Activation of water by permethyltungstenocene; evidence for the oxidative addition of water

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Water oxidatively adds to photogenerated [W(η^5-C_5Me_5)$_2$] to form [WH(OH)(η^5-C_5Me_5)$_2$]; continued irradiation converts [WH(OH)(η^5-C_5Me_5)$_2$] to [WO(η^5-C_5Me_5)$_2$].

Oxidative addition is a potentially important reaction for the activation of water in solar energy conversion schemes and in other homogeneous catalytic cycles involving water.[1–3] Here, we report the oxidative addition of water to [W(η^5-C_5Me_5)$_2$] and, by analogy, to [Mo(η^5-C_5H_5)$_2$]. Oxidative addition reactions of water are uncommon for both thermodynamic and kinetic reasons.[4] In fact, only a few well characterized systems involving oxidative addition of water to organometallic complexes have been reported. For example, Milstein *et al.*[2] demonstrated the oxidative addition of water to several iridium(i) complexes [eqn. (1)] and Yoshida[1] reported the oxidative addition of water to rhodium(i) hydrido complexes [*e.g.* eqn. (2)].

$$[Ir(PMe_3)_4]^+ + H_2O \rightarrow cis\text{-}[Ir(PMe_3)_4(H)(OH)]^+ \qquad (1)$$

$$[RhH(PPr^i_3)]_3 + H_2O \xrightarrow{py} [RhH_2(py)_2(PPr^i_3)_2(OH)] \qquad (2)$$

Oxidative addition of water has been proposed in several other studies,[3,5] generally as part of longer reaction pathways, but these reactions are not understood mechanistically, and oxidative addition has not been established with certainty in these systems.

Our interest in the oxidative addition of water to [Mo(η^5-C_5H_5)$_2$] was piqued when, as part of a water-splitting project, we found that irradiation of [MoH$_2$(η^5-C_5H_5)$_2$] in acetonitrile–water formed [MoO(η^5-C_5H_5)$_2$] and H_2 in quantitative yield.[6]

$$[MoH_2(\eta^5\text{-}C_5H_5)_2] + H_2O \xrightarrow[MeCN]{h\nu} [MoO(\eta^5\text{-}C_5H_5)_2] + 2H_2 \qquad (3)$$

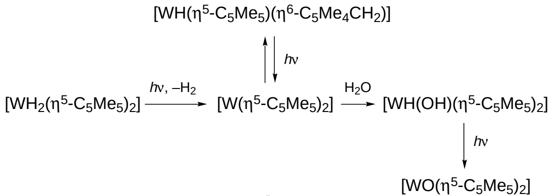
It is well established that irradiation of [MH$_2$(η^5-C_5H_5)$_2$] (M = Mo, W) forms H_2 and [M(η^5-C_5H_5)$_2$],[7] and a consideration of possible mechanisms for reaction (3) led us to hypothesize that oxidative addition of water to [Mo(η^5-C_5H_5)$_2$] was involved. In order to investigate this hypothesis, we studied the photochemistry of the related [WH$_2$(η^5-C_5Me_5)$_2$] molecule rather than [MoH$_2$(η^5-C_5H_5)$_2$] because [WH(OH)(η^5-C_5Me_5)$_2$] is a relatively stable molecule, whereas [MoH(OH)(η^5-C_5H_5)$_2$] has not been reported.[8] {Note that the[WH(OH)(η^5-C_5Me_5)$_2$] was prepared by $LiAlH_4$ reduction of [WO(η^5-C_5Me_5)$_2$], not by reaction of water with the [W(η^5-C_5Me_5)$_2$] intermediate.}

Irradiation of [WH$_2$(η^5-C_5Me_5)$_2$] in CD_3CN (37 mm; $\lambda > 340$ nm) in the presence of water (3.7 m) for 7.5 h caused a colour change from yellow to yellow–green.†‡ ^1H and ^{13}C NMR analysis (Table 1) of the solution showed the presence of the oxidative addition product [WH(OH)(η^5-C_5Me_5)$_2$] (12%), as well as [WO(η^5-C_5Me_5)$_2$] (12%), [WH(η^5-C_5Me_5)$_2$(η^6-$C_5Me_4CH_2$)] (9%), and unreacted [WH$_2$(η^5-C_5Me_5)$_2$] (67%), eqn. (4) and Scheme 1. [WH(η^5-C_5Me_5)(η^6-$C_5Me_4CH_2$)] is the known intramolecular C–H oxidative addition product that forms from the [W(η^5-C_5Me_5)$_2$] intermediate.§ The formation of this product indicates that [W(η^5-C_5Me_5)$_2$] is forming as an intermediate in the reaction, as planned. Continued irradiation of the reaction solution for a total of 15 h caused the solution to turn green (λ_{max} = 596 nm), at which point ^1H and ^{13}C NMR analysis showed [WH(OH)(η^5-C_5Me_5)$_2$] (27%), an increased amount of [WO(η^5-C_5Me_5)$_2$] (59%), and unreacted [WH$_2$(η^5-C_5Me_5)$_2$] (14%).

$$[WH_2(\eta^5\text{-}C_5Me_5)_2] \xrightarrow[CD_3CN\text{–}H_2O]{h\nu} [WH(OH)(\eta^5\text{-}C_5Me_5)_2] + [WO(\eta^5\text{-}C_5Me_5)_2] + [WH(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)] \qquad (4)$$

The results above show that water oxidatively adds to the photogenerated [W(η^5-C_5Me_5)$_2$] intermediate, and they also suggest that [WH(OH)(η^5-C_5Me_5)$_2$] is an intermediate on the pathway from [WH$_2$(η^5-C_5Me_5)$_2$] to [WO(η^5-C_5Me_5)$_2$]. Consistent with this latter hypothesis, irradiation of [WH(OH)(η^5-C_5Me_5)$_2$]¶ (28 mm; $\lambda > 340$ nm) in CD_3CN–H_2O ([H_2O] = 3.7 m) for 7.5 h gave [WO(η^5-C_5Me_5)$_2$] as the only product {38% yield with 62% [WH(OH)(η^5-C_5Me_5)$_2$] still unreacted}, eqn. (5).

$$[WH(OH)(\eta^5\text{-}C_5Me_5)_2] \xrightarrow[CD_3CN\text{–}H_2O]{h\nu} [WO(\eta^5\text{-}C_5Me_5)_2] \qquad (5)$$



Scheme 1

Table 1 ^1H NMR chemical shifts in various solvents

	Assignment	[WH$_2$(η^5-C_5Me_5)$_2$]	[WO(η^5-C_5Me_5)$_2$]	[WH(OH)-(η^5-C_5Me_5)$_2$]	[WH(η^5-C_5Me_5)-(η^6-$C_5Me_4CH_2$)][a]
C_6D_6	C_5Me_5	1.98	1.87	1.81	1.86
	W–OH			−0.51	
	W–H	−11.25		−11.05	−11.94
CD_3CN	C_5Me_5	1.95	1.90	1.82	1.87
	W–OH			−0.88	
	W–H	−11.86		−11.47	−12.39
CD_3CN–H_2O	C_5Me_5	1.95	1.92	1.85	1.87
(15/1)	W–H	−12.01		−11.57	−12.43

[a] For comparison to the other complexes, only the C_5Me_5 and hydride resonances are reported in this Table. For the complete spectrum, see footnote ¶.

Also consistent with the hypothesis, irradiation (λ > 340 nm; 7.5 h) of $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ (22 mm) in dry CD_3CN gave $[WO(\eta^5\text{-}C_5Me_5)_2]$ (19%), $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ (10%), and a small amount of $[WH(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)]$ (1%), with 70% of $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ still unreacted.[‖]

$$[WH(OH)(\eta^5\text{-}C_5Me_5)_2 \xrightarrow[CD_3CN]{h\nu} [WO(\eta^5\text{-}C_5Me_5)_2] + [WH_2(\eta^5\text{-}C_5Me_5)_2] + [WH(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)] \qquad (6)$$

Several additional experiments provided further insights into the reactions presented in Scheme 1. Irradiation (λ > 340 nm) of $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ (37 mm) for 7.5 h in CD_3CN containing only small amounts of water (59 mm) gave $[WH(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)]$ (58%) as the major product along with a small amount of $[WO(\eta^5\text{-}C_5Me_5)_2]$ (3%) and unreacted $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ (39%). {Irradiation (λ > 340 nm) of $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ (22 mm) for 23 h in dry CD_3CN gave $[WH(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)]$ as the only product.} The formation of $[WH(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)]$ was reversible, however, as irradiation of this compound in CD_3CN (16 mm; λ > 340 nm) for 7.5 h in the presence of a large excess of water (3.7 m) gave $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ (21%) and $[WO(\eta^5\text{-}C_5Me_5)_2]$ (79%). Continued irradiation for a total of 18 h gave complete conversion to $[WO(\eta^5\text{-}C_5Me_5)_2]$. In the reverse reaction, it is suggested that reductive elimination of a C–H bond occurs to give $[W(\eta^5\text{-}C_5Me_5)_2]$, which then reacts with H_2O to form $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ and then $[WO(\eta^5\text{-}C_5Me_5)_2]$.

The mechanism for the conversion of $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ to $[WO(\eta^5\text{-}C_5Me_5)_2]$ is uncertain. One possibility is a mechanism suggested by Bercaw and Parkin for the thermal conversion of $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ to $[WO(\eta^5\text{-}C_5Me_5)_2]$ (at 80 °C).[10] Their mechanism is shown in reactions (7) and (8).

$$2\ [WH(OH)(\eta^5\text{-}C_5Me_5)_2] \rightarrow [WH_2(\eta^5\text{-}C_5Me_5)_2] + [W(OH)_2(\eta^5\text{-}C_5Me_5)_2] \qquad (7)$$

$$2\ [W(OH)_2(\eta^5\text{-}C_5Me_5)_2] \rightarrow [WO(\eta^5\text{-}C_5Me_5)_2] + H_2O \qquad (8)$$

The products of reaction (6) are consistent with this pathway. According to this mechanism $[WH(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)]$ is formed in a secondary photolysis by irradiation of $[WH_2(\eta^5\text{-}C_5H_5)_2]$, not by a route involving reductive elimination of water from $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$. It is not obvious, however, why the mechanism would be photochemically activated. Another possible mechanism is a 1,2-elimination of H_2 from $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$. Consistent with this pathway is the observation that $[WO(\eta^5\text{-}C_5Me_5)_2]$ is the only product formed by irradiation of $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ in the presence of an excess of water [eqn. (5)]. However, the formation of $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ in eqn. (6) is not accounted for by this mechanism.

In summary, the spectroscopic observation of $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ provides convincing evidence for the oxidative addition of water to $[W(\eta^5\text{-}C_5Me_5)_2]$ and by analogy to $[Mo(\eta^5\text{-}C_5H_5)_2]$. The $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ molecule is photoreactive and it is converted to $[WO(\eta^5\text{-}C_5Me_5)_2]$. We are continuing to investigate the mechanisms of these reactions and their applications to water splitting.

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Footnotes

[†] $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ and $[WO(\eta^5\text{-}C_5Me_5)_2]$ were prepared by literature procedures.[8]

Spectroscopic data: $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ (see also Table1 and refs. 8 and 9). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 MHz, in ppm relative to $SiMe_4$): δ 12.40 (s, CH_3), 90.09 (s, *C*CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 12.42 (s, CH_3), 91.05 (s, *C*CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN–H_2O; 15 : 1): δ 12.10 (s, CH_3), 90.96 (s, *C*CH_3). EIMS (70 eV): *m/z* 454 (M^+ −2, 100% with correct isotope pattern). UV–VIS (MeCN) λ_{max} = 281 nm (ε = 7221 $dm^3\ mol^{-1}\ cm^{-1}$).

$[WO(\eta^5\text{-}C_5Me_5)_2]$ (see also Table 1). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 11.72 (s, CH_3), 99.02 (s, *C*CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN–H_2O; 15 : 1): δ 11.49 (s, CH_3), 99.38 (s, *C*CH_3). UV–VIS (MeCN) λ_{max} = 596 nm (ε = 113 $dm^3\ mol^{-1}\ cm^{-1}$). In addition to the NMR spectra, the band at 596 nm was a useful diagnostic that indicates the formation of $[WO(\eta^5\text{-}C_5Me_5)_2]$ in a reaction.

[‡] A typical photolysis experiment was performed as follows. To an NMR tube attached to a stopcock was loaded 10 mg of $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ (21.9 μmol) and CD_3CN (0.6 ml) in a dry box. Distilled water (40 μl, 2.2 mmol), which had been degassed by three freeze–pump–thaw (FPT) cycles, was syringed into the tube under N_2. After the resulting solution was degassed by two FPT cycles, the tube was flame-sealed. During the photolysis, the solution in the NMR tube was cooled with ice–water and shaken frequently. The solutions were irradiated using a high-pressure Hg arc lamp (200 W) fitted with a water filter and a UV cutoff filter (Corning Glass CS 0-52). When the chemical resonances of $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ overlapped with those of solvents, the amount of $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ was estimated by subtracting integrations corresponding to solvent, which in turn were calculated using their ratios to added $SiMe_4$ in stock NMR solvents.

[§] The complex $[WH(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)]$ was reported to form from $[W(\eta^5\text{-}C_5Me_5)_2]$ in (*a*) photolysis of $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ in pentane,[9] (*b*) reaction of $[W(H)Cl(\eta^5\text{-}C_5Me_5)_2]$ with MeLi in toluene at 100 °C,[8] (*c*) reaction of $[WCl_2(\eta^5\text{-}C_5Me_5)_2]$ with MeLi in C_6D_6 at 80 °C,[8] and (*d*) reaction of $[WCl_2(\eta^5\text{-}C_5Me_5)_2]$ with Na–Hg in thf.[9b]

[¶] The preparation of $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ was modified from the literature procedure[8] as follows. Diethyl ether (20 ml) was added to a mixture of $[WO(\eta^5\text{-}C_5Me_5)_2]$ (240 mg; 0.51 mmol) and $LiAlH_4$ (180 mg; 4.75 mmol) at −77 °C. The reaction mixture was warmed to room temp. and stirred for 2 h, producing an orange–brown solution. After unreacted $LiAlH_4$ was filtered off, and solvent was removed, the residual solid was chromatographed on basic alumina.[6b] The first fraction (hexanes) was $[WH(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)]$ (45.9 mg, 0.10 mmol, 19.6%). The second fraction (hexanes–ether = 1 : 1) was $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ (9.3 mg, 0.02 mmol, 3.9%), and the third fraction was a negligible amount of unreacted $[WO(\eta^5\text{-}C_5Me_5)_2]$. The last fraction (ether–thf = 1 : 1) was $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ (51.5 mg, 0.11 mmol, 21.4%). ^1H NMR data for $[WH(\eta^5\text{-}C_5Me_5)(\eta^5,\eta^1\text{-}C_5Me_4CH_2)]$ in CD_3CN: δ 1.87 [15 H, s, $C_5(Me_5)$], 1.51, 1.80 and 2.06 [each 3 H, s, $C_5(Me)_4CH_2$], 2.01 [3H, d, $C_5(Me)_4CH_2$, $J_{HW(H)}$ = 3 Hz], 2.87 and 3.08 [each 1 H, m, $C_5(Me)_4CH_2$], −12.39 (1 H, br m, J_{WH} = 93 Hz). Spectroscopic data for $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ (see also Table 1). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 13.14 (s, *C*H_3), 108.43 (s, *C*CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN–H_2O; 15 : 1): δ 13.36 (s, CH_3), 109.30 (s, *C*CH_3). IR (KBr pellet, cm^{-1}): 2973m, 2904s, 2860m, 2725w, 1906m (WH), 1378s, 1265m, 1102w, 1070w, 1024m, 934w, 872m, 801m, 692w. The resonance of the OH proton could be located at δ −0.51 (C_6D_6), which broadens upon addition of a stoichiometric amount of water or ethanol, and disappears with addition of an excess of water.

[‖] Further irradiation for a total of 30 h produced a solution containing a decreased amount of $[WH_2(\eta^5\text{-}C_5Me_5)_2]$ (1%), an increased amount of $[WH(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)]$ (18%), $[WO(\eta^5\text{-}C_5Me_5)_2]$ (49%), and unreacted $[WH(OH)(\eta^5\text{-}C_5Me_5)_2]$ (42%).

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