, 1988, 7, 2053.
 - 2 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729; J. L. Petersen, D. L. Lichtenberger, R. F. Fenske, and L. F. Dahl, *ibid.*, 1975, **97**, 6433; H. H. Brintzinger, L. L. Lohr, Jr., and K. L. Tang Wong, *ibid.*, 1975, **97**, 5146; H. H. Brintzinger and L. S. Bartell, *ibid.*, 1970, **92**, 1105.
 - 3 J. C. Green, M. L. H. Green, and C. K. Prout, *J. Chem. Soc., Chem. Commun.*, 1972, 421; (b) J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, 1974, **96**, 2248; 1975, **97**, 6416; 1975, **97**, 6422; J. C. Green, S. E. Jackson, and B. Higginson, *J. Chem. Soc., Dalton Trans.*, 1975, 403; A. J. Schultz, K. L. Stearley, J. M. Williams, R. Mink, and G. D. Stucky, *Inorg. Chem.*, 1977, **16**, 3303.
 - 4 Theoretical calculations have demonstrated that the protonation of $[(C_5H_5)Fe(CO)_2]_2(\mu-CO)(\mu-CH_2)$ at the methylene ligand and not the Fe-Fe bond is charge and not orbital controlled, B. E. Bursten and R. H. Cayton, *J. Am. Chem. Soc.*, 1987, **109**, 6053.
 - 5 Dihydrogen complexes have been recently reviewed, G. J. Kubas, *Acc. Chem. Res.*, 1988, **21**, 120.
 - 6 X. L. R. Fontaine, E. H. Fowles, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1988, 482.
 - 7 M. S. Chinn and D. M. Heinekey, *J. Am. Chem. Soc.*, 1987, **109**, 5865.
 - 8 D. M. Heinekey, N. G. Payne, and G. K. Schulte, *J. Am. Chem. Soc.*, 1988, **110**, 2303; B. Chaudret, personal communication.
 - 9 Similarly, HBF_4 oxidises $(C_5Me_5)_2Mo(CH_3)_2$ to $[(C_5Me_5)_2Mo(CH_3)_2]^+$. J. C. Green, M. L. H. Green, and C. P. Morley, *J. Organomet. Chem.*, 1982, **233**, C4.
 - 10 Closed trihydrogen species have been studied theoretically to account for the observed exchange processes in bis-dihydrogen complexes. J. K. Burdett, J. R. Phillips, M. R. Pourian, M. Poliakov, J. J. Turner, and R. Upmacis, *Inorg. Chem.*, 1987, **26**, 3054.
-