An Intramolecular W–H···O=C Hydrogen Bond? Electrosynthesis and X-Ray Crystallographic Structure of $[WH_3(\eta^1\text{-}OCOMe)(Ph_2PCH_2CH_2PPh_2)_2]$

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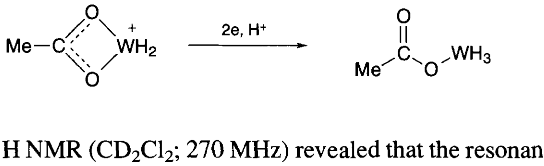
Electrochemical reduction of $[WH_2(\eta^2\text{-}OCOMe)(dppe)_2]^+$ in the presence of protons leads to the formation of $[WH_3(\eta^1\text{-}OCOMe)(dppe)_2]$: NMR and X-ray crystallographic data suggest this complex possesses an unprecedented W–H···O=C intramolecular hydrogen bond.

Controlled potential electrolysis of $[WH_2(\eta^2\text{-}OCOMe)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–MeCN containing one equivalent of $MeCO_2H$ at a vitreous carbon cathode maintained at -2.1 V *vs.* ferrocenium–ferrocene affords bright yellow microcrystalline $[WH_3(\eta^1\text{-}OCCOMe)(dppe)_2]$ **1** in excellent yield (91%),† eqn. (1) (diphosphine ligands omitted for clarity).



(1)

^1H NMR (CD_2Cl_2; 270 MHz) revealed that the resonances of two of the three H ligands of **1** were unexceptionally centred at $\delta = -2.78$ ($^2J_{PH} \approx 31$ Hz) whereas that of the third occurred at a substantially lower field, δ 2.92. ^1H Relaxation measurements (298 K) gave $T_1 = 255$ and 300 ms for the low and high field resonances respectively, as is consistent with the presence of classical hydride ligands. Variable-temperature ^1H NMR spectroscopy over the range -20 to $+40$ °C in CD_2Cl_2 and between $+20$ and $+70$ °C in $(CD_3)_2SO$ established that the complex was stereochemically rigid with no interchange of the hydridic sites. Above 70 °C slight line broadening and decomposition occurred.

Hydrogen bonding and/or longer range dipole–dipole interactions of the hydride with carboxylate O atoms are expected to cause deshielding of hydride. Either or both would explain the occurrence of the low field hydride resonance. Solution IR spectroscopy of the trihydride showed $\nu(C{=}O)$ at 1620 cm^{-1} which is in the frequency range typical for η^1-carboxylate ligands but is otherwise uninformative.

To obtain further information, an X-ray crystallographic analysis of $[WH_3(\eta^1\text{-}OCOMe)(dppe)_2]$ was undertaken.‡ A view of the structure of the trihydride is shown in Fig. 1, the three hydride ligands were located and refined satisfactorily. The W atom has dodecahedral coordination with the two chelating diphosphine ligands spanning the 'equatorial' B-sites; the hydrides and acetate occupy the A-sites.

The carboxylate ligand adopts the η^1-coordination mode with the carbonyl oxygen sitting over one of the hydride ligands at a distance of 2.33(6) Å. This distance is shorter than the sum of the van der Waals radii of O and H (2.6 Å) and is indicative of weak hydrogen bonding. The proximity of the O and H atoms presumably accounts for the low field resonance observed in the ^1H NMR spectrum.

The normal to the acetate ligand plane lies only 13.7(4)° from the normal to the dodecahedral plane of W, P(1), P(3), O(5) and H(6), and the C(51)–C(5)–O(51)···H(6) torsion angle is 165(2)°. Thus the unique hydride atom, H(6), lies close to the plane encompassing conventional sp^2 hybridised carbonyl oxygen lone pairs. Adopting the projection of Taylor *et al.*[4] for hydrogen bonds to carbonyl groups, as shown in Fig. 2(*a*), θ is 75° and ϕ in this projection is $-6°$.

Such angles are not at all abnormal for intramolecular hydrogen bonds. In a bivariate statistical analysis of X-ray and neutron diffraction data reported for 152 C=O···H intramolecular hydrogen-bonding systems, nearly 20% of samples lie within the confines of $70 < \theta < 90°$ and $0 > \phi > -10°$.[4]

Values of C=O···H $\leqslant$ 90° are relatively common where intramolecular geometric restraints are operative[4] giving rise to arrangements such as shown in Fig. 2(*b*): we suggest that the evidence presented herein is consistent with an analogous type of interaction, Fig. 2(*c*).

Finally, we note that the pendant acetate ligand, besides distinguishing one hydride from the other two, is also responsible for the unprecedented reactivity of this complex towards deuterons: deuteronation of **1** leads to selective release

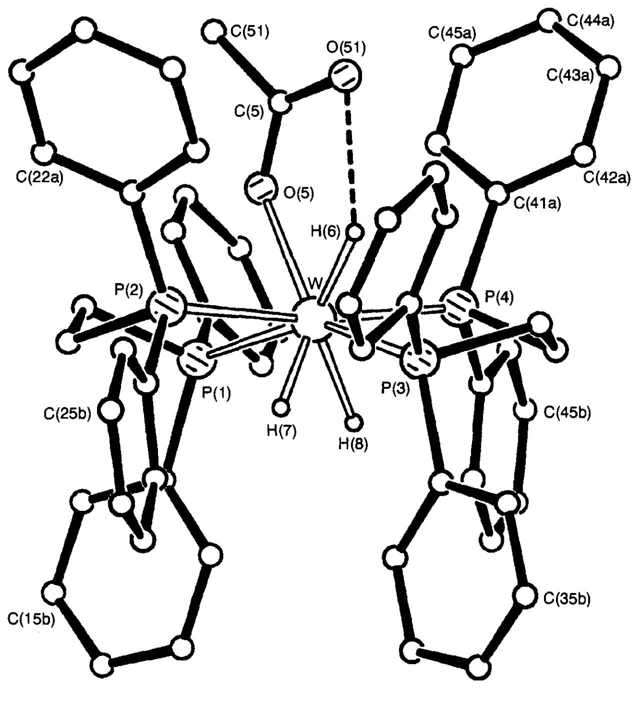


Fig. 1 Crystal structure of $[WH_3(\eta^1\text{-}OCOMe)(dppe)_2]$

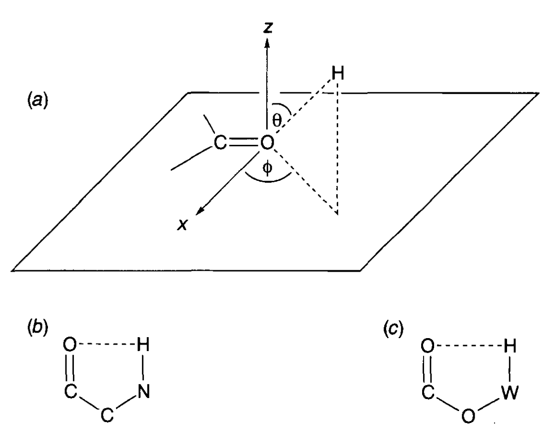


Fig. 2 (*a*) representation of C=O···H hydrogen bonding defining angles θ and ϕ according to ref. 4; (*b*) representation of a common intramolecular hydrogen bonding motif; (*c*) analogous representation for hydride **1**, θ = 75° and $\phi = -6°$, C=O···H 84.4(16)°, see text

of H_2 rather than to a mixture of HD, H_2 and D_2 as is unexceptionally the case with other polyhydrides.[5]

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Footnotes

† Microanalytical and spectroscopic data are fully consistent with the formulation of **1**.

‡ *X-Ray crystallography*: crystal structure analysis of $[WH_3(\eta^1\text{-OCOMe})(dppe)_2]\cdot MeCN$. Crystal data: $C_{54}H_{54}O_2P_4W\cdot C_2H_3N$, M = 1083.8 monoclinic, space group $P2_1/c$ (no. 14), a = 14.383(1), b = 16.673(2), c = 20.883(1) Å, β = 90.891(6)°, U = 5007.6 Å^3, Z = 4, D_c = 1.437 g cm^3, $F(000)$ = 2200, μ(Mo-Kα) = 25.2 cm^{-1}, λ(Mo-Kα) = 0.71069 Å. Fine, yellow, square-prismatic needle crystals. One *ca.* 0.13 × 0.13 × 0.33 mm, mounted on a glass fibre and coated with epoxy resin examined photographically; then on CAD4 diffractometer, with monochromated radiation, for accurate cell parameters and diffraction intensity measurements (θ_{max} = 20°). Data processed with corrections for Lorentz-polarisation effects, slight crystal deterioration, absorption and to eliminate negative intensities. 4652 Unique reflections (3351 with $I > 2\sigma_I$) into SHELX system[6] for structure determination (heavy-atom method) and refinement; at convergence, R = 0.054, R_g = 0.041[6] for all 4652 reflections weighted $w = (\sigma_F^2 + 0.00020F^2)^{-1}$. The three hydride ligands were found in appropriate locations, with peak heights *ca.* 0.5–0.7 e Å^{-3} in a difference Fourier map; the other major peaks in that map, to *ca.* 0.7 e Å^{-3} were all closer to the W atom and in chemically unreasonable positions. The hydride ligands were refined independently and successfully in the diphosphine ligands, all the hydrogen atoms were included in idealised positions; the methyl H-atoms in the carboxylate were refined with geometric constraints. For all hydrogen atoms, isotropic thermal parameters were refined freely. All non-hydrogen atoms were refined anisotropically.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre. See Information for Authors, Issue No. 1.

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