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HALIDE, HYDRIDE, ALKYL, OXO AND RELATED DERIVATIVES OF BIS(PENTAMETHYLCYCLOPENTADIENYL)TUNGSTEN(IV)

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Abstract—A "wet" entry into permethyltungstenocene chemistry is provided by $Cp^*_2WCl_2$ ($Cp^* = \eta^5$-C_5Me_5), prepared by reduction of $Cp^*WCl_4(PMe_3)$ with Mg followed by metathesis with MCp^* (M = Li, K). $Cp^*_2WCl_2$ may be converted to a variety of other permethyltungstenocene derivatives and thus, $Cp^*_2WH_2$, $Cp^*_2W(H)Cl$. $Cp^*_2W(CH_3)_2$, $Cp^*_2W(CH_3)Cl$, $Cp^*_2W(CH_3)H$, $Cp^*_2W(CH_2C_6H_5)H$, $Cp^*_2W(\eta^2$-$CH_2O)$ and $Cp^*_2W{=}O$ have been isolated. The dihydride derivative, $Cp^*_2WH_2$, is readily protonated to give $[Cp^*_2WH_3]^+$. The protonation occurs by attack at *both* the W—H bonds (and not the d^2 tungsten centre), forming an η^3-trihydrogen species, $[Cp^*_2W(\eta^3$-$H_3)]^+$, prior to collapsing to the trihydride cation, $[Cp^*_2WH_3]^+$. The central and lateral hydride ligands of $[Cp^*_2WH_3]^+$ exchange sites by an intramolecular mechanism in preference to a deprotonation/protonation mechanism. The oxo ligand of $Cp^*_2W{=}O$ undergoes facile isotopic exchange with $H_2{}^{18}O$ and $H_2{}^{17}O$. $Cp^*_2W{=}O$ is oxidized by $H_2O_{2(aq)}$ and by O_2 to give (η^5-C_5Me_5)(η^1-C_5Me_5)$W(=O)_2$ and (η^5-C_5Me_5)$W(=O)_2(OC_5Me_5)$, respectively. (η^5-C_5Me_5)(η^1-C_5Me_5)$W(=O)_2$ possesses both *penta*hapto and *mono*hapto pentamethylcyclopentadienyl ligands which exchange on the NMR timescale with $\Delta G^\ddagger = 10(1)$ kcal mol^{-1} at -60°C. (η^5-C_5Me_5)$W(=O)_2(OC_5Me_5)$ is formed by insertion of an oxygen atom from dioxygen into the W—C_5Me_5 bond. The two oxo ligands of (η^5-C_5Me_5)(η^1-C_5Me_5)$W(=O)_2$ and (η^5-C_5Me_5)$W(=O)_2(OC_5Me_5)$ exhibit a strong *trans* influence, resulting in a coordination geometry of the pentamethylcyclopentadienyl ligand which is more properly described as (η^1,η^4-C_5Me_5). The oxo ligand of $Cp^*_2W{=}O$ may be abstracted by a variety of reagents. Thus, both H_2 and Me_2SiH reduce $Cp^*_2W{=}O$ to $Cp^*_2WH_2$, and Me_3SiCl converts $Cp^*_2W{=}O$ to $Cp^*_2WCl_2$. In contrast, the reaction between $Cp^*_2W{=}O$ and CH_3I gives the oxo-methyl cation, $[Cp^*_2W(=O)CH_3][I]$, which is deprotonated by KH to give initially the *tetra*hapto-coordinated η^4-1,2,3,4-tetramethylfulvene complex, $Cp^*(\eta^4$-$C_5Me_4{=}CH_2)W(=O)(CH_3)$, which subsequently isomerizes to *dihapto*-coordinated *exo*-methylene tautomer, $Cp^*(\eta^2$-$CH_2{=}C_5Me_4)W(=O)(CH_3)$.

The group 6 "bent metallocene" derivatives, Cp_2MX_2 and Cp_2ML ($Cp = \eta^5$-C_5H_5; M = Mo, W; X = halide, hydride, alkyl, etc.; L = CO, PR_3, etc.), first reported by Wilkinson, Green, McCleverty and Pratt in 1961,[1] have been amongst the most important compounds in the development of synthetic, mechanistic, structural and theoretical organotransition metal chemistry. For example, structural studies provided experimental evidence to test the validity of the various molecular orbital descriptions for bent metallocene derivatives.[2] In addition, the tungstenocene system has exhibited a wealth of chemistry which has provided information on many fundamental transformations including: (i) the first example of the photochemical reductive elimination of dihydrogen, (ii) the insertion of $[Cp_2W]$ into sp^3 C—H bonds (i.e. alkane activation), (iii) the first evidence for α-H elimination for $[Cp_2W{-}CH_3]^+$, (iv) ring opening of a tungstenacyclobutane derivative to give an alkylidene–olefin intermediate, which subsequently led to proposal of the Green–Rooney mechanism for olefin polymerization, and (v) the development of rules for predicting the regioselectivity of nucleophilic addition to organometallic cations.[3]

Our research group has had a long-standing interest in studying fundamental organometallic

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transformations including α and β migratory insertion/elimination, reductive elimination/oxidative addition and sigma bond metathesis. In this regard the permethylmetallocene derivatives of scandium, titanium, zirconium, hafnium, niobium and tantalum have proven to be particularly well-suited to structural and mechanistic studies due to their enhanced solubilities, stabilities and crystallizabilities, as compared with the (η^5-C_5H_5) analogues.[4] Moreover, the steric bulk of their (η^5-C_5Me_5) ligands inhibits bimolecular decomposition pathways, thus allowing isolation of compounds such as $Cp^*_2Ta(=CH_2)H$[4h] ($Cp^* = \eta^5$-C_5Me_5), the first isolable example of an alkylidene hydride derivative. In order to extend our mechanistic studies at "bent permethylmetallocene" centres to the less electropositive transition elements to the right of the Periodic Table, we have long sought a convenient synthetic route to the permethyltungstenocene system. In view of the extensive chemistry of the unsubstituted [(η^5-$C_5H_5)_2W$] system leading to the formation of dimers via intermolecular attack at the C—H bonds of the (η^5-C_5H_5) ligands of other metal centres,[5] we again anticipated a substantial increase in stability for the (η^5-C_5Me_5) analogue. Although the tungstenocene system has been known for more than 25 years, corresponding synthetic approaches to permethyltungstenocene derivatives have been uniformly unsuccessful, and the only previously reported synthesis of $Cp^*_2WH_2$ is the recently described metal vapour synthesis method involving co-condensation of Cp*H with W atoms.[6] Herein we describe a conventional synthesis of $Cp^*_2WCl_2$ and the synthesis, structure and reaction chemistry of other derivatives of permethyltungstenocene derived therefrom.

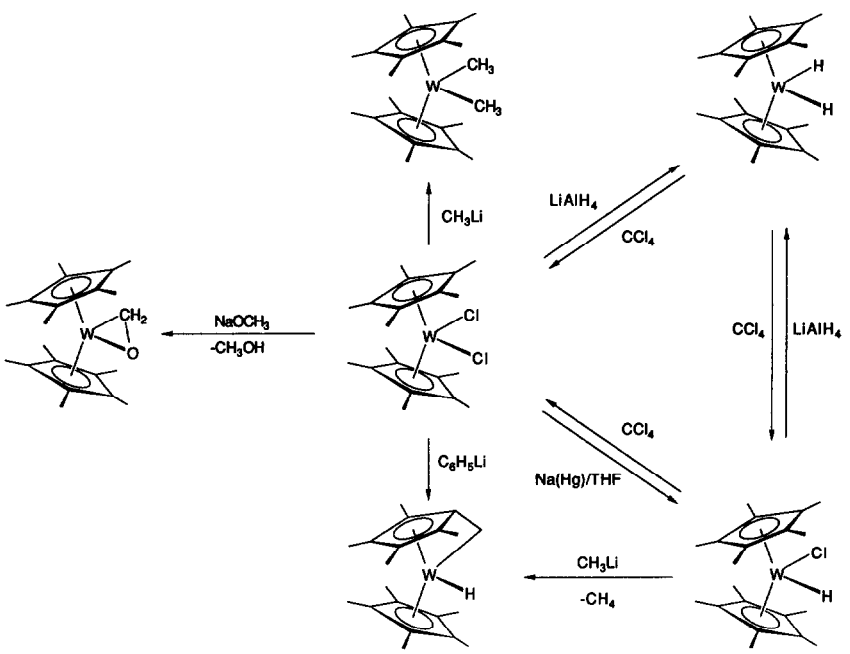
RESULTS AND DISCUSSION

Halide, hydride, alkyl and formaldehyde derivatives of permethyltungstenocene

(1) *Synthetic studies.* $Cp^*_2WCl_2$ is synthesized in *ca* 30% yield from $Cp^*WCl_4(PMe_3)$[7] by a two-step process involving (i) reduction by Mg (0.5 equivalent) followed by (ii) reaction with either LiCp* or KCp*. This approach is also successful for the mixed-ring derivative (η^5-C_5Me_5)(η^5-$C_5Me_4CH_2CH_2CH_3$)WCl_2.

$$Cp^*WCl_4(PMe_3) \xrightarrow{0.5\,Mg/THF} \{Cp^*WCl_3(PMe_3)(MgCl_2)_{0.5}\} \xrightarrow[(M = Li, K)]{MCp^*/C_6H_5CH_3/145°C} Cp^*_2WCl_2.$$

$Cp^*_2WCl_2$ provides an entry to a variety of other permethyltungstenocene derivatives (Scheme 1). For example, the reaction of $Cp^*_2WCl_2$ with $LiAlH_4$ generates $Cp^*_2WH_2$ in which $Cp^*_2W(H)Cl$ is observed as an intermediate. A more convenient synthesis of $Cp^*_2W(H)Cl$ is the reduction of $Cp^*_2WCl_2$ by Na(Hg) in THF. The origin of the hydride ligand is uncertain, but it is likely that it



Scheme 1. Syntheses of permethyltungstenocene derivatives from $Cp^*_2WCl_2$.

arises by abstraction from the solvent.† The dimethyl derivative, $Cp^*_2W(CH_3)_2$, is isolated from the reaction of $Cp^*_2WCl_2$ with CH_3Li in toluene at 80°C. In contrast, the reaction of $Cp^*_2WCl_2$ with $NaOCH_3$ gives the η^2-formaldehyde derivative, $Cp^*_2W(\eta^2\text{-}CH_2O)$. This reaction occurs with elimination of methanol and, thus, may proceed via the dimethoxy derivative, $[Cp^*_2W(OCH_3)_2]$, followed by 1,3-elimination of CH_3OH.‡

$$Cp^*_2WCl_2 \xrightarrow{NaOCH_3} [Cp^*_2W(OCH_3)_2] \xrightarrow{-CH_3OH} Cp^*_2W(\eta^2\text{-}CH_2O).$$

Other η^2-formaldehyde derivatives of tungsten, namely $W(PMe_3)_4(\eta^2\text{-}CH_2O)H_2$[9] and $W(\eta^4\text{-}C_4H_6)(\eta^2\text{-}CH_2O)(PMe_3)_3$,[10] as well as the molybdenocene derivative, $Cp_2Mo(\eta^2\text{-}CH_2O)$,[11] have recently been reported.

The metallated derivative, $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$,§ is formed by the reaction of $Cp^*_2WCl_2$ with C_6H_5Li. The simple metathesis produce (very sterically crowded) $Cp^*_2W(C_6H_5)_2$, is not obtained nor is it observed as an intermediate; rather, as evidenced by the formation of biphenyl, phenyllithium appears to act as a reducing agent. $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ is also obtained by the reaction of the hydrido-chloride derivative, $Cp^*_2W(H)Cl$, with CH_3Li at 110°C. The latter reaction is observed to proceed via elimination of methane from the initial metathesis product, $Cp^*_2W(CH_3)H$, by ^1H NMR spectroscopy.

$$Cp^*_2W(H)Cl \xrightarrow{CH_3Li/110°C} [Cp^*_2W(CH_3)H] \xrightarrow{-CH_4} Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH.$$

The W^{IV} compound $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ is not as reactive as the analogous Ta^V compound, $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)TaH_2$, which is an effective source of the 16-electron intermediate, $[Cp^*_2Ta\text{—}H]$.[12] It does, however, react with H_2 (4 atm) to give $Cp^*_2WH_2$ at 220°C.

$$Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH + H_2 \longrightarrow Cp^*_2WH_2.$$

$Cp^*_2WH_2$ is converted sequentially to the hydrido-chloride, $Cp^*_2W(H)Cl$, and the dichloride derivative, $Cp^*_2WCl_2$ upon treatment with CCl_4. Furthermore, $Cp^*_2WCl_2$ and $Cp^*_2WH_2$ react at 220°C to form $Cp^*_2W(H)Cl$ as an equilibrium mixture.

$$Cp^*_2WH_2 + Cp^*_2WCl_2 \rightleftharpoons 2Cp^*_2W(H)Cl \quad K_{eq} \approx 21(1) \text{ at } 220°C.$$

The methyl–chloride derivative, $Cp^*_2W(CH_3)Cl$, is conveniently obtained by selected cleavage of one of the W—CH_3 bonds of $Cp^*_2W(CH_3)_2$ upon treatment with one equivalent of HCl, generated *in situ* by the reaction of Me_3SiCl (one equivalent) with H_2O (0.5 equivalent). $Cp^*_2W(CH_3)Cl$ is another useful precursor to permethyltungstenocene derivatives and exhibits a variety of reaction pathways as shown in Scheme 2. Simple substitution reactions occur with CH_3Li and $LiAlH_4$ to give $Cp^*_2(CH_3)_2$ and $Cp^*_2W(CH_3)H$, respectively. In contrast to these metathesis reactions, the reaction of $Cp^*_2W(CH_3)Cl$ with C_6H_5Li does not give $Cp^*_2W(CH_3)(C_6H_5)$ but rather $Cp^*_2W(CH_2C_6H_5)H$. A plausible reaction sequence would involve nucleophilic attack by LiC_6H_5 at the methylidene ligand of an intermediate cation, $[Cp^*_2W(=CH_2)H]^+$, generated by α-H elimination from the intermediate $[Cp^*_2W\text{—}CH_3]^+$, e.g.

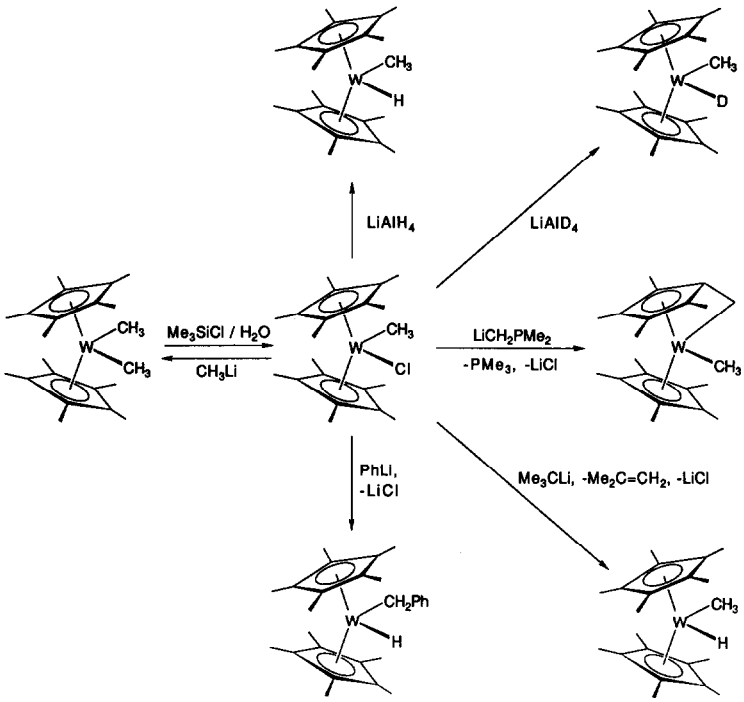
$$Cp^*_2W(CH_3)Cl \xrightarrow{-Cl^-} [Cp^*_2W\text{—}CH_3]^+ \rightleftharpoons [Cp^*_2W(=CH_2)H]^+ \xrightarrow[-Li^+]{C_6H_5Li} Cp^*_2W(CH_2C_6H_5)H.$$

A similar mechanism has been proposed for the formation of $[Cp_2W(CH_2PR_3)H][PF_6]$ from $[Cp_2W(CH_3)(PR_3)][PF_6]$.[13] The mechanism of this reaction is to be contrasted with the reaction of $Cp^*_2W(CH_3)Cl$ with $LiAlH_4$ to give $Cp^*_2W(CH_3)H$. For this latter reaction, a similar mechanism may have, in principle, occurred since the product of a direct metathesis mechanism and that of an α-H elimination mechanism are identical. However, the reaction of $Cp^*_2W(CH_3)Cl$ with $LiAlD_4$ provides $Cp^*_2W(CH_3)D$, in support of the direct metathesis reaction. A further reaction pathway is demonstrated by the reaction of $Cp^*_2W(CH_3)Cl$ with $LiCH_2PMe_2$ in which dehydrohalogenation occurs, but the overall result is that of deprotonation of one of the Cp* methyl groups, and not [W—CH_3], to give $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)W(CH_3)$. The reaction of $Cp^*_2W(CH_3)Cl$ with other organolithium reagents lead to complex mixtures. For example, CH_2CH_3MgBr or Me_3CLi gives *inter alia* $Cp^*_2W(CH_3)H$ with the elimination of olefin.

† Smaller quantities of $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ are also formed by this reduction but $Cp^*_2W(H)Cl$ may be readily separated by crystallization from pentane.

‡ The formation of η^2-thioaldehyde and η^2-imine complexes by 1,3-elimination of CH_4 from $Cp_2Zr(SCH_2R)(CH_3)$[8a] and from $Cp^*Ta(NMe_2)(CH_3)_3$[8b] have been observed.

§ $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ and $Cp^*\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2\}W$ have been prepared previously by photolytic elimination of H_2 from $Cp^*_2WH_2$.[6]



Scheme 2. Synthesis and reaction chemistry of $Cp_2^*W(CH_3)Cl$.

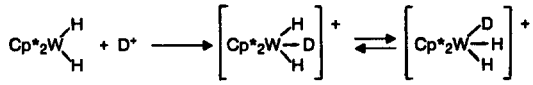
(2) *The mechanism of the protonation of* $Cp_2^*WH_2$: *evidence for a trihydrogen species.* The tungstenocene derivative, Cp_2WH_2, has previously been shown to react with a variety of electrophiles,[14] e.g. BX_3 (X = F, Cl),[15] H^+,[1a] and R_3Al.[16] Similarly, the dihydride, $Cp_2^*WH_2$, is readily protonated by a variety of acids including $HBF_4 \cdot Et_2O$, $HCl_{(aq)}$ and $[Me_3NH][BPh_4]$ to give the trihydride cation, $[Cp_2^*WH_3]^+$.

$$Cp_2^*WH_2 + HX \longrightarrow [Cp_2^*WH_3][X] \, (X = Cl, BF_4, BPh_4).$$

The $[Cp_2^*WH_3]^+$ cation is characterized by two resonances in the ^1H NMR spectrum in D_2O at δ −4.50 (doublet) and δ −5.42 (triplet) corresponding to the central and lateral protons, respectively. The small $^2J_{H-H}$ coupling constant, *ca* 3 Hz, is indicative that the species is formally a trihydride, not a dihydrogen–hydride derivative, $[Cp_2^*W(\eta^2\text{-}H_2)H]^+$. Interestingly, the central hydride ligand exhibits an 11 Hz greater $^1J_{W-H}$ coupling constant ($^1J_{W-H}$ = 66 Hz) than the lateral hydride ligands ($^1J_{W-H}$ = 57 Hz), possibly reflecting a greater a_1 (and thus greater tungsten 6*s*) contribution in the bonding to the central hydride ligand. The trihydride derivative is readily deprotonated by $KOH_{(aq)}$ to regenerate $Cp_2^*WH_2$.

$$[Cp_2^*WH_3]^+ + KOH_{(aq)} \longrightarrow Cp_2^*WH_2 + H_2O + K^+.$$

Some rather unexpected features of this protonation/deprotonation mechanism are revealed by examining the stereochemistry of D^+ addition to $Cp_2^*WH_2$. Treatment of a suspension of $Cp_2^*WH_2$ in D_2O with a solution of DCl/D_2O affords, as the kinetic product, the isotopomer with the deuterium predominantly occupying the *central* position, $[Cp_2^*W(H)(D)(H)]^+$ (*ca* 90%, 1 min), and a much smaller fraction of the laterally deuterated isotopomer, $[Cp_2^*W(H)(H)(D)]^+$ (*ca* 10%, 1 min). Subsequent exchange of the lateral and central hydride ligands occurs over a period of several hours, accompanied by further incorporation of deuterium from excess DCl/D_2O (*vide infra*).



The relatively small doublet ($^2J_{H-H}$ = 3 Hz) attributable to the central hydrogen of $[Cp_2^*W(H)(H)(D)]^+$ initially observed in the ^1H NMR spectrum (resonance H_2O in Fig. 1) is particularly indicative of the strong preference for central protonation. Possible pathways for the protonation of $Cp_2^*WH_2$ with D^+ are shown in Scheme 3. Pathways (a) and (b) involve direct protonation at the tungsten centre in the lateral and central positions, respectively. On the basis of *ground* state orbital control arguments, an electrophile would be

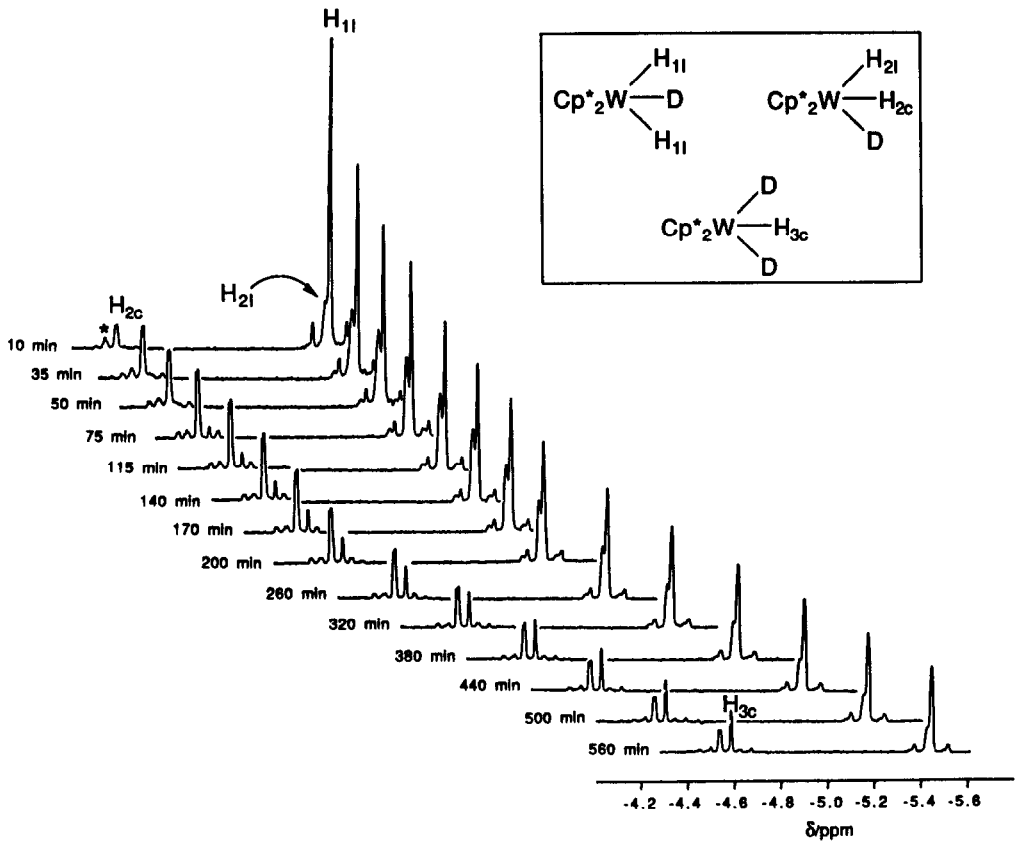
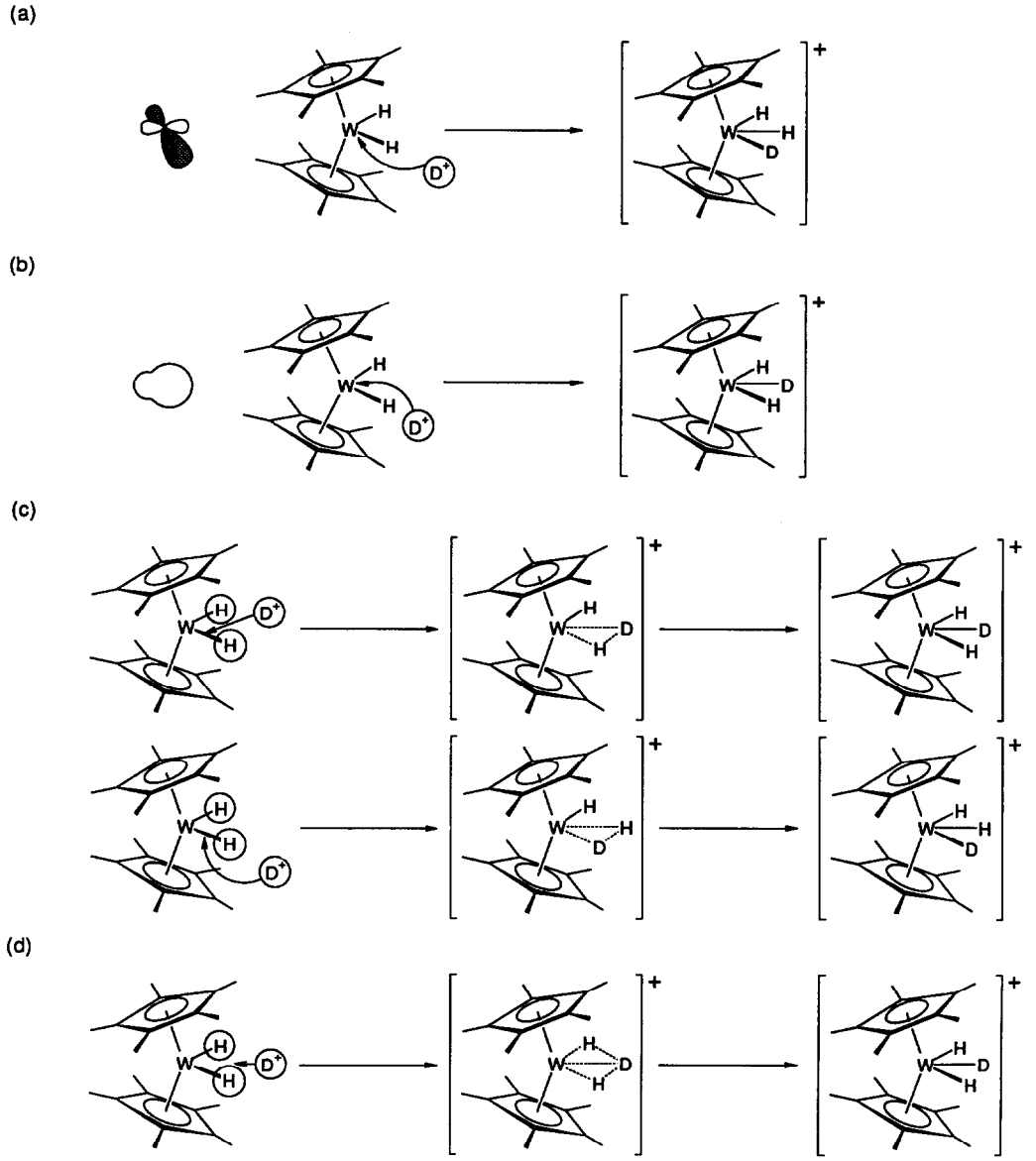


Fig. 1. Evolution of the hydride region of the ^{1}H NMR spectrum for the product of $Cp_2^*WH_2$ with DCl in D_2O (* denotes central hydride of $[Cp_2^*WH_3]^+$).

predicted to attack *initially* the HOMO. The first bonding description of the bent metallocene system was provided by Dahl and Ballhausen[17] in which it was implied that the lone pair of electrons on the metal centre of Cp_2WH_2 resided in an orbital which is directed between the two hydrogen ligands. If this proposal is correct, the observed stereochemistry of the deuteration reaction would be consistent with orbital-controlled electrophilic attack at the HOMO of $Cp_2^*WH_2$. However, the Ballhausen–Dahl description has been questioned. On the basis of the CH_3—Re—CH_3 bond angle in a related derivative, $(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_5Me)Re(CH_3)_2$, Alcock suggested that, in fact, the lone pair resides in an orbital lateral to the methyl ligands.[18] This suggestion has been overwhelmingly supported by (i) structural studies by Green *et al.* on a series of d^0, d^1 and d^2 Cp_2MX_2 derivatives, which showed that the X—M—X bond angle *decreases* across the series, thus suggesting that the additional d electrons occupy an orbital which lies *laterally* to the two X ligands,[2] (ii) single crystal electron paramagnetic studies on Cp_2VS_5 and $(\eta^5\text{-}C_5H_4CH_3)_2VCl_2$, which indicate that the unpaired electron occupies a lateral orbital[19] and (iii) a combined molecular orbital/photoelectron spectroscopy study.[20] Thus, Green *et al.*[2] proposed a new bonding description for Cp_2MX_2 which comprised elements of both the Ballhausen–Dahl and Alcock models and also resembled the Brintzinger[21] description. Additional support for a lateral HOMO is provided by the calculations of Lauher and Hoffmann[22] and Dahl *et al.*;[23] the validity of their description is underscored by the observation that the H—Mo—H bond angle of 75.5(3)° in Cp_2MoH_2, as determined by neutron diffraction,[24] is very close to that predicted ($\approx$ 78°) for a d^2 molecule.[19] The conclusions of these quantitative studies are summarized in a qualitative MO diagram for $Cp_2^*WH_2$, shown in Fig. 2.† The $2a_1$ HOMO is a tungsten-localized lateral orbital that interacts minimally with the two hydride ligands. Thus, protonation following orbital control would be expected to proceed by path (a) (Scheme 3), giving the lateral d_1-isotopomer, $[Cp_2^*W(H)(H)(D)]^+$. However, observation of the central d_1-isotopomer, $[Cp_2^*W(H)(D)(H)]^+$, which arises by attack along

† Based on the results of refs 22 and 23.



Scheme 3. Possible pathways for protonation of $Cp^*_2WH_2$. (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.

the pseudo-C_2 axis, signals a more subtle situation. There is no occupied, metal-based central orbital in Fig. 2, which therefore rules out path (b) (Scheme 3) as a dominant mechanistic pathway.

Whereas one might be tempted to once again question the conclusions concerning the spatial disposition of the lone pair orbital for $Cp^*_2WH_2$, the alternative protonation pathways [Scheme 3(c) and 3(d)] should be first considered. Protonation at one or both of the hydride ligands is likely, particularly if they are sites of higher negative charge than the tungsten centre. Thus, protonation is subject to charge control (i.e. at $W—H^{\delta-}$) rather than orbital control (at the HOMO).† Protonation of a tungsten–hydrogen bond of $Cp^*_2WH_2$ would initially generate the dihydrogen–hydride cation, $[Cp^*_2W(\eta^2\text{-}H_2)H]^+$, which subsequently collapses to the trihydride cation. Protonation of a Re—H bond for the d^0 complex $Re(PR_3)_2H_7$ has been discussed

† Theoretical calculations have demonstrated that the protonation of $[CpFe(CO)_2]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ at the methylene ligand and not the Fe—Fe bond is charge and not orbital controlled.[25]

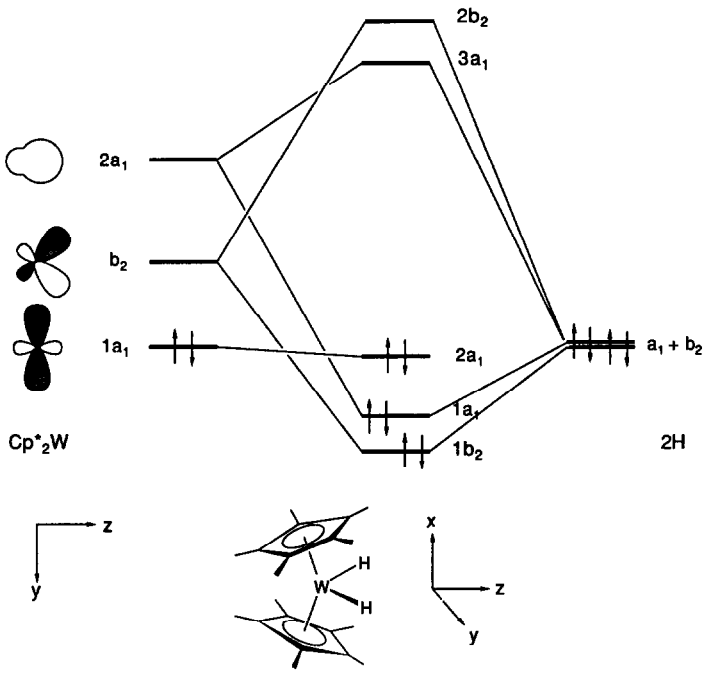


Fig. 2. A qualitative MO diagram for $Cp_2^*WH_2$.

recently.[26]† Moreover, a sequence closely analogous to that proposed for $Cp_2^*WH_2$ has been recently reported for the protonation/deprotonation of $(\eta^5\text{-}C_5H_5)(Me_2PCH_2CH_2PMe_2)RuH$; protonation occurs at the Ru—H bond (rather than at the d^6 metal centre) to afford $[(\eta^5\text{-}C_5H_5)(Me_2PCH_2CH_2PMe_2)Ru(\eta^2\text{-}H_2)]^+$, which subsequently equilibrates with $[(\eta^5\text{-}C_5H_5)(Me_2PCH_2CH_2PMe_2)RuH_2]^+$.[27]‡

Selective protonation of a single W—H bond of $Cp_2^*WH_2$ from the "inside" of the H—W—H angle, rather than from a lateral position could possibly be strongly preferred; however, the factors distating such a preference are not obvious. Alternately, it could be argued that the preferentially central protonation is a consequence of the proton initially interacting with *both* hydride ligands [Scheme 3(d)], producing the trihydrogen cation $[Cp_2^*W(\eta^3\text{-}H_3)]^+$, which subsequently collapses to the trihydride cation. The rather acute (*ca* 75°) H—W—H angle simultaneously offers both hydrides to electrophilic attack. In this regard, a trihydrogen adduct has recently been invoked to account for the unusual NMR behaviour for $[(\eta^5\text{-}C_5H_5)(PMe_3)IrH_3]^+$.[28] An equivalent molecular orbital picture is that attack occurs at the second highest occupied molecular orbital (SHOMO), that of $1a_1$ symmetry (Fig. 2). Thus, in view of the extensive structural, spectroscopic and theoretical studies cited above, pathway (d) (Scheme 3) appears to best reconcile the stereochemical preferences for central protonation of $Cp_2^*WH_2$.§

The kinetic product $[Cp_2^*W(H)(D)(H)]^+$ undergoes subsequent rearrangement to the lateral d_1-isotopomer $[Cp_2^*W(H)(H)(D)]^+$, and further exchange with the solvent (DCl/D_2O) resulting in the formation of d_2, and d_3 derivatives (Fig. 1). Examination of the time evolution of the ^1H NMR spectra for this mixture reveals that conversion of the central d_1-isotopomer, $[Cp_2^*W(H)(D)(H)]^+$, to the lateral d_1-isotopomer, $[Cp_2^*W(H)(H)(D)]^+$ occurs much faster than deuterium incorporation from DCl/D_2O. Since $[Cp_2^*WH_3]^+$ may be cleanly deprotonated to Cp_2WH_2 by $KOH_{(aq)}$, a possible mechanism for the isomerization process would be deprotonation of the central position¶ of $[Cp_2^*W(H)(D)(H)]^+$ generating $Cp_2^*WH_2$, followed

† An alternative explanation is that protonation occurs at the d^2 metal centre of the dihydrogen derivative, $Re(PR_3)_2(\eta^2\text{-}H_2)H_5$, with which $Re(PR_3)_2H_7$ may be in equilibrium.

‡ It was also shown that deprotonation of the dihydrogen derivative, $[CpRu(dmpe)(\eta^2\text{-}H_2)]^+$, is faster than that for the dihydride, $[CpRu(dmpe)H_2]^+$, as expected by the principle of microscopic reversibility.

§ We note that the product obtained from Cp_2WH_2 and R_3Al is also the result of attack at the central position; however, there is no evidence that this is the kinetic product of the reaction (ref. 16).

¶ Deprotonation from the central position is favoured over the lateral position according to the principle of microscopic reversibility.

by addition of D^+ at the lateral position.†

$$[Cp^*_2W(H)(D)(H)]^+ \rightleftharpoons [Cp^*_2WH_2] + D^+ \rightleftharpoons [Cp^*_2W(H)(H)(D)]^+.$$

It is important to recognize, however, that the observed build up of $[Cp^*_2W(H)(H)(D)]^+$ is *inconsistent* with this mechanism, since (i) the rate of conversion of $[Cp^*_2W(H)(D)(H)]^+$ to $[Cp^*_2W(H)(H)(D)]^+$ involves deprotonation of the central position and reprotonation *laterally*, whereas the subsequent conversion of $[Cp^*_2W(H)(H)(D)]^+$ to the d^2-isotopomer, $[Cp^*_2W(H)(D)(D)]^+$ involves deprotonation from the central position and reprotonation *centrally*; the latter must be much faster to account for the initial predominance of $[Cp^*_2W(H)(D)(H)]^+$, and (ii) the large pool of deuterium virtually assures addition of D^+ rather than H^+ to any $Cp^*_2W(X)Y$ (X, Y = H, D). Moreover, the normal, substantial k_H/k_D expected for deprotonation[29] further contributes to the faster conversion of $[Cp^*_2W(H)(H)(D)]^+$ to $[Cp^*_2W(H)(D)(D)]^+$, relative to its formation from $[Cp^*_2W(H)(D)(H)]^+$. The data shown in Fig. 1 clearly show that $[Cp^*_2W(H)(H)(D)]^+$ does, in fact, build up in concentration, and does so substantially faster than the overall conversion of the d_1-isotopomer $[Cp^*_2WH_2D]^+$ to the d_2-isotopomer, $[Cp^*_2WHD_2]^+$, and the d_3-isotopomer, $[Cp^*_2WD_3]^+$, the latter two resulting in an overall decrease in the total intensity of the hydride resonances in the ^1H NMR spectrum.

An additional pathway for the direct *intramolecular* interconversion of the two d_1-isotopomers which does not involve a deprotonation mechanism, is clearly required to accommodate the observed build up of $[Cp^*_2W(H)(H)(D)]^+$.

$$[Cp^*_2W(H)(D)(H)]^+ \rightleftharpoons [Cp^*_2W(H)(H)(D)]^+.$$

A kinetic analysis of these rate data reveals that the intramolecular exchange process for $[Cp^*_2W(H)(D)(H)]^+ \rightarrow [Cp^*_2W(H)(H)(D)]^+$ is approximately an order of magnitude faster than deprotonation.‡ A possible direct pathway for the intramolecular exchange would involve pseudorotation out of the equatorial plane of the bent sandwich structure; however, we are unaware of a precedent for such a process. More likely mechanisms, shown in Scheme 4, include (i) intermediacy of a dihydrogen adduct which rotates, (ii) the intermediacy of a (closed) trihydrogen§ adduct which rotates, and (iii) migration of the hydride ligand to the Cp* ligand to give an η^4-diene intermediate, $[Cp^*(\eta^4\text{-}C_5Me_5H)WHD]^+$, a "Tarzan" type swing over the deuterium, followed by return to the metal centre. Hydride and alkyl group migrations to and from cyclopentadienyl (and arene) ligands have previously been observed and postulated for other reactions.[31] Our data do not allow a distinction between these possibilities.

Syntheses and reactivity of the oxo derivatives $Cp^*_2W{=}O$, $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$, $Cp^*W(=O)_2(OCp^*)$ *and* $Cp^*W(\eta^2\text{-}O_2)(=O)(CH_3)$

In view of the increasing interest in organometallic compounds containing oxo and peroxo ligands,[32] we have explored the reactivity of some of these permethyltungstenocene derivatives with reagents such as water, hydrogen peroxide and dioxygen. Some of this work has been communicated.[33]

(1) *Mono-oxo tungsten derivatives: oxo transfer reactions from tungsten and evidence for* 1,2*-addition and elimination processes.* Access to oxo-derivatives of permethyltungstenocene is provided by the reaction of $Cp^*_2WCl_2$ with $KOH_{(aq)}$ in THF which gives $Cp^*_2W{=}O$ as a deep-green crystalline material (Scheme 5) or, alternatively, by the reaction of $Cp^*_2W(\eta^2\text{-}CH_2O)$ with H_2O.

$$Cp^*_2W(\eta^2\text{-}CH_2O) + H_2O \longrightarrow Cp^*_2W{=}O + CH_3OH.$$

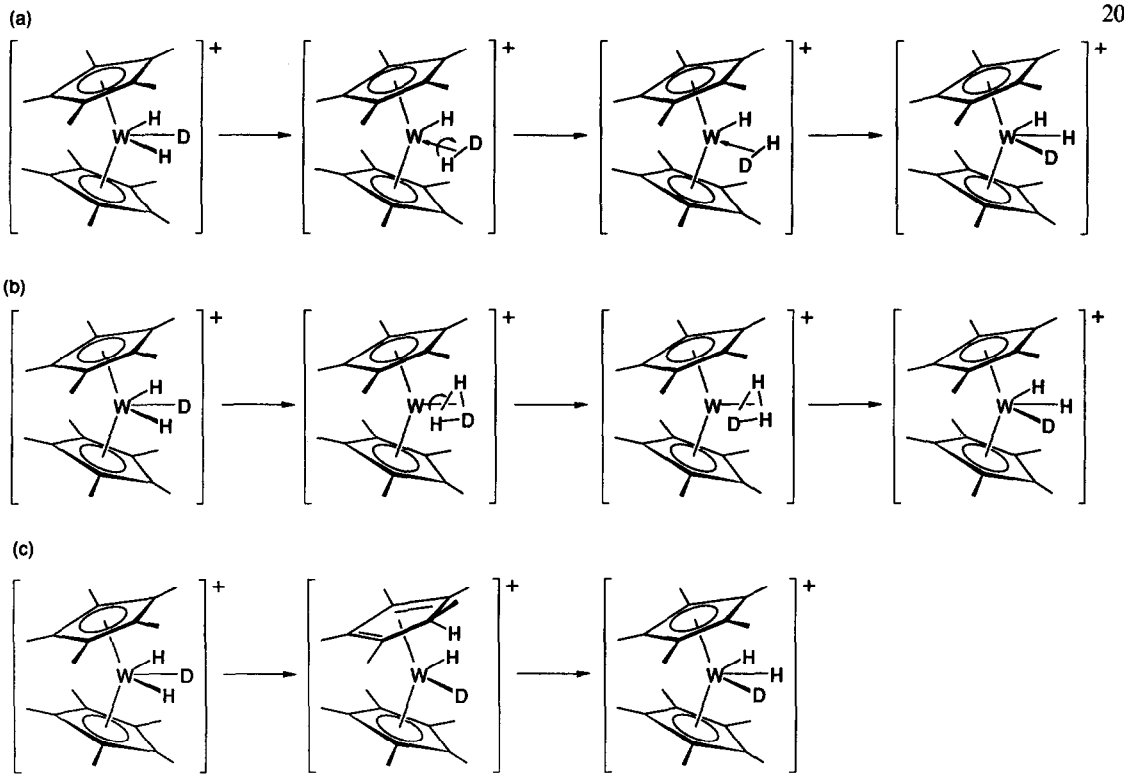
$Cp^*_2W{=}O$ is a member of a relatively rare class of oxo-derivatives in which the metal centre is closed-shell (18-electron) in the absence of oxygen lone-pair donation.¶ We propose to denote these as "class b" M=O derivatives in order to distinguish them from the more common "class a" ($M{=}O \leftrightarrow M^-{\equiv}O^+$) derivatives, for which lone-pair donation from oxygen to the metal centre imparts triple $M^-{\equiv}O^+$ bond character, and hence a stronger bond, obtains. Therefore, it appeared reasonable to consider the possibility that the oxo ligand in $Cp^*_2W{=}O$ could be more weakly bound

† Protonation at the central site is clearly favoured, however, protonation at the lateral site may occur, albeit at a much slower rate.

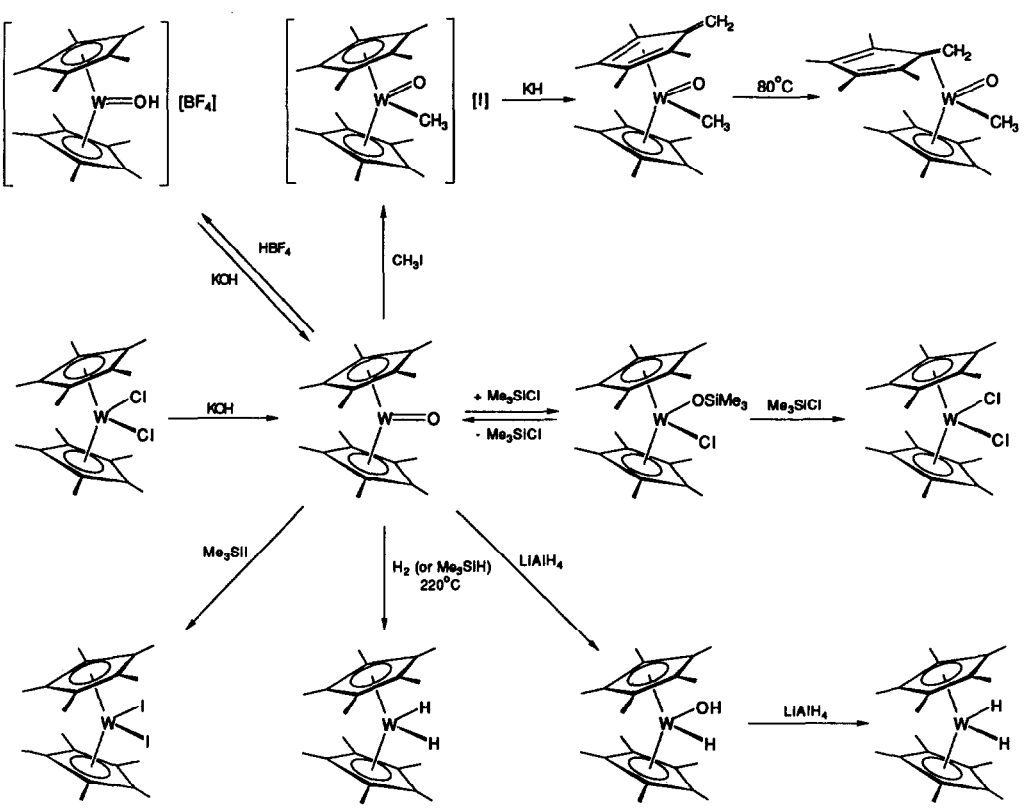
‡ Data were fit using the program "GEAR" [T. Beukelman, J. Chesick, R. J. McKinney and F. J. Weigert, PC Version 1.31 (1987)] and the approximate rate constants obtained are: $[Cp^*_2W(H)(D)(H)]^+ \rightarrow [Cp^*_2WH_2] + D^+$, $k \approx 1.2 \times 10^{-3}$ s^{-1}; $[Cp^*_2W(H)(D)(H)]^+ \rightarrow [Cp^*_2W(H)(H)(D)]^+$, $k \approx 1 \times 10^{-2}$ s^{-1}.

§ Closed trihydrogen species have been studied theoretically to account for the observed exchange processes in bis-dihydrogen complexes.[30]

¶ Other 18-electron oxo-derivatives include $Cp^*_2Ta(=O)R$ (R=H, CH_3), $Cp_2Nb(=O)(CH_3)$, $Cp_2M{=}O$ (M=Mo, W) and $Cp^*Re(=O)_3$.



Scheme 4. Possible intramolecular exchange mechanisms for the rearrangement central d_1-$[Cp_2^*W(H)(D)(H)]^+ \rightarrow$ lateral d_1-$[Cp_2^*W(H)(H)(D)]^+$. (a) Exchange via an η^2-dihydrogen intermediate. (b) Exchange via an η^3-trihydrogen intermediate. (c) Exchange via H (or D) migration to the Cp* ligand.



Scheme 5. Synthesis and reaction chemistry of $Cp_2^*W{=}O$.

than other tungsten oxo ligands and, thus, exceptionally reactive.

The comparatively weak W=O bond is evident from both its spectroscopic features and its chemical reactivity. Thus, $Cp_2^*W{=}O$ is characterized by a strong $\nu(W{=}O)$ in its IR spectrum at 860 cm^{-1} (820 cm^{-1} for $Cp_2^*W{=}^{18}O$) compared with $\nu(M{\equiv}O) \approx 930$–$1000\ cm^{-1}$ for class a. An illustrative comparison of $\nu(M{-}O)$ stretching frequencies is that the 14-electron, class a, derivative, CH_3ReO_3,[34] shows absorptions at 999 and 960 cm^{-1}, almost 100 cm^{-1} higher than those of the 18-electron, class b, derivative, Cp^*ReO_3 (909 and 878 cm^{-1}).[35]

The high reactivity of the oxo ligand in $Cp_2^*W{=}O$ is demonstrated by the oxygen exchange reaction with labelled H_2^*O. A solution of $Cp_2^*W{=}^{18}O$ in pentane undergoes facile isotopic exchange with $H_2{}^{16}O$ giving $Cp_2^*W{=}^{16}O$ within 1 h at room temperature (IR spectroscopy). This reaction presumably proceeds via the dihydroxy derivative, $[Cp_2^*W(^{16}OH)(^{18}OH)]$, which may be envisaged to be formed by the overall 1,2-addition† of the $H^{16}O{-}H$ bond across the $W{=}^{18}O$ double bond. The microscopic chemical reverse, i.e. 1,2-elimination of $H_2{}^{18}O$ from this symmetric intermediate, allows exchange of oxygen atoms to occur.

$$Cp_2^*W{=}^{18}O + H_2{}^{16}O \rightleftharpoons [Cp_2^*W(^{18}OH)(^{16}OH)] \rightleftharpoons Cp_2^*W{=}^{16}O + H_2{}^{18}O.$$

Similarly, treatment of $Cp_2^*W{=}^{16}O$ with excess $H_2{}^{17}O$ (*ca* 50% enriched) results in the formation of $Cp_2^*W{=}^{17}O$ as monitored by ^{17}O NMR spectroscopy (δ 760 ppm in C_6D_6 relative to external $H_2{}^{17}O$).‡ The kinetics of this exchange in THF solution at 25°C have been measured and the second-order rate constant for oxygen exchange is approximately $2(1) \times 10^{-4}\ s^{-1}\ M^{-1}$, larger than representative values reported for anionic and cationic complexes in aqueous solutions.§

Similarly, the isoelectronic, d^0, oxo-derivative, $Cp_2^*Ta(=O)H$, which is a class b oxo-derivative, ($\nu(Ta{=}O) = 850\ cm^{-1}$), undergoes rapid exchange of oxygen atoms with labelled $H_2{}^*O$. For this example, the hydride ligand acts as a second probe to study the exchange reaction. Thus, the isotopomer, $Cp_2^*Ta(=^{18}O)H$, was treated with $D_2{}^{16}O$ and the exchange process was monitored by IR spectroscopy. The results clearly demonstrate that exchange of the oxo ligand occurred for the exclusion of the hydride ligand. This is consistent with the mechanism outlined for the exchange reaction of $Cp_2^*W{=}O$ with H_2O in which a reaction occurs only at the M=O double bond, possibly in a concerted manner.

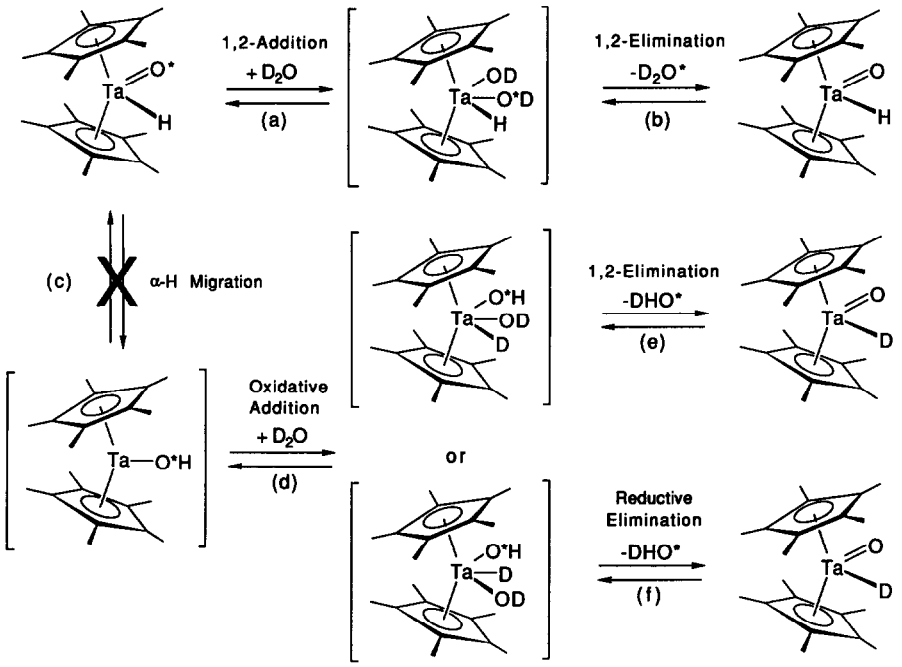
$$Cp_2^*Ta(=^{18}O)H + D_2{}^{16}O \rightleftharpoons [Cp_2^*Ta(^{18}OD)(^{16}OD)H] \rightleftharpoons Cp_2^*Ta(=^{16}O)H + D^{18}OH.$$

The observation of no exchange of deuterium into the tantalum hydride position has two implications: (i) the reaction does not involve an initial α-H migration from Ta to oxygen to generate a 16-electron, $[Cp_2^*Ta{-}OH]$, intermediate which reacts with H_2O by oxidative addition [Scheme 6, steps (c) and (d)], since this mechanism would ultimately lead to the exchange of the tantalum hydride for deuterium. We have noted previously that the α-H migration for $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4Ph)Ta(=O)H$ is much slower (as yet unobserved) than that for the methylidene hydride derivative, $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4Ph)Ta(=CH_2)H$.[38] Accordingly, treatment of $Cp_2^*Ta(=CH_2)H$ with D_2O gives $Cp_2^*Ta(=O)D$ and CH_3D (via oxidative addition of DO—D to $[Cp_2^*TaCH_3]$), and *not* $Cp_2^*Ta(=O)H$ and CH_2D_2. (ii) The dihydroxy–hydride intermediate, $[Cp_2^*Ta(^{18}OD)(^{16}OD)H]$, loses water by a 1,2-elimination pathway [Scheme 6, step (b)] and *not* by reductive elimination. Reductive elimination would generate $[Cp_2^*Ta{-}^{18}OD]$ from which α-D elimination would result in exchange of the tantalum hydride for deuterium. The 1,2-addition/elimination reactions involving HO—H and [Ta=O] are likely encouraged by interaction of the hydrogen with a lone electron pair of the oxo ligand, at least in the early stages of the reaction. Moreover, the 1,2-elimination pathway ensures that the tungsten centre will remain as 18-electron, d^0, throughout the process and does not necessitate the formation

† The terms 1,2-addition and 1,2-elimination are not meant to imply a concerted mechanism, but are only intended to indicate the overall transformation.

‡ Published data on ^{17}O chemical shifts are thus far limited so that no firm conclusions can be presently drawn regarding the ^{17}O chemical shifts for the different classes (a and b) of oxo ligands. For reference, ^{17}O chemical shifts for some other oxo (terminal and bridging) derivatives are given in ref. 36.

§ We are not aware of similar measurements of the rates for oxygen exchange in other *neutral* oxo compounds; however, the ^{18}O exchange kinetics for ionic complexes *in aqueous solution* have been reviewed. Typical second-order rate constants ($\approx$ 25°C, corrected for $[H_2O]$) include: $[ReO_4]^-$, $10^{-8}\ s^{-1}\ M^{-1}$; *trans*-$[Re(en)_2O_2]^+$, $10^{-6}\ s^{-1}\ M^{-1}$; $[WO_4]^{2-}$, $10^{-2}\ s^{-1}\ M^{-1}$. It should be noted that for all these examples the rate laws are complex, and the rates are very pH dependent.[37]



Scheme 6. Possible mechanisms for the exchange of the oxo ligand in $Cp_2^*Ta(=^{18}O)H$ with D_2O.

of the high energy 16-electron, d^2, intermediate, $[Cp_2^*Ta—OH]$. A reaction which follows the same pathway, i.e. 1,2-addition/elimination, is the hydrolysis of $Cp_2^*Ta(=NC_6H_5)H$ with D_2O, which gives $Cp_2^*Ta(=O)H$, not $Cp_2^*Ta(=O)D$ (^1H NMR spectroscopy).

$$Cp_2^*Ta(=NC_6H_5)H + D_2O \longrightarrow Cp_2^*Ta(=O)H + C_6H_5ND_2.$$

An observation of relevance to these oxo exchange reactions is provided by the reaction of $Cp_2^*W=O$ with Me_3SiCl. The initial product is $Cp_2^*W(OSiMe_3)Cl$ which is formed via a 1,2-addition of the Si—Cl bond across the W=O double bond.

$$Cp_2^*W=O + Me_3SiCl \rightleftharpoons Cp_2^*W(OSiMe_3)Cl \longrightarrow 0.5Cp_2^*W=O + 0.5Cp_2^*WCl_2 + 0.5(Me_3Si)_2O.$$

$Cp_2^*W(OSiMe_3)Cl$ reacts further with Me_3SiCl giving $Cp_2^*WCl_2$ and $(Me_3Si)_2O$. Furthermore, the 1,2-addition of a Si—Cl bond across the W=O double bond is reversible, as for the reaction of $Cp_2^*W=O$ with $H_2{}^*O$. Thus, the reaction of $Cp_2^*W=O$ with Me_3SiCl (are equivalent) gives initially an equilibrium mixture with $Cp_2^*W(OSiMe_3)Cl$ which subsequently decomposes with the elimination of $(Me_3Si)_2O$ to form $Cp_2^*WCl_2$ (0.5 equivalent) and $Cp_2^*W=O$ (0.5 equivalent).† In a similar fashion, the reaction of $Cp_2^*W=O$ with Me_3SiI can be used to prepare $Cp_2^*WI_2$.

The exceptional reactivity of $Cp_2^*W=O$ is also illustrated by its reduction to $Cp_2^*WH_2$ by either H_2 or Me_3SiH, although the conditions are rather forcing (*ca* 200°C). This reduction can be achieved more readily by reaction with $LiAlH_4$, in which the hydroxy–hydride derivative, $Cp_2^*W(H)(OH)$, may be isolated as the first-formed product. This reduction of $Cp_2^*W=O$ to the hydroxy hydride derivative, $Cp_2^*W(OH)H$ illustrates the similarity of this W=O double bond with the C=O double bond in ketones and aldehydes. Further similarities are that (i) both dihydroxy derivatives, $[Cp_2^*W(OH)_2]$ and $[R_2C(OH)_2]$, are unstable with respect to elimination of water and formation of the X=O (X = Cp_2^*W, R_2C) double bond, and (ii) as for ketones and aldehydes, $Cp_2^*W=O$ reacts with the glycol, $(CH_2OH)_2$ to form the glycolate, $Cp_2^*W(\eta^2\text{-}O,O—OCH_2CH_2O)$.‡

† This reaction is somewhat more complicated, since variable, small quantities, of a silicon product (at present unidentified, but possibly Me_6Si_2), other than $(Me_3Si)_2O$ are formed.

‡ $Cp_2^*W(OCH_2CH_2O)$ has not been isolated and has only been characterized by ^1H NMR data (in C_6D_6): δ 1.83 (s, Cp*), δ 3.07 (—OCH_2CH_2O—).

In addition to these reactions which result in oxygen atom transfer from tungsten, $Cp^*_2W{=}O$ has also proved to be a valuable starting material for other oxo derivatives of (pentamethylcyclopentadienyl)tungsten as illustrated in Scheme 5. $Cp^*_2W{=}O$ reacts with HBF_4 to generate the ionic species $[Cp^*_2W{=}OH][BF_4]$. The reaction is reversible and treatment with KOH regenerates $Cp^*_2W{=}O$. $Cp^*_2W{=}O$ also reacts with MeI to give an ionic derivative, $[Cp^*_2W(=O)CH_3][I]$, which is characterized by $\nu(W{=}O) = 868\ cm^{-1}$, similar to that of $Cp^*_2W{=}O$ ($\nu(W{=}O) = 860\ cm^{-1}$). However, it is interesting to note that in contrast to the reactions of $Cp^*_2W{=}O$ with Me_3SiCl and HBF_4, nucleophilic attack at CH_3I occurs by the d^2 tungsten centre, not the oxygen ligand. In addition, this reaction with CH_3I is not reversible. Thus, the d_3-derivative, $[Cp^*_2W(=O)CD_3][I]$, does not undergo exchange of methyl groups when treated with CH_3I.

$$[Cp^*_2W(=O)CD_3][I] + CH_3I \not\rightarrow [Cp^*_2W(=O)CH_3][I] + CD_3I.$$

Furthermore, the isoelectronic tantalum derivative, $Cp^*_2Ta(=O)H$, does not react under similar conditions with MeI since the metal centre is d^0 and no longer nucleophilic.[39]

A suspension of $[Cp^*_2W(=O)CH_3][I]$ in THF is readily deprotonated by KH. The initial product is the η^4-1,2,3,4-tetramethylfulvene derivative, $Cp^*(\eta^4\text{-}C_5Me_4{=}CH_2)W(=O)(CH_3)$, obtained by deprotonation of the methyl group of the Cp* ligand as opposed to the W—CH_3 group. The uncoordinated *exo*-$(CH_3C)_4C{=}CH_2$ double bond of the η^4-1,2,3,4-tetramethylfulvene ligand is characterized by a strong absorption at 1600 cm^{-1} in the IR spectrum and resonances in the ^{13}C NMR spectrum at δ 163.0 and 102.2 ppm, assignable to $\eta^4\text{-}(CH_3C)_4C{=}CH_2$ and $\eta^4\text{-}(CH_3C)_4C{=}CH_2$, respectively, only slightly shifted from the free ligand values of δ 155.4 and 109.8, respectively. This η^4-derivative undergoes isomerization to the η^2-*exo*-$CH_2{=}C_5Me_4$ derivative, $Cp^*(\eta^2\text{-}CH_2{=}C_5Me_4)W(=O)(CH_3)$, at 80°C. An analogous η^2-*exo*-$CH_2{=}C_5Me_4$ derivative, $Pd(\eta^2\text{-}CH_2{=}C_5Me_4)(PMe_3)_2$, has recently been reported and its X-ray crystal structure determined.[40] The ^{13}C NMR data for $Cp^*(\eta^2\text{-}CH_2{=}C_5Me_4)W(=O)CH_3$ provide strong evidence for η^2-coordination of the tetramethylfulvene ligand: the resonances assignable to the $(\eta^2\text{-}CH_2{=}C_5Me_4)$ ligand of $Pd(\eta^2\text{-}CH_2{=}C_5Me_4)(PMe_3)_2$ and $Cp^*(\eta^2\text{-}CH_2{=}C_5Me_4)W(=O)CH_3$ are similar (Table 2) and are significantly different from both the η^4-derivative, $Cp^*(\eta^4\text{-}C_5Me_4{=}CH_2)W(=O)CH_3$ and the free ligand, $C_5Me_4{=}CH_2$. Notably, the $\{CH_2{=}C_5Me_4\}$ methylene carbon atom is observed at δ 40.1 (in C_6D_6) for $Cp^*(\eta^2\text{-}CH_2{=}C_5Me_4)W(=O)CH_3$ and at 35.8–43.6 (in $(CD_3)_2CO$) for $Pd(\eta^2\text{-}CH_2{=}C_5Me_4)L_2$ (L = PMe_3, PEt_3, P $(OMe)_3$], whereas for the η^4-derivative, $Cp^*(\eta^4\text{-}C_5Me_4{=}CH_2)W(=O)(CH_3)$, and the free ligand, $CH_2{=}C_5Me_4$, the methylene carbon atom is observed to be approximately 60 ppm to lower field at δ 102.2 and 109.8 (in C_6D_6), respectively. Furthermore, the uncoordinated ring carbon atoms, $\{(MeC)_4C{=}CH_2\}$, of $Cp^*(\eta^2\text{-}CH_2{=}C_5Me_4)W(=O)CH_3$, δ 129.7–135.2, are only slightly shifted from the values of the free ligand, δ 123.7–138.7.

Deprotonation of the d_3-isotopomer, $[Cp^*_2W(=O)CD_3][I]$, gives $Cp^*(\eta^4\text{-}C_5Me_4{=}CH_2)W(=O)CD_3$ and upon heating, $Cp^*(\eta^2\text{-}CH_2{=}C_5Me_4)W(=O)CD_3$, providing evidence that the reaction does not proceed via initial deprotonation of the W—CH_3 group followed by a rearrangement.

(2) *Dioxo derivatives: the formation of η^1-pentamethylcyclopentadienyl derivative.* The dioxo derivative, $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$, is obtained by the reaction of $Cp^*_2W{=}O$ with the oxo-transfer reagents, $H_2O_{2(aq)}$ or Me_3CO_2H (Scheme 7). $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$ is also formed by the reaction of $Cp^*_2WH_2$ with $H_2O_{2(aq)}$.

$$Cp^*_2WH_2 \xrightarrow{H_2O_{2(aq)}} (\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2.$$

Interestingly, this compound does not react with excess H_2O_2 to give the peroxo derivative, $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)$, in contrast to the reaction of $Cp^*W(=O)_2CH_3$ with H_2O_2 which gives $Cp^*W(=O)(\eta^2\text{-}O_2)CH_3$.[41] $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$ has been structurally characterized by X-ray diffraction techniques (Fig. 3).[47]

Although compounds of the type $(\eta^5\text{-}C_5R_5)W(=O)_2(R')$ have recently been characterized by X-ray diffraction,[43] the principal interest in the structure of $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$ arises from the bonding modes of the pentamethylcyclopentadienyl ligands. In particular, one of these ligands adopts a *monohapto*, $(\eta^1\text{-}C_5Me_5)$, bonding mode. Where *monohapto* bonding modes are now common for C_5H_5 ligands,[44] the η^1-bonding mode of one of the pentamethylcyclopentadienyl ligands in $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$ represents the first example of a transition metal-coordinated η^1-Cp* ligand. The other pentamethylcyclopentadienyl ligand, while being bonded in a *pentahapto*, $(\eta^5\text{-}C_5Me_5)$, manner is, however, asymmetric with the ligand being displaced in the direction of the oxo ligands so that the structure is more aptly described as $(\eta^1,\eta^4\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$ (*vide infra*).

Table 1. ^{1}H NMR data[a]

Assignment	δ (ppm)	Coupling (Hz)
$Cp^*_2WCl_2$		
η^5-$C_5(CH_3)_5$	1.68	s
$Cp^*_2WI_2$		
η^5-$C_5(CH_3)_5$	1.97	s
$Cp^*(\eta^5$-$C_5Me_4CH_2CH_2CH_3)WCl_2$		
η^5-$C_5(CH_3)_5$	1.70	s
η^5-$C_5(CH_3)_4(CH_2CH_2CH_3)$		
2(CH_3)	1.80	s
2(CH_3)	1.69	s
η^5-$C_5(CH_3)_4(CH_2CH_2CH_3)$	1.96	m
η^5-$C_5(CH_3)_4(CH_2CH_2CH_3)$	1.34	m
η^5-$C_5(CH_3)_4(CH_2CH_2CH_3)$	0.83	t, $^3J_{H-H} = 7.3$
$Cp^*_2W(H)Cl$		
η^5-$C_5(CH_3)_5$	1.81	s
W—*H*	−11.91	s, $^1J_{W-H} = 97$
$Cp^*_2W(\eta^2$-$CH_2O)$		
η^5-$C_5(CH_3)_5$	1.72	s
η^2-CH_2O	2.01	s[b]
$Cp^*(\eta^5,\eta^1$-$C_5Me_4CH_2)WH$		
η^5-$C_5(CH_3)_5$	1.86	s
η^5,η^1-$C_5(CH_3)_4CH_2$		
1(CH_3)	2.21	d, $J_{H-W(H)} = 3$
1(CH_3)	2.01	s
1(CH_3)	1.59	s
1(CH_3)	1.52	s
η^5,η^1-$C_5(CH_3)_4CH_2$		
1H	3.50	t, $^2J_{H-H} = 2$
1H	3.13	m
W—*H*	−11.94	s (broad), $^1J_{W-H} = 93$
$Cp^*_2W(CH_3)_2$		
η^5-$C_5(CH_3)_5$	1.51	s
$W(CH_3)_2$	−0.54	s
$Cp^*_2W(CH_3)Cl$		
η^5-$C_5(CH_3)_5$	1.60	s
W—CH_3	−0.09	s
$Cp^*_2W(CH_3)H$		
η^5-$C_5(CH_3)_5$	1.76	s
W—CH_3	−0.16	s
W—*H*	−10.86	s, $^1J_{W-H} = 105$
$Cp^*_2W(CH_2C_6H_5)(H)$		
η^5-$C_5(CH_3)_5$	1.72	s
W—CH_2Ph	2.32	s
W—$CH_2C_6H_5$		
1H(*para*)	7.07	t, $^3J_{H-H} = 7.5$
2H(*meta*)	7.25	t, $^3J_{H-H} = 7.5$
2H(*ortho*)	7.49	d, $^3J_{H-H} = 7.5$
W—*H*	−11.09	s, $^1J_{W-H} = 100$

(*continued*)

Table 1 (*continued*)

	Assignment	δ (ppm)	Coupling (Hz)
$Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)W(CH_3)$			
	$\eta^5\text{-}C_5(CH_3)_5$	1.65	s
	$\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2$		
	$1(CH_3)$	1.68	s
	$1(CH_3)$	1.64	s
	$1(CH_3)$	1.56	s
	$1(CH_3)$	1.52	s
	$\eta^5,\eta^1\text{-}C_5(CH_3)_4CH_2$		
	1H	3.39	d, $^2J_{H-H} = 2$
	1H	2.59	d, $^2J_{H-H} = 2$
	$W—CH_3$	−0.63	s
$[Cp_2^*WH_3][BF_4]$			
D_2O	$\eta^5\text{-}C_5(CH_3)_5$	2.03	s
	1 W—*H* (central)	−4.50	t, $^2J_{H-H} = 3$, $^1J_{W-H} = 66$
	2 W—*H* (lateral)	−5.42	d, $^2J_{H-H} = 3$, $^1J_{W-H} = 57$
$(CD_3)_2CO$	$\eta^5\text{-}C_5(CH_3)_5$	2.25	s
	1 W—*H* (central)	−4.21	t, $^2J_{H-H} = 3$, $^1J_{W-H} = 66$
	2 W—*H* (lateral)	−5.19	d, $^2J_{H-H} = 3$, $^1J_{W-H} = 57$
Isotopic shifts:			
	W—*H* of $[Cp_2^*W(H)(H)(H)]^+$	−4.21	t, $^2J_{H-H} = 3$
	W—*H* of $[Cp_2^*W(H)(H)(D)]^+$	−4.25	d, $^2J_{H-H} = 3$
	W—*H* of $[Cp_2^*W(D)(H)(D)]^+$	−4.30	s
$[Cp_2^*WH_3][BPh_4]$			
$CDCl_3$	$\eta^5\text{-}C_5(CH_3)_5$	2.09	s
	1 W—*H* (central)	−4.20	t, $^2J_{H-H} = 3$, $^1J_{W-H} = 69$
	2 W—*H* (lateral)	−5.34	d, $^2J_{H-H} = 3$, $^1J_{W-H} = 57$
	$[BPh_4]$		
	ortho	7.43	s (broad)
	meta	7.03	t, $^3J_{H-H} = 7$
	para	6.88	t, $^3J_{H-H} = 7$
$Cp_2^*W{=}O$			
	$\eta^5\text{-}C_5(CH_3)_5$	1.87	s
$[Cp_2^*W(=O)(CH_3)][I]$			
D_2O	$\eta^5\text{-}C_5(CH_3)_5$	1.94	s
	$W—CH_3$	0.94	s
$CDCl_3$	$\eta^5\text{-}C_5(CH_3)_5$	2.13	s
	$W—CH_3$	1.07	s
$Cp_2^*W(OH)H$			
	$\eta^5\text{-}C_5(CH_3)_5$	1.81	s
	W—*H*	−11.08	s, $^2J_{W-H} = 114$
	W—O*H*[c]		
$[Cp_2^*W(=OH)][BF_4]$			
D_2O	$\eta^5\text{-}C_5(CH_3)_5$	1.88	s
	W=O*H*[c]		
$Cp_2^*W(OSiMe_3)Cl$			
	$\eta^5\text{-}C_5(CH_3)_5$	1.71	s
	$W—OSi(CH_3)_3$	0.45	s
$(\eta^1\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_5)W(=O)_2$			
C_6D_6, 25°C	$\eta^5\text{-}C_5(CH_3)_5$	1.80	s

(*continued*)

Table 1 (*continued*)

	Assignment	δ (ppm)	Coupling (Hz)
C_7D_8, 25°C	η^5-$C_5(CH_3)_5$	1.80	s
C_7D_8, −90°C	η^5-$C_5(CH_3)_5$	1.52	s
	η^1-$C_5(CH_3)_5$		
	$1(CH_3)$	2.56	s
	$2(CH_3)$	2.00	s
	$2(CH_3)$	1.92	s
$(\eta^5$-$C_5Me_5)W(=O)_2(OC_5Me_5)$			
	η^5-$C_5(CH_3)_5$	1.85	s
	η^1-$C_5(CH_3)_5$		
	$1(CH_3)$	1.40	s
	$2(CH_3)$	1.62	q, partially resolved, $^5J_{C-H} = 1$
	$2(CH_3)$	1.78	q, partially resolved, $^5J_{C-H} = 1$
$Cp^*W(\eta^4$-$C_5Me_4{=}CH_2)W(=O)(CH_3)$			
	η^5-$C_5(CH_3)_5$	1.57	s
	η^4-$C_5(CH_3)_4{=}CH_2$	2.83	s
		2.59	s
		1.47	s
		1.55	s
	η^4-$C_5(CH_3)_4{=}CH_2$	4.54	s
		4.40	s
	$W-CH_3$	1.44	s[d]
$Cp^*W(\eta^2$-$C_5Me_4{=}CH_2)W(=O)(CH_3)$			
	η^5-$C_5(CH_3)_5$	1.56	s
	η^4-$C_5(CH_3)_4{=}CH_2$	2.55	s
		2.33	s
		1.97	s
		0.89	s
	η^2-$C_5(CH_3)_4{=}CH_2$	3.48	d, $^2J_{H-H} = 9$
		1.57	d,[e] $^2J_{H-H} = 9$
	$W-CH_3$	0.60	s[d]

[a] In C_6D_6 unless specified otherwise.
[b] Assignment tentative.
[c] Not located.
[d] Identified by preparation of the d_3-methyl derivative.
[e] Located by irradiation at δ 3.48 ppm.

Interestingly, at room temperature the resonances due to the Cp* ligands of $(\eta^5$-$C_5Me_5)(\eta^1$-$C_5Me_5)W(=O)_2$ are equivalent in the ^1H NMR spectrum. However, cooling to −90°C freezes out the solid-state structure. The data accumulated from the ^1H NMR variable temperature experiments are shown in Fig. 4. The studies suggest that the exchange process proceeds via η^1–η^5 ligand exchange and that 1,2-sigmatropic shifts of the η^1-C_5Me_5 ligand do not occur on a significantly faster timescale. An approximate barrier for this rearrangement process is 10(1) kcal mol^{-1} at −60°C.

The IR spectrum of $(\eta^5$-$C_5Me_5)(\eta^1$-$C_5Me_5)W(=O)_2$ is characterized by two W=O stretches, $\nu(WO_2)_{sym} = 895\ cm^{-1}$ and $\nu(WO_2)_{asym} = 935\ cm^{-1}$ [Fig. 5(a)]. The IR spectrum of the isotopomer. $(\eta^5$-$C_5Me_5)(\eta^1$-$C_5Me_5)W(=^{18}O)(=^{16}O)$ [Fig. 5(b)] shows two bands assigned to the W=O vibrations with $\nu(W^{16}O^{18}O)_{sym} = 860\ cm^{-1}$ and $\nu(W^{16}O^{18}O)_{asym} = 920\ cm^{-1}$. The difference in the symmetric and asymmetric stretches of the $(\eta^5$-$C_5Me_5)(\eta^1$-$C_5Me_5)W(=^{18}O)(=^{16}O)$ and $(\eta^5$-$C_5Me_5)(\eta^1$-$C_5Me_5)W(=^{16}O)_2$ isotopomers are $\Delta\nu_{sym} = 35\ cm^{-1}$ and $\Delta\nu_{asym} = 15\ cm^{-1}$. This difference of the shifts of the symmetric and asym-

Table 2. ^{13}C NMR data[a]

Assignment	δ (ppm)	Coupling (Hz)
$Cp^*_2WCl_2$		
η^5-$C_5(CH_3)_5$	11.6	q, $^1J_{C-H} = 128$
η^5-$C_5(CH_3)_5$	105.1	s
$Cp^*(\eta^5$-$C_5Me_4CH_2CH_2CH_3)WCl_2$		
η^5-$C_5(CH_3)_5$	11.4	q, $^1J_{C-H} = 128$
η^5-$C_5(CH_3)_5$	105.3	s
η^5-$C_5(CH_3)_4(CH_2CH_2CH_3)$		
2C	11.7	q, $^1J_{C-H} = 128$
2C	11.8	q, $^1J_{C-H} = 128$
η^5-$C_5(CH_3)_4(CH_2CH_2CH_3)$		
2C	103.8	s
1C	106.2	s
2C	107.6	s
η^5-$C_5(CH_3)_4(CH_2CH_2CH_3)$		
1C	24.4	t, $^1J_{C-H} = 126$
1C	28.6	t, $^1J_{C-H} = 130$
η^5-$C_5(CH_3)_4(CH_2CH_2CH_3)$	14.7	q, $^1J_{C-H} = 126$
$Cp^*_2W(H)Cl$		
η^5-$C_5(CH_3)_5$	12.1	q, $^1J_{C-H} = 127$
η^5-$C_5(CH_3)_5$	97.7	s
$Cp^*_2W(\eta^2$-$CH_2O)$		
η^5-$C_5(CH_3)_5$	11.3	q, $^1J_{C-H} = 127$
η^5-$C_5(CH_3)_5$	95.9	s
η^2-CH_2O	45.3	t, $^1J_{C-H} = 159$
$Cp^*(\eta^5,\eta^1$-$C_5Me_4CH_2)WH$		
η^5-$C_5(CH_3)_5$	12.2	
η^5-$C_5(CH_3)_5$	92.2	
η^5,η^1-$C_5(CH_3)_4CH_2$		
1(CH_3)	9.3	
1(CH_3)	10.0	
1(CH_3)	12.6	
1(CH_3)	15.1	
η^5,η^1-$C_5(CH_3)_4CH_2$		
1C	86.1	
1C	87.9	
1C	91.8	
1C	96.8	
1C	109.4	
η^5,η^1-$C_5(CH_3)_4CH_2$	36.1	
$Cp^*_2W(CH_3)_2$		
η^5-$C_5(CH_3)_5$	10.2	q, $^1J_{C-H} = 127$
η^5-$C_5(CH_3)_5$	93.6	s
$W(CH_3)_2$	−6.9	q, $^1J_{C-H} = 123$ $^1J_{W-C} = 76$
$Cp^*_2W(CH_3)Cl$		
η^5-$C_5(CH_3)_5$	10.8	q, $^1J_{C-H} = 127$
η^5-$C_5(CH_3)_5$	99.3	s
W—CH_3	−8.3	q, $^1J_{C-H} = 125$
$Cp^*_2W(CH_3)H$		
η^5-$C_5(CH_3)_5$	11.2	q, $^1J_{C-H} = 127$
η^5-$C_5(CH_3)_5$	91.9	s

(*continued*)

Table 2 (*continued*)

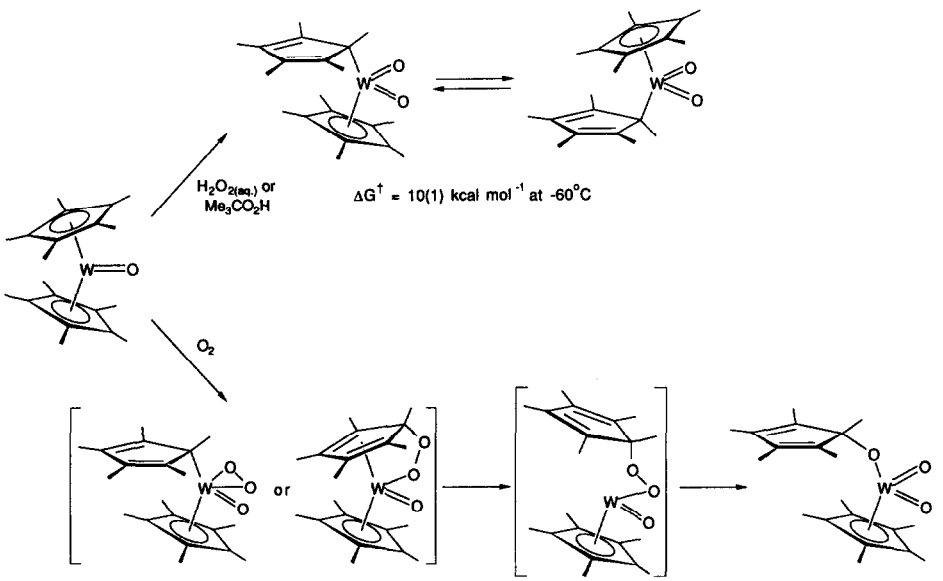
	Assignment	δ (ppm)	Coupling (Hz)
	W—CH_3	−22.1	dq, $^1J_{C-H}$(q) = 123, $^2J_{C-W(H)}$(d) = 7, $^1J_{W-C}$ = 67
$Cp^*_2W(CH_2C_6H_5)(H)$			
	η^5-$C_5(CH_3)_5$	11.4	q, $^1J_{C-H}$ = 127
	η^5-$C_5(CH_3)_5$	92.9	s
	W—CH_2Ph	4.2	t, $^1J_{C-H}$ = 122
	W—$CH_2C_6H_5$		
	1C(*ipso*)	153.5	s
	2C(*ortho*)	126.7	dd, $^1J_{C-H}$ = 156, $^4J_{C-H}$ = 7
	2C(*meta*)	134.0	d, $^1J_{C-H}$ = 155
	1C(*para*)	122.7	dt, $^1J_{C-H}$(d) = 160, $^3J_{C-H}$(t) = 8
$[Cp^*_2WH_3][X]$[b]			
	η^5-$C_5(CH_3)_5$	10.3	q, $^1J_{C-H}$ = 129
	η^5-$C_5(CH_3)_5$	102.2	s
$Cp^*_2W{=}O$			
	η^5-$C_5(CH_3)_5$	13.6	q, $^1J_{C-H}$ = 127
	η^5-$C_5(CH_3)_5$	107.6	s
$[Cp^*_2W(=O)(CH_3)][I]$			
$CDCl_3$	η^5-$C_5(CH_3)_5$	11.4	q, $^1J_{C-H}$ = 127
	η^5-$C_5(CH_3)_5$	121.8	s
	W—CH_3	17.9	q, $^1J_{C-H}$ = 134
$Cp^*_2W(OH)H$			
	η^5-$C_5(CH_3)_5$	11.3	q, $^1J_{C-H}$ = 127
	η^5-$C_5(CH_3)_5$	93.0	s
$(\eta^1$-$C_5Me_5)(\eta^5$-$C_5Me_5)W(=O)_2$			
C_7D_8, 25°C	η^5-$C_5(CH_3)_5$	12.8	Broad (fluxional)
	η^5-$C_5(CH_3)_5$[c]		
C_7D_8, −90°C	η^5-$C_5(CH_3)_5$	10.1	q
	η^5-$C_5(CH_3)_5$	117.4	s
	η^1-$C_5(CH_3)_5$		
	2C	11.2	q
	2C	12.5	q
	1C	30.5	q
	η^1-$C_5(CH_3)_5$		
	1C	83.3	s
	2C	134.0	s
	2C[d]		
$(\eta^5$-$C_5Me_5)W(=O)_2(OC_5Me_5)$			
	η^5-$C_5(CH_3)_5$	11.0	q, $^1J_{C-H}$ = 127
	η^5-$C_5(CH_3)_5$	118.5	s
	η^1-$C_5(CH_3)_5$		
	1(CH_3)	23.9	q, $^1J_{C-H}$ = 127
	2(CH_3)	10.2	q, $^1J_{C-H}$ = 125
	2(CH_3)	11.4	q, $^1J_{C-H}$ = 125
	η^1-$C_5(CH_3)_5$		
	1C	93.4	s
	2C	134.7	s
	2C	137.3	s

(*continued*)

Table 2 (*continued*)

Assignment	δ (ppm)	Coupling (Hz)
$Cp^*W(\eta^4\text{-}C_5Me_4{=}CH_2)W(=O)(CH_3)$		
$\eta^5\text{-}C_5(CH_3)_5$	8.9	q, $^1J_{C-H} = 128$
$\eta^5\text{-}C_5(CH_3)_5$	112.7	s
$\eta^4\text{-}C_5(CH_3)_4{=}CH_2$	24.6	q, $^1J_{C-H} = 126$
	19.4	q, $^1J_{C-H} = 126$
	13.8	q, $^1J_{C-H} = 128$
	10.2	q, $^1J_{C-H} = 128$
$\eta^4\text{-}C_5(CH_3)_4{=}CH_2$	163.0	s
	144.7	s
	129.8	s
	84.7	s
	62.9	s
$\eta^4\text{-}C_5(CH_3)_4{=}CH_2$	102.2	t, $^1J_{C-H} = 156$
$W{-}CH_3$	15.2	q, $^1J_{C-H} = 125$
$Cp^*W(\eta^2\text{-}C_5Me_4{=}CH_2)W(=O)(CH_3)$		
$\eta^5\text{-}C_5(CH_3)_5$	10.4	q, $^1J_{C-H} = 128$
$\eta^5\text{-}C_5(CH_3)_5$	111.6	s
$\eta^4\text{-}C_5(CH_3)_4{=}CH_2$	11.8	q, $^1J_{C-H} = 126$
	11.2	q, $^1J_{C-H} = 126$
	10.6	q, $^1J_{C-H} = 126$
	9.6	q, $^1J_{C-H} = 126$
$\eta^4\text{-}C_5(CH_3)_4{=}CH_2$	135.2	s
	133.7	s
	129.9	s
	129.7	s
	84.4	s
$\eta^4\text{-}C_5(CH_3)_4{=}CH_2$	40.1	t, $^1J_{C-H} = 149$
$W{-}CH_3$	20.9	q, $^1J_{C-H} = 127$

[a] In C_6D_6 unless specified otherwise.
[b] In dilute $DCl_{(aq)}$.
[c] Not observed due to fluxionality.
[d] Obscured by solvent.



Scheme 7. The formation of dioxo derivatives from $Cp^*_2W{=}O$.

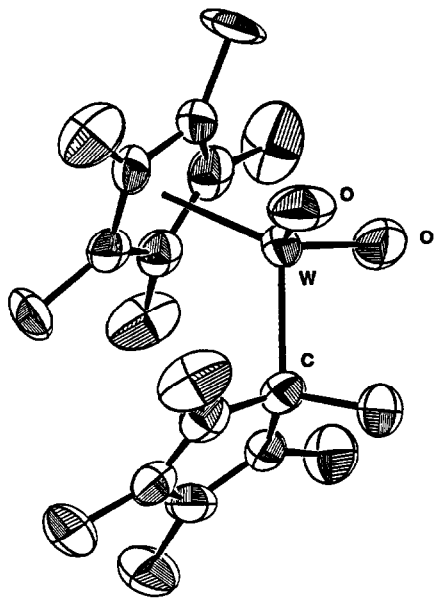


Fig. 3. The molecule structure of $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$.

metric vibrations is to be expected because of the different contributions of the tungsten motion to the symmetric and asymmetric vibrations. Essentially, the symmetric stretch corresponds more to the motion of the oxo ligands than does the asymmetric stretch, which has a significant contribution from the motion of the tungsten atom. Thus, the motion of the tungsten atom in the asymmetric vibration diminishes the effect of isotopic substitution of the oxo ligands and results in a shift of only 15 cm^{-1}, compared with 35 cm^{-1} for the symmetric stretch.

The reaction of $Cp_2^*W{=}{}^{18}O$ with $H_2O_{2(aq)}$ results in the formation of an approximately 2:1 mixture of the isotopomers $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=^{18}O)(=^{16}O)$ and $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=^{16}O)_2$. Other studies on the reactions of transition metal derivatives with $H_2O_{2(aq)}$[45] have shown that the products are often η^2-peroxo, $[M]\text{-}(\eta^2\text{-}O_2)$, derivatives obtained via a metathesis reaction. Thus, it was considered that the reaction of $Cp_2^*W{=}O$ with H_2O_2 may have proceeded via an η^2-peroxo intermediate, $[Cp_2^*W(\eta^2\text{-}O_2)]$, which ring-opened to give the dioxo derivative, i.e.

$$Cp_2^*W{=}{}^*O \xrightarrow[-H_2{}^*O]{H_2O_2} [Cp_2^*W(\eta^2\text{-}O_2)] \longrightarrow (\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2.$$

If this mechanism were correct, then the product of $Cp_2^*W{=}{}^{18}O$ and $H_2{}^{16}O_{2(aq)}$ would be exclu-

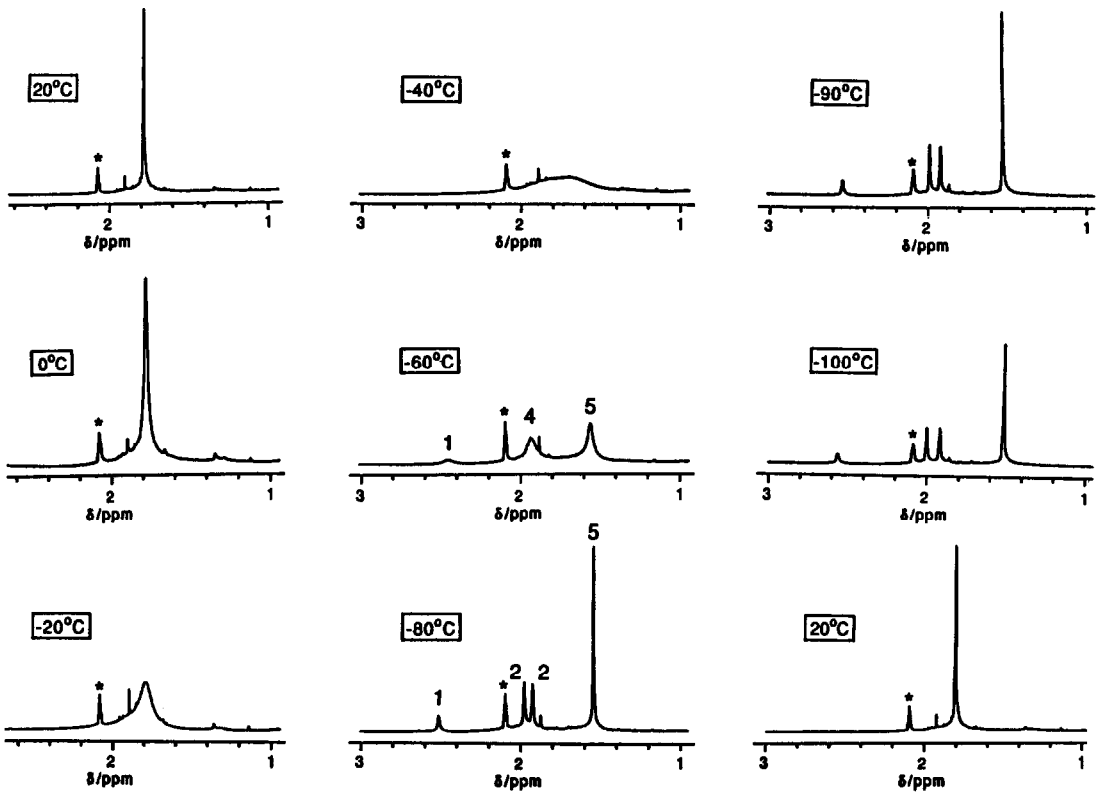


Fig. 4. Variable temperature ^1H NMR spectra of $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$ in d_8-toluene (* denotes residual protio solvent; numbers above peaks indicate the respective number of methyl groups).

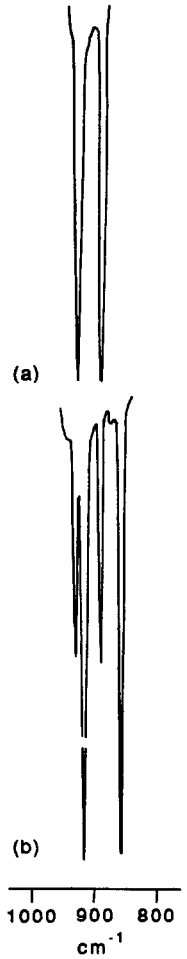


Fig. 5. IR absorptions of the W=O ligands in (a) (η^5-C_5Me_5)(η^1-C_5Me_5)W(=^{16}O)$_2$ and (b) a 2:1 mixture of (η^5-C_5Me_5)(η^1-C_5Me_5)W(=^{16}O)(=^{18}O) and (η^5-C_5Me_5)(η^1-C_5Me_5)W(=^{16}O)$_2$.

sively the isotopomer (η^5-C_5Me_5)(η^1-C_5Me_5)W(=^{16}O)$_2$. However, as described above, the reaction of Cp^*_2W=^{18}O with $H_2{}^{16}O_{2(aq)}$ results in the formation of an approximately 2:1 mixture of the isotopomers (η^5-C_5Me_5)(η^1-C_5Me_5)W(=^{18}O)(=^{16}O) and (η^5-C_5Me_5)(η^1-C_5Me_5)W(=^{16}O)$_2$. The presence of (η^5-C_5Me_5)(η^1-C_5Me_5)W(=^{18}O)(=^{16}O) demonstrates conclusively that the reaction does not proceed via an η^2-peroxo intermediate, Cp^*_2W(η^2-O_2), in which the η^2-peroxo ligand is derived from H_2O_2.

Since Cp^*_2W=O also reacts with Me_3CO_2H to yield (η^5-C_5Me_5)(η^1-C_5Me_5)W(=O)$_2$ (and Me_3COH), a reaction involving Cp^*_2W(OH)(OOR) (R = H, CMe_3), which subsequently eliminates ROH, seems likely. This mechanism would be expected to give only (η^5-C_5Me_5)(η^1-C_5Me_5)W(=^{16}O)(=^{18}O). The origin of *ca* 33% of (η^5-C_5Me_5)(η^1-C_5Me_5)W(=^{16}O)$_2$ may arise from either prior exchange of Cp^*_2W=^{18}O with $H_2{}^{16}O$, or may signal an alternate reaction pathway in which the 2:1 ratio results from decomposition of some intermediate containing three exchangeable oxygen atoms, e.g.

$$Cp^*(\eta^1\text{-}Cp^*)W(^*OH)(OH)(=O) \rightleftharpoons Cp^*(\eta^1\text{-}Cp^*)W(^*OH)(=O)(OH) \rightleftharpoons Cp^*(\eta^1\text{-}Cp^*)W(=^*O)(OH)(OH).$$

We note that (η^5-C_5Me_5)(η^1-C_5Me_5)W(=O)$_2$ does not undergo facile oxygen exchange with labelled $H_2{}^*O$, in contrast to that observed for the mono-oxo derivative, Cp^*_2W=O. Since (η^5-C_5Me_5)(η^1-C_5Me_5)W(=O)$_2$ is a class a oxo derivative, slower exchange is anticipated.

Cp^*_2W=O undergoes a remarkably clean reaction with O_2 to form white, crystalline, Cp^*W(=O)$_2$(OCp*) (Scheme 7). Cp^*W(=O)$_2$(OCp*) has been characterized by an X-ray crystal structure determination and the molecular structure is shown in Fig. 6.[46] In principle, a cyclopentadienyl ligand can bond to a single transition metal centre in a variety of modes, namely η^5-, η^3-,η^1-,η^3,η^2- and η^1,η^4-. In this respect, the bonding between the tungsten atom and the ($\eta^{"5"}$-C_5Me_5) ligand is particularly interesting: while primarily *pentahapto*, η^5-, in character, there is some unmistakable *monohapto*, η^1-, component. Thus, one of the inner-ring carbon atoms, C_α, is displaced from the plane of the other ring atoms, towards W, by about 0.05 Å. This carbon

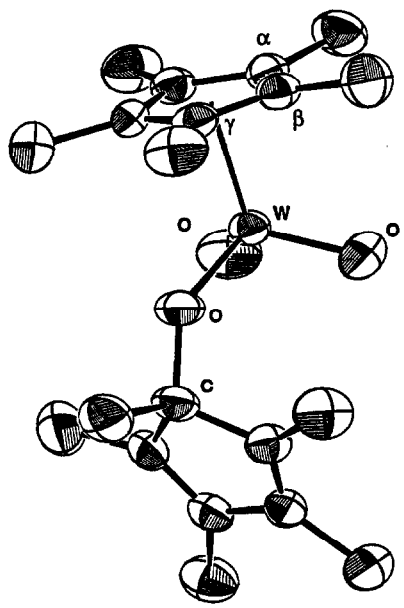


Fig. 6. The molecular structure of ($\eta^{"5"}$-C_5Me_5)W(=O)$_2$(OC_5Me_5).

atom is appreciably pyramidal and the W—C_α distance of 2.334(4) Å is approximately 0.1–0.15 Å shorter than the other W—C distances of this ligand. Indeed, this W—C_α distance is only 0.13 Å longer than the value of 2.20 Å for the W—C distance to the (η^1-C_5Me_5) ligand in (η^5-C_5Me_5)(η^1-C_5Me_5)W(=O)$_2$. There is also considerable localization of the double bonds in the η^{5}-C_5Me_5 η^1 ligand: the C_β—C_γ bonds at 1.396(4) Å, while considerably longer than a pure double bond or the corresponding bonds in the η^1-C_5Me_5 ligand bonded to oxygen, are significantly shorter than the other ring bonds. These observations suggest that the W—(η^5-C_5Me_5) interaction is a mixture of η^5- and η^1-bonding and that the ligand is more aptly described as bonding in an η^1,η^4-fashion.

We note that many of these same features are observed for the (η^5-C_5Me_5) ligand in the structure of the related compound, (η^5-C_5Me_5)(η^1-C_5Me_5)W(=O)$_2$, which differs from (η^5-C_5Me_5)W(=O)$_2$(OC_5Me_5) in that the W atom is directly bonded to the (η^1-C_5Me_5) ligand, rather than being bonded through an oxygen atom. In this complex the W atom is appreciably closer (at about 2.32 Å) to one of the atoms of the (η^5-C_5Me_5) than to the other four, and in each case the ring atom is *trans* to the W—C single bond of the (η^1-C_5Me_5) ligand.

The origin of the asymmetry of the bonding of the (η^5-C_5Me_5) ligand in (η^5-C_5Me_5)(η^1-C_5Me_5)W(=O)$_2$ and (η^5-C_5Me_5)W(=O)$_2$(OC_5Me_5) may be attributed to the strong *trans* influence of two oxo ligands. The ligands *trans* to each oxo ligand may be viewed to be the double bond components of the (η^5-C_5Me_5) ligand. The strong W=O bonding weakens the *trans* tungsten–ligand bonding, and thus lengthening of the bonds to these four carbon atoms results. Other evidence that the oxo ligand exerts a strong *trans* influence is provided by the structures of (η^5-C_5Me_5)Re(=O)Cl_2 and (η^5-C_5Me_5)Re(=O)$(CH_3)_2$.[47] In these examples, the presence of only one oxo ligand results in the lengthening of two Re—ring carbon bonds, so that only one double bond component within the pentamethylcyclopentadienyl ligand obtains. Thus, by extension, the rhenium-(η^5-C_5Me_5) bonding for these structures takes on some η^3,η^2- (i.e. allyl, olefin) character.

The reaction between Cp^*_2W=O and O_2 has been examined by the use of ^{16}O, ^{17}O and ^{18}O labels. Thus, the product of the reaction of $Cp^*_2W=^{18}O$ with $^{16}O_2$ has been studied by IR spectroscopy, and the product of the reaction of $Cp^*_2W=^{17}O$ with $^{16}O_2$ has been studied by ^{17}O NMR spectroscopy. The results show that the oxygen atom which is inserted between the tungsten atom and the Cp* ligand arises from the O_2 rather than the oxo ligand of Cp^*_2W=O. Two potential pathways for the formation of (η^5-C_5Me_5)W(=O)$_2$(OC_5Me_5) involve (i) the formation of an η^2-peroxo intermediate, i.e. (η^5-C_5Me_5)(η^1-C_5Me_5)W(=O)(η^2-O_2), followed by migration of the (η^1-C_5Me_5) ligand to (η^2-O_2), and (ii) attack at both the Cp* ligand and W by O_2 leading to a bridging peroxo species and thus C—O bond formation in the initial stages (Scheme 7). However, the available data does not permit the distinction between these two mechanisms. We note that a potential model for this reaction is the acid-catalysed conversion of Cp^*_2Ta(η^2-O_2)CH_3 to Cp^*_2Ta(=O)OCH_3.[48]

$$Cp^*_2Ta(\eta^2\text{-}O_2)CH_3 \xrightarrow{H^+(catalyst)} Cp^*_2Ta(=O)OCH_3.$$

In order to examine this possibility further, and also to examine the transfer of an oxygen to a methyl group on tungsten, the previously reported oxo–peroxo methyl compound, Cp*W(=O)(η^2-O_2)CH_3,[41] was synthesized by a new procedure involving the oxidation of Cp*W$(CO)_3CH_3$ with $H_2O_{2(aq)}$.

$$Cp^*W(CO)_3CH_3 \xrightarrow{H_2O_{2(aq)}} Cp^*W(=O)(\eta^2\text{-}O_2)CH_3.$$

This compound is analogous to one of the potential intermediates shown in Scheme 7. However, this complex does not *cleanly* undergo a transformation of the type shown and so no firm conclusions regarding the mechanism can be drawn at this time.

The W—OCp* bond in Cp*W(=O)$_2$(OCp*) can be cleaved with Me_3SiCl to give Cp*W(=O)$_2$Cl.[41,43]

$$Cp^*W(=O)_2(OCp^*) \xrightarrow{Me_3SiCl} Cp^*W(=O)_2Cl.$$

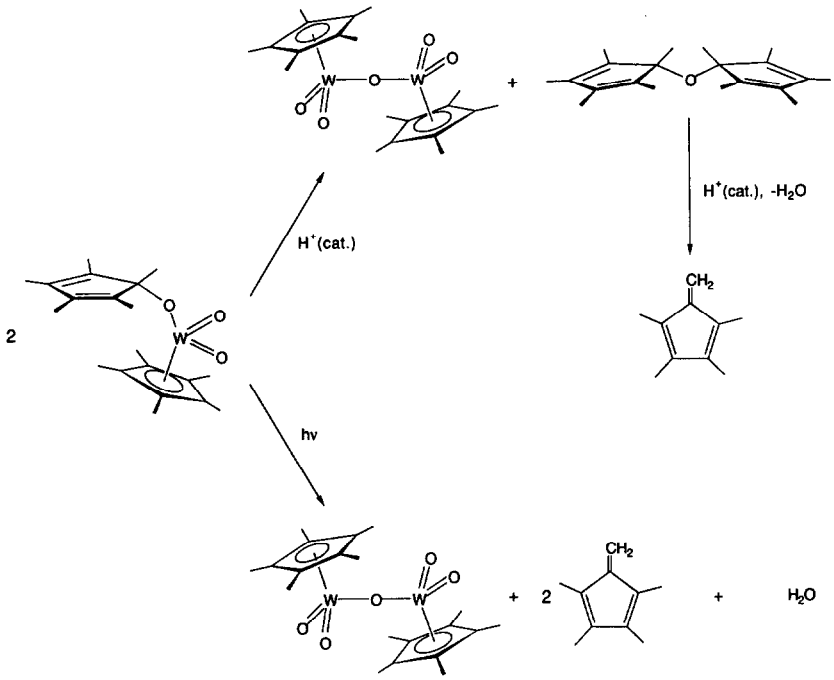
Cp*W(=O)$_2$(OCp*) undergoes an acid-catalysed rearrangement to generate the dimer, [Cp*W(=O)$_2$]$_2$O (0.5 equivalent), and the ether, $(C_5Me_5)_2O$, which has been spectroscopically characterized but not isolated. The ether undergoes a further acid-catalysed dehydration to give tetramethylfulvene, $C_5Me_4CH_2$.† This overall process can also be effected photochemically as summarized in Scheme 8.

EXPERIMENTAL

General considerations

All manipulations were performed using a combination of glovebox, high-vacuum or Schlenk tech-

† The organic derivatives $(C_5Me_5)_2O$ and $C_5Me_4CH_2$ have only been spectroscopically characterized and not isolated pure. 1,2,3,4-tetramethylfulvene has been previously reported.[49]



Scheme 8. Acid-catalysed and photochemical conversion of $Cp^*W(=O)_2(OCp^*)$ to $[Cp^*W(=O)_2]_2O$.

niques.[50] Solvents were purified and degassed by standard procedures. C_6D_6 was purified by vacuum transfer from activated molecular sieves (4 Å, Linde) and then from "titanocene".[51]

^1H, ^2H, ^{13}C and ^{17}O NMR spectra were measured on Varian EM-390 (90 MHz), JEOL FX90Q (90 MHz), JEOL GX400Q (400 MHz) and Brucker WM500 (500 MHz) spectrometers and ^1H and ^{13}C NMR data for the compounds are reported in Tables 1 and 2. IR spectra were recorded on a Beckman 4240 spectrophotometer. Elemental analyses and mass spectra were obtained by Mr L. Henling and Mr F. Harvey of the CIT analytical department.

Cp^*WCl_4 and $Cp^*WCl_4(PMe_3)$ were prepared as described previously.[7]

Preparation of $Cp^*_2WCl_2$

(a) *From* $Cp^*WCl_4(PMe_3)$. A mixture of $Cp^*WCl_4(PMe_3)$ (30 g, 55.9 mmol) and Mg (0.68 g, 28.3 mmol) was treated with THF (75 cm^3) at −78°C and stirred as it was allowed to warm to room temperature. A red solution was obtained after *ca* 30 min. The mixture was stirred for a further 12 h after which the solvent was removed under reduced pressure giving a red–orange solid. Cp*Li (10 g, 70.4 mmol) and toluene (*ca* 50 cm^3) were added and the mixture was heated at *ca* 145°C for 4 days. The solvent was removed and the residue was washed with petroleum ether (b.p. 35–60°C, 5 × 100 cm^3). This solid was placed in a Soxhlet extractor and extracted with toluene. The toluene extract was allowed to cool to room temperature overnight forming green crystals which were separated and washed with pentane, giving $Cp^*_2WCl_2$ (3 g). A second crop (0.5 g) was also obtained. The residue in the thimble of the Soxhlet extractor was extracted with CH_2Cl_2. The CH_2Cl_2 was removed from the extract under reduced pressure giving a further quantity of $Cp^*_2WCl_2$ (2.5 g). Total yield $Cp^*_2WCl_2$ 6 g (21%). Elemental analysis (found/calc.): C 46.4 (45.7), H 5.7 (5.7)%. Mass spectrum: $m/e = 526$ for $Cp^*_2W^{184}Cl^{35}Cl^{37}$. IR data (Nujol mull, KBr plates, cm^{-1}): 1490(w,br), 1060(w), 1015(s).

(b) *From* Cp^*WCl_4. A suspension of Cp^*WCl_4 (20 g, 43.4 mmol) in toluene (40 cm^3) was treated with PMe_3 (7 cm^3, *ca* 64 mmol) and stirred for 12 h at room temperature. The solvent was removed under reduced pressure giving $Cp^*(WCl_4(PMe_3)$ as a green powder. Mg (0.54 g, 22.5 mmol) was added and THF (50 cm^3) were added at −78°C. The mixture was stirred as it was allowed to warm to room temperature, giving a red solution which deposited red crystals. The THF was removed under reduced pressure after *ca* 2 h. KCp* (11 g, 62.9 mmol) and toluene (100 cm^3) were added and the mixture was heated at *ca* 145°C in a glass ampoule. Portions of the solvent were removed under vacuum periodically (initially after 2 h). Green crystals could be observed to be present after 16 h. After 2 days the volatile components were removed and the residue

was washed with pentane (5×100 cm^3) and placed in a Soxhlet extractor and extracted with toluene. Green crystals were deposited and were filtered and washed with pentane giving $Cp^*_2WCl_2$ (5 g). A further 800 mg was isolated from the toluene filtrate and 200 mg was isolated by extraction of the residue in the Soxhlet thimble with CH_2Cl_2. Total yield $Cp^*_2WCl_2$, 6 g (26%).

Preparation of $Cp^*(\eta^5\text{-}C_5Me_4CH_2CH_2CH_3)WCl_2$

A suspension of Cp^*WCl_4 (2.1 g, 4.6 mmol) in toluene (10 cm^3) was treated with PMe_3 (0.8 cm^3, *ca* 7.4 mmol) and stirred for 2 h at room temperature. The solvent was removed under reduced pressure giving $Cp^*WCl_4(PMe_3)$ as a green powder. Mg (0.059 g, 2.4 mmol) was added and THF (20 cm^3) added at −78°C. The mixture was stirred as it was allowed to warm to room temperature, giving a red solution which deposited red crystals. The THF was removed under reduced pressure after *ca* 4 h. $Li(C_5Me_4CH_2CH_2CH_3)$ (0.77 g, 4.5 mmol) and toluene (30 cm^3) were added and the mixture was heated at *ca* 145°C in a glass ampoule. Portions of the solvent were removed under vacuum periodically. After 3 days the volatile components were removed and the residue was washed with pentane (4×100 cm^3) extracted into hot toluene and allowed to cool to −78°C. Green crystals were deposited and were filtered and washed with pentane giving $Cp^*(\eta^5\text{-}C_5Me_4CH_2CH_2CH_3)WCl_2$ (250 mg, 10%). Elemental analysis (found/calc.): C 47.4(47.7), H 5.7(6.2)%.

Preparation of $Cp^*_2WH_2$

A mixture of $Cp^*_2WCl_2$ (500 mg, 0.95 mmol) and $LiAlH_4$ (300 mg, 7.9 mmol) was treated with Et_2O (40 cm^3) at −78°C. The mixture was stirred and warmed to room temperature. After 2 h the $Cp^*_2WCl_2$ had dissolved and an orange solution phase was present. The mixture was stirred for a total of 3 days giving a pale yellow solution phase which was cooled to 0°C and slowly treated with Et_2O saturated with H_2O (60 cm^3) and then H_2O (2 cm^3). The mixture was filtered and the solvents removed under reduced pressure. The residue was extracted into pentane and crystallized at −78°C giving yellow needles which were isolated by filtration and dried *in vacuo* giving $Cp^*_2WH_2$ (300 mg, 69%).

When the reaction was hydrolysed after 2 h, the product isolated was a mixture of $Cp^*_2WH_2$ and $Cp^*_2W(H)Cl$. Reduction of $Cp^*_2W(H)Cl$ under similar conditions for 2 days gave $Cp^*_2WH_2$.

Preparation of $Cp^*_2W(H)Cl$

A mixture of $Cp^*_2WCl_2$ (400 mg, 0.76 mmol), Na (100 mg, 4.35 mmol) and Hg (5 cm^3) was treated with THF (20 cm^3) at −78°C. The mixture was stirred and allowed to warm to room temperature. After 18 h the mixture was filtered and the solvent was removed from the filtrate under reduced pressure. The residue was extracted into pentane, concentrated and placed at −78°C giving light brown needles of $Cp^*_2W(H)Cl$ (180 mg, 48%). Elemental analysis (found/calc.): C 49.9 (48.9), H 6.3 (6.3)%. IR data (Nujol mull, KBr plates, cm^{-1}): 2710(w), 1940(m) [W—H], 1065(w), 1020(s).

Preparation of $Cp^*_2W(CH_3)_2$

$Cp^*_2WCl_2$ (2 g, 3.8 mmol) and CH_3Li (400 mg, 18.2 mmol) were treated with toluene (20 cm^3) and heated at 80°C for 2 h giving a red–orange solution. The mixture was filtered and the toluene removed under reduced pressure. The residue was extracted into pentane and cooled to −78°C giving orange needles of $Cp^*_2W(CH_3)_2$ (1.2 g, 65%). Elemental analysis (found/calc.): C 54.4 (54.6), H 7.3 (7.4)%. IR data (Nujol mull, KBr plates, cm^{-1}): 2715(w), 1060(w), 1020(s).

Preparation of $Cp^*_2W(\eta^2\text{-}CH_2O)$

A mixture of $Cp^*_2WCl_2$ (900 mg, 1.7 mmol) and $NaOCH_3$ (400 mg, 7.4 mmol) was heated in toluene (20 cm^3) at 80°C for 2 days giving a red–orange solution. The solvent was removed under reduced pressure and the residue was extracted into pentane and crystallized at −78°C giving brown needles of $Cp^*_2W(\eta^2\text{-}CH_2O)$ (480 mg, 58%). The product was contaminated by small quantities of $Cp^*_2W{=}O$. Elemental analysis (found/calc.): C 51.7 (52.3), H 6.5 (6.6)%.

Preparation of $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$

(a) A mixture of $Cp^*_2W(H)Cl$ (180 mg, 0.37 mmol) and CH_3Li (150 mg, 6.8 mmol) were treated with toluene (20 cm^3) and heated at 100°C for 16 h. The solvent was removed under reduced pressure and the residue crystallized from pentane at −78°C giving yellow–orange crystals of $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ (120 mg, 72%). Elemental analysis (found/calc.): C 52.9 (52.9), H 6.4 (6.6)%.

(b) A mixture of $Cp^*_2WCl_2$ (*ca* 15 mg) and CH_3Li (*ca* 10 mg) in C_6D_6 (*ca* 0.5 cm^3) in a NMR tube was heated at 80°C for 1 h and was observed by ^1H NMR spectroscopy to generate $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ via $Cp^*_2W(CH_3)H$.

(c) A mixture of $Cp^*_2WCl_2$ (*ca* 15 mg) and C_6H_5Li (*ca* 10 mg) in C_6D_6 (*ca* 0.5 cm^3) in a NMR tube was heated at 80°C for 4 h and was observed by ^1H NMR spectroscopy to generate $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$.

Reaction of $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ *with* H_2

A solution of $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WH$ (*ca* 15 mg) in C_6D_6 (*ca* 0.5 cm^3) was sealed in a NMR tube under H_2 (*ca* 4 atm at 25°C) and heated at 220°C for 24 h. Observation by ^1H NMR spectroscopy demonstrated the formation of $Cp^*_2WH_2$.

Interconversion of $Cp^*_2WH_2$ *and* $Cp^*_2W(H)Cl$

(a) A solution of $Cp^*_2WH_2$ (*ca* 10 mg) in C_6D_6 (*ca* 0.5 cm^3) in a NMR tube was treated with CCl_4 and observed by ^1H NMR spectroscopy to generate sequentially $Cp^*_2W(H)Cl$ and $Cp^*_2WCl_2$, accompanied by the formation of $CHCl_3$.

(b) A solution of $Cp^*_2W(H)Cl$ (*ca* 10 mg) in C_6D_6 (*ca* 0.5 cm^3) in a NMR tube was treated with excess CCl_4 and observed by ^1H NMR spectroscopy to generate, cleanly, $Cp^*_2WCl_2$ and $CHCl_3$ after 30 min at room temperature.

(c) A mixture of $Cp^*_2WH_2$ and $Cp^*_2WCl_2$ (*ca* 1 : 1 molar ratio) in C_6D_6 was heated at 220°C for 1 day to give an equilibrium mixture with $Cp^*_2W(H)Cl$ ($K \approx 21$).

Preparation of $Cp^*_2W(CH_3)Cl$

A stirred solution of $Cp^*_2W(CH_3)_2$ (600 mg, 1.24 mmol) in toluene (20 cm^3) was treated with Me_3SiCl (157×10^{-3} cm^3, 1.68 mmol) and then H_2O (11×10^{-3} cm^3, 0.61 mmol). The solvent was removed under reduced pressure after 1 h at room temperature and the residue was washed with pentane (3×10 cm^3) to give $Cp^*_2W(CH_3)Cl$ as a red–brown crystalline solid (570 mg, 91%). Elemental analysis (found/calc.): C 50.5 (50.0), H 6.6 (6.5)%. IR data (Nujol mull, KBr plates, cm^{-1}): 2710(w), 1060(w), 1020(s).

Reaction of $Cp^*_2W(CH_3)Cl$ *with* CH_3Li; *formation of* $Cp^*_2W(CH_3)_2$

A solution of $Cp^*_2W(CH_3)Cl$ (*ca* 15 mg) in C_6D_6 (*ca* 0.5 cm^3) in a NMR tube was treated with CH_3Li (*ca* 10 mg). The reaction was monitored by ^1H NMR spectroscopy to give $Cp^*_2W(CH_3)_2$ after 30 min at room temperature.

Preparation of $Cp^*_2W(CH_3)H$

A mixture of $Cp^*_2W(CH_3)Cl$ (250 mg, 0.50 mmol) and $LiAlH_4$ (150 mg, 3.95 mmol) was treated with Et_2O at −78°C and the mixture stirred as it was allowed to warm to room temperature. The mixture was stirred for 4 h and cooled to 0°C before adding H_2O (*ca* 2 cm^3) dropwise. The mixture was filtered and the solvent removed under reduced pressure. The residue was extracted into pentane, concentrated and placed at −78°C. The orange crystals which were deposited were a mixture of $Cp^*_2W(CH_3)H$ and $Cp^*_2W(CH_3)_2$ (70 mg, *ca* 30%, ratio *ca* 4 : 1). The solvent was removed from the filtrate under reduced pressure giving $Cp^*_2W(CH_3)H$ (*ca* 30 mg, 13%, <5% $Cp^*_2W(CH_3)_2$). Elemental analysis (found/calc.): C 53.7 (53.6), H 7.2 (7.2)%. IR data (Nujol mull, KBr plates, cm^{-1}): 2715(w), 1900(m) [W—H], 1160(w), 1100(w), 1065(w), 1020(s), 790(w).

The reaction was repeated under similar conditions using $LiAlD_4$ as the reducing agent and D_2O for the hydrolysis. In this case the product of the reaction was identified as $Cp^*_2W(CH_3)D$ by ^1H and ^2H NMR spectroscopy.

Preparation of $Cp^*_2W(CH_2C_6H_5)H$

A mixture of $Cp^*_2W(CH_3)Cl$ (110 mg, 0.22 mmol) and C_6H_5Li (50 mg, 0.60 mmol) was treated with toluene (5 cm^3) and stirred at room temperature for 1 h. The mixture was filtered and the solvent removed under reduced pressure. The residue was extracted into pentane, concentrated and placed at −78°C. The orange crystals which were deposited were a mixture of $Cp^*_2W(CH_3)_2$ and $Cp^*_2W(CH_2Ph)H$ (30 mg, *ca* 50 : 50). The solvent was removed from the filtrate under reduced pressure to give pure $Cp^*_2W(CH_2Ph)H$ (*ca* 70 mg, 59%). Elemental analysis (found/calc.): C 59.0 (59.3), H 6.9 (7.0)%.

Preparation of $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)WCH_3$

A solution of $Cp^*_2W(CH_3)Cl$ (*ca* 20 mg) in C_6D_6 (0.5 cm^3) was treated with $LiCH_2PMe_2$ (10 mg). The products were observed by ^1H NMR spectroscopy to be $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)W(CH_3)$ and PMe_3 after 18 h at room temperature. The solvent was removed under reduced pressure and the residue was extracted into pentane. The mixture was filtered and the pentane removed from the filtrate under reduced pressure to give a yellow–orange solid, $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)W(CH_3)$ (*ca* 15 mg).

Reaction of $Cp^*_2W(CH_3)Cl$ *with* CH_3CH_2MgBr *and* Me_3CLi; *formation of* $Cp^*_2W(CH_3)H$

A solution of $Cp^*_2W(CH_3)Cl$ (*ca* 15 mg) in C_6D_6 (*ca* 0.5 cm^3) was treated with an excess of either CH_3CH_2MgBr or Me_3CLi and the reaction was monitored by ^1H NMR spectroscopy. In each case $Cp^*_2W(CH_3)H$, *inter alia*, was observed to be formed.

Preparation of $[Cp^*_2WH_3][BF_4]$

(a) A solution of $Cp^*_2WH_2$ (30 mg, 0.07 mmol) in Et_2O (5 cm^3) was treated dropwise with a solution of HBF_4 in Et_2O until a white precipitate was formed in a colourless solution. The mixture was filtered and the residue was washed with Et_2O and dried *in vacuo* giving a white powder, $[Cp^*_2WH_3][BF_4]$ (*ca* 30 mg, 84%). Elemental analysis (found/calc.): C 43.7 (44.1), H 6.0 (6.1)%. IR data (Nujol mull, KBr plates, cm^{-1}): 2720(w), 1985(m), [W—H], 1945(m) [W—H], 1800(w,br), 1570(m,br), 1280(w), 1050(s,br), 880(w), 860(w), 825(m), 720(m), 515(w).

(b) A mixture of $Cp^*_2WH_2$ (*ca* 20 mg) and $[Me_3NH][BPh_4]$ (*ca* 30 mg) was treated with $(CD_3)_2CO$ (*ca* 0.5 cm^3). A white solid was deposited which was separated by filtration giving $[Cp^*_2WH_3][BPh_4]$.

(c) A solution of $Cp^*_2WH_2$ (*ca* 20 mg) in Et_2O (*ca* 5 cm^3) was treated with excess $HCl_{(aq)}$ giving a fine white precipitate. The solvents were removed under reduced pressure giving a white solid, $[Cp^*_2WH_3][X]$ (X = Cl or HCl_2).

Protonation of $Cp^*_2WH_2$ *with* D^+

A suspension of $Cp^*_2WH_2$ (*ca* 15 mg) in D_2O (*ca* 0.5 cm^3) in a NMR tube was treated with a solution of DCl in D_2O. The $Cp^*_2WH_2$ dissolved giving a colourless solution. ^1H NMR spectroscopy demonstrated that the D^+ reacted initially at the central position giving d_1-$[Cp^*_2W(H)(D)(H)]^+$. Further exchange processes giving lateral d_1-$[Cp^*_2W(H)(H)(D)]^+$, d_2-$[Cp^*_2WHD_2]^+$ and d_3-$[Cp^*_2WD_3]^+$ occurred over a period of hours.

Deprotonation of $[Cp^*_2WH_3][BF_4]$

A solution of $[Cp^*_2WH_3][BF_4]$ (*ca* 15 mg) in H_2O (1 cm^3) was treated with a solution of $KOH_{(aq)}$ until a yellow precipitate was obtained. The water was removed under reduced pressure and the residue was extracted into pentane. The mixture was filtered and the pentane was removed from the filtrate under reduced pressure giving pure $Cp^*_2WH_2$ (*ca* 10 mg).

Preparation of $Cp^*_2W{=}O$

(a) A stirred suspension of $Cp^*_2WCl_2$ (1.0 g, 1.9 mmol) and KOH (0.27 g, 4.8 mmol) in THF (20 cm^3) was treated with H_2O (5 cm^3). The mixture was stirred for 1 h at room temperature giving a deep green THF solution above the colourless aqueous layer. The solvents were removed under reduced pressure and the residue was extracted into pentane, concentrated and cooled to −78°C giving dark green crystals of $Cp^*_2W{=}O$ (610 mg, 36%). Elemental analysis (found/calc.): C 51.2 (51.1), H 6.4 (6.4)%. ^{17}O NMR data (12 MHz, C_6D_6): δ 760 ppm. IR data (Nujol mull, KBr plates, cm^{-1}): 2710(w), 1060(w), 1025(m), 860(vs) [W=O] {820 $W{=}P^{18}$}.

The isotopically labelled derivative $Cp^*_2W{=}{}^{18}O$ (*ca* 90–95%) was obtained by a modification of the above procedure using $K^{18}OH/H_2{}^{18}O$. $Cp^*_2W{=}{}^{17}O$ was obtained by the exchange of $Cp^*_2W{=}{}^{16}O$ with $H_2{}^{17}O$ (*ca* 45%).

(b) A solution of $Cp^*_2W(\eta^2\text{-}CH_2O)$ (20 mg) in C_6D_6 (0.5 cm^3) was treated with H_2O (excess). The products were observed by ^1H NMR spectroscopy to be $Cp^*_2W{=}O$ and CH_3OH. $Cp^*_2W{=}{}^{17}O$ was also prepared by a large scale modification of this reaction.

Oxo exchange reactions of $Cp^*_2W{=}O$ *with* $H_2{}^*O$

(a) A solution of $Cp^*_2W{=}{}^{18}O$ (30 mg) in pentane (*ca* 5 cm^3) was stirred with excess $H_2{}^{16}O$ for 1 h at room temperature. The solvents were removed and the product was demonstrated to be $Cp^*_2W{=}{}^{16}O$ by IR spectroscopy.

(b) A solution of $Cp^*_2W{=}{}^{16}O$ (*ca* 50 mg) in pentane (5 cm^3) was stirred with excess $H_2{}^{17}O$ (45%) for 3 h at room temperature. The volatile components were removed and the formation of enriched $Cp^*_2W{=}{}^{17}O$ was demonstrated by ^{17}O NMR spectroscopy.

(c) A solution of $Cp^*_2W{=}{}^{17}O$ (*ca* 25 mg) in THF (*ca* 0.5 cm^3) was treated with $H_2{}^{16}O$ (*ca* 10 equivalents). Exchange of the labelled oxygen atoms was observed by ^{17}O NMR spectroscopy (δ 770 ppm in THF relative to external $H_2{}^{17}O$).

Exchange reaction of $Cp^*_2Ta(={}^{18}O)H$ *with* $D_2{}^{16}O$

A solution of $Cp^*_2Ta(={}^{18}O)H$ (50 mg) in pentane (*ca* 10 cm^3) was stirred with D_2O (*ca* 0.1 cm^3) for 3 h at room temperature. The solvents were removed and the product was identified as $Cp^*_2Ta(={}^{16}O)H$ by IR spectroscopy.

Reaction of $Cp^*_2Ta(=NC_6H_5)H$ *with* D_2O; *formation of* $Cp^*_2Ta(=O)H$

A solution of $Cp^*_2Ta(=NC_6H_5)H$ (*ca* 20 mg) in C_6D_6 (*ca* 0.5 cm^3) in a NMR tube was treated with excess D_2O. After 24 h at room temperature the products were observed to be $Cp^*_2Ta(=O)H$ and $PhND_2$ by ^1H NMR spectroscopy.

Reaction of $Cp^*_2W{=}O$ *with* Me_3SiCl; *formation of* $Cp^*_2W(OSiMe_3)Cl$ *and* $Cp^*_2WCl_2$

(a) A solution of $Cp^*_2W{=}O$ (*ca* 10 mg) in C_6D_6 (*ca* 0.5 cm^3) in a NMR tube was treated with excess Me_3SiCl. An immediate reaction occurred and the products $Cp^*_2WCl_2$ and $(Me_3Si)_2O$ were identified by ^1H NMR spectroscopy.

(b) A solution of $Cp^*_2W{=}O$ (*ca* 10 mg) in C_6D_6 (*ca* 0.5 cm^3) in a NMR tube was treated with Me_3SiCl (one equivalent) and was observed by ^1H NMR spectroscopy to generate an equilibrium mixture with $Cp^*_2W(OSiMe_3)Cl$ (*ca* 80% $Cp^*_2W(OSiMe_3)Cl$ initially). Over the period of 36 h, this mixture converted to equimolar amounts of $Cp^*_2W{=}O$ and $Cp^*_2WCl_2$.

Preparation of $Cp^*_2WI_2$

A solution of $Cp^*_2W{=}O$ (50 mg, 0.11 mmol) in toluene (10 cm^3) was treated with Me_3SiI (excess) at room temperature. The solvent was removed after 1 h and the residue washed with pentane (3×10 cm^3) to give a green crystalline solid, $Cp^*_2WI_2$ (50 mg, 67%). Elemental analysis (found/calc.): C 30.3 (33.9), H 4.0 (4.2)%.

Reaction of $Cp^*_2W{=}O$ *with* H_2 *and* Me_2SiH; *formation of* $Cp^*_2WH_2$

A solution of $Cp^*_2W{=}O$ (*ca* 15 mg) in C_6D_6 (*ca* 0.5 cm^3) in a NMR tube was sealed under either H_2 or Me_3SiH and heated at 220°C for *ca* 15 and 6 h, respectively. In each case the product was observed to be $Cp^*_2WH_2$ by ^1H NMR spectroscopy.

Reaction of $Cp^*_2W{=}O$ *with* $LiAlH_4$; *formation of* $Cp^*_2W(OH)H$ *and* $Cp^*_2WH_2$

A mixture of $Cp^*_2W{=}O$ (150 mg, 0.32 mmol) and $LiAlH_4$ (150 mg, 3.95 mmol) was treated with Et_2O (*ca* 20 cm^3) at −78°C. The mixture was stirred as it was allowed to warm to *ca* −20°C. An orange solution was obtained after *ca* 15 min. At this temperature the mixture was treated slowly with Et_2O saturated with H_2O (*ca* 30 cm^3) and then H_2O (1 cm^3). The mixture was filtered and the solvents removed from the filtrate under reduced pressure. The residue was extracted into pentane and crystallized at −78°C giving tan crystals, $Cp^*_2W(OH)H$ (70 mg, 47%). Elemental analysis (found/calc.): C 51.3 (50.9), H 6.7 (6.8)%. ^{17}O NMR data (12 MHz, C_6D_6): δ −110 ppm, $\nu_{1/2} \approx 330$ Hz). IR data (Nujol mull, KBr plates, cm^{-1}): 3600(w) [W—OH], 2715(w), 1905(m) [W—H], 1150(w), 1075(sh), 1060(w), 1025(m), 935(w), 900(w), 790(w). Prolonged reaction times at room temperature produces $Cp^*_2WH_2$.

$Cp^*_2W(OD)D$ was prepared by a similar method using $LiAlD_4$ and D_2O.

Preparation of $[Cp^*_2W(=OH)][BF_4]$

A solution of $Cp^*_2W{=}O$ (120 mg, 0.26 mmol) in Et_2O (10 cm^3) was treated with $HBF_4 \cdot Et_2O$ (excess) at −78°C. The mixture was warmed to room temperature and deposited a white solid which was isolated by filtration and washed with Et_2O giving $[Cp^*_2W{=}OH][BF_4]$ (*ca* 75 mg, 50%). Elemental analysis (found/calc.): C 40.7 (43.0), H 5.3 (5.6)%. IR data (Nujol mull, KBr plates, cm^{-1}): 3340(s,br) [WO—H], 2725(vw), 1285(w), 1210(m), 1050(vs,br), 970(m), 920(m), 875(m), 845(m), 800(vw), 760(w), 720(w), 550(w), 510(m).

Reaction of $[Cp^*_2W(=OH)][BF_4]$ *with* $KOH_{(aq)}$; *formation of* $Cp^*_2W{=}O$

$[Cp^*_2W(=OH)][BF_4]$ (*ca* 50 mg, 0.09 mmol) in THF (5 cm^3) was stirred with excess $KOH_{(aq)}$ for 2 h giving a green solution. The solvents were removed under reduced pressure and the residue was extracted into pentane. The mixture was filtered and the pentane removed under reduced pressure giving a green solid (*ca* 20 mg, 48%) which was identified as $Cp^*_2W{=}O$ by ^1H NMR spectroscopy.

Preparation of $[Cp^*_2W(=O)CH_3][I]$

A solution of $Cp^*_2W{=}O$ (150 mg, 0.32 mmol) in toluene (3 cm^3) was treated with CH_3I (0.2 cm^3, 3.2 mmol) and the mixture was stirred. After *ca* 5 min a yellow microcrystalline deposit started to form. The stirring was continued for 12 h. The mixture was filtered and the solid was washed with pentane (3×2 cm^3) and dried *in vacuo* giving yellow crystals $[Cp^*2W(=O)CH_3][I]$ (150 mg, 77%). $[Cp^*2W(=O)CD_3][I]$ was obtained by a similar procedure using CD_3I. Elemental analysis (found/calc.): C 41.3 (41.2), H 5.4 (5.4)%. IR data (Nujol mull, KBr plates, cm^{-1}): 2715(vw), 1250(vw), 1075 (vw,br), 1020(m), 868(s) [W=O], 790(w), 715(w).

Attempted exchange reaction of $[Cp^*_2W(=O)CD_3][I]$ *with* CH_3I

A solution of $[Cp^*_2W(=O)CD_3][I]$ (*ca* 20 mg) in $CDCl_3$ (*ca* 0.5 cm^3) in a NMR tube was treated with CH_3I (*ca* 10 equivalents). The mixture was heated at 80°C for 18 h. There was no evidence for the formation of the isotopomer, $[Cp^*_2W(=O)CH_3][I]$, by ^1H NMR spectroscopy.

Preparation of $Cp^*(\eta^4\text{-}C_5Me_4{=}CH_2)W(=O)CH_3$

A suspension of $[Cp^*_2W(=O)CH_3][I]$ (*ca* 50 mg, 0.08 mmol) and KH (*ca* 10 mg, 0.25 mmol) in THF (*ca* 5 cm^3) was stirred for 2 h at room temperature giving an orange solution phase. The THF was removed under reduced pressure and the residue was extracted into pentane. The mixture was filtered and the pentane removed under reduced pressure giving orange–red crystals of $Cp^*(\eta^4\text{-}C_5Me_4{=}CH_2)(=O)CH_3$ (*ca* 20 mg, 50%). Elemental analysis (found/calc.): C 52.5 (52.1), H 6.7 (6.6)%. IR data (Nujol mull, KBr plates, cm^{-1}): 3080(w), 2715(w), 1600(s), 1400(m), 1325(w), 1280(w), 1160(m), 1110(vw), 1035(m), 945(vs), 925(w), 845(s), 835(vw), 715(vw), 695(w).

$Cp^*(\eta^4\text{-}C_5Me_4{=}CH_2)W(=O)CD_3$ was obtained by a similar procedure using $[Cp^*_2W(=O)CD_3][I]$ and NaH.

Preparation of $Cp^*(\eta^2\text{-}CH_2{=}C_5Me_4)W(=O)CH_3$

A solution of $Cp^*(\eta^4\text{-}C_5Me_4{=}CH_2)W(=O)CH_3$ (*ca* 25 mg, 0.05 mmol) in C_6D_6 was heated at 80°C for 3 h giving $Cp^*(\eta^2\text{-}CH_2{=}C_5Me_4)(=O)CH_3$ quantitatively as determined by ^1H NMR spectroscopy. The solvent was removed under reduced pressure giving $Cp^*(\eta^2\text{-}CH_2{=}C_5Me_4)W(=O)CH_3$ as a red–orange solid. IR data (Nujol mull, KBr plates, cm^{-1}): 2715(vw), 1505(w), 1410(w), 1175(w), 1020(m), 960(s), 945(m), 795(vw), 715(w).

$Cp^*(\eta^2\text{-}CH_2{=}C_5Me_4)W(=O)CD_3$ was obtained by a similar procedure from $Cp^*(\eta^4\text{-}C_5Me_4{=}CH_2)W(=O)CD_3$.

Preparation of $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$

(a) A stirred solution of $Cp^*_2W{=}O$ (200 mg, 0.43 mmol) in pentane (15 cm^3) was treated dropwise with *ca* 30% H_2O_2 (0.1 cm^3, *ca* 1.0 mmol) at room temperature. The green solution became yellow and a pale yellow solid was deposited. After 1 h the volatile components were removed under reduced pressure and the residue was extracted into pentane, concentrated and placed at −78°C giving yellow crystals of $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$ (*ca* 180 mg, 87%). Elemental analysis (found/calc.): C 48.8 (49.4), H 5.9 (6.2)%. ^{17}O NMR data (12 MHz, C_6D_6, 25°C): δ 738 ppm. IR data (Nujol mull, KBr plates, cm^{-1}): 2710(w), 1620(w), 1505(w), 1220(m), 1160(w), 1115(w), 1065(sh), 1045(sh), 1025(m), 945(vs) [W=O], 895(vs) [W=O], {920 and 860 for $W^{18}O^{16}O$ isotopomer}, 800(w), 710(w).

(b) A solution of $Cp^*_2W{=}O$ (*ca* 20 mg) in C_6D_6 (0.5 cm^3) was treated with Me_3CO_2H (excess) and observed by ^1H NMR spectroscopy to give $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$ after *ca* 5 min at room temperature.

(c) A solution of $Cp^*_2WH_2$ (*ca* 20 mg) in C_6D_6 (0.5 cm^3) was treated with *ca* 30% $H_2O_{2(aq)}$ (excess). $(\eta^2\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$ was formed immediately, as evidenced by ^1H NMR spectroscopy.

Preparation of $(\eta^5\text{-}C_5Me_5)W(=O)_2(OC_5Me_5)$

A solution of $Cp^*_2W{=}O$ (200 mg, 0.43 mmol) in pentane (10 cm^3) at −78°C was placed under O_2 (1 atm) and was stirred as it was allowed to warm to room temperature. Upon reaching room temperature the initially green solution had become colourless. The solution was concentrated after 30 min and cooled to −78°C giving white (or very pale yellow) crystals of $(\eta^5\text{-}C_5Me_5)W(=O)_2(OC_5Me_5)$ (200 mg, 94%). Elemental analysis (found/calc.): C 47.5 (47.8), H 5.8 (6.0)%. ^{17}O NMR data (12 M Hz, C_6D_6): δ 685 ppm $Cp^*W(=O)_2OCp^*$. IR data (Nujol mull, KBr plates, cm^{-1}): $Cp^*_2W(=^{16}O)_2$ ($^{16}OC_5Me_5$) 2730(w), 1675(w), 1505(m), 1360(m), 1315(vw), 1295(vw), 1260(s), 1140(m), 1065(vs), 1035(s), 1005(vs), 950(vs), 915(vs), 890(vs), 810(m), 800(m), 715(w), 700(s), 600(w), 465(w). $Cp^*_2W(=^{18}O)(=^{16}O)(^{16}OC_5Me_5)$ 2730(w), 1740(vw), 1675(w), 1505(m,sh), 1360(m), 1315(vw), 1295(vw), 1260(s), 1140(m), 1065(vs), 1035(s), 1005(vs), 945(vs), 910(vs), 895(m), 875(vw), 860(vs), 810(m), 800(m), 715(vw), 700(s), 610(w), 465(w).

Preparation of $Cp^*W(\eta^2\text{-}O_2)(=O)CH_3$

A solution of $Cp^*W(CO)_3CH_3$ (300 mg, 0.77 mmol) in $CHCl_3$ (2 cm^3) was treated with $H_2O_{2(aq)}$ (*ca* 0.2 cm^3, 30%, *ca* 2 mmol) and stirred for 24 h at room temperature. The volatile components were removed under reduced pressure and the residue was washed with pentane giving a pale yellow powder of $Cp^*W(\eta^2\text{-}O_2)(=O)CH_3$ (250 mg, 85%).

Reaction of $(\eta^5\text{-}C_5Me_5)W(=O)_2(OC_5Me_5)$ *with* Me_3SiCl; *formation of* $Cp^*W(=O)_2Cl$

A solution of $(\eta^5\text{-}C_5Me_5)W(=O)_2(OC_5Me_5)$ (*ca* 25 mg) in C_6D_6 (*ca* 0.5 cm^3) in a NMR tube was

treated with excess Me_3SiCl. After 8 h at room temperature the product was observed to be quantitatively $Cp^*W(=O)_2Cl$ by ^1H NMR spectroscopy. The product was also characterized by IR spectroscopy.

Acid-catalysed decomposition of $(\eta^5\text{-}C_5Me_5)W(=O)_2(OC_5Me_5)$

A solution of $(\eta^5\text{-}C_5Me_5)W(=O)_2(OC_5Me_5)$ (*ca* 15 mg, 0.03 mmol) in C_6D_6 (*ca* 0.5 cm^3) in a NMR tube was treated with a catalytic quantity of *p*-TsOH (*ca* 0.5 mg, 0.003 mmol). The initial products were observed to be $[Cp^*W(=O)_2]_2O$ and $(C_5Me_5)_2O$ by ^1H NMR and IR spectroscopy. Further reaction resulted in dehydration of $(C_5Me_5)_2O$ to $C_5Me_4{=}CH_2$.

$(C_5Me_5)_2O$. ^1H NMR data (400 MHz, C_6D_6): δ 1.19, s, 1 (CH_3) of $C_5(CH_3)_5$; δ 1.60, q, partially resolved, $^5J_{C-H} = 1$, 2 (CH_3); δ 1.73, q, partially resolved, $^5J_{C-H} = 1$, 2 (CH_3). ^{13}C NMR data (100 MHz, C_6D_6): δ 21.9, q, $^1J_{C-H} = 128$, 1 (CH_3); δ 9.6, q, $^1J_{C-H} = 128$, 2 (CH_3); δ 11.4, q, $^1J_{C-H} = 128$, 2 (CH_3); 84.1, s 1*C*; 132.6, s, 2*C*; 139.9, s, 2*C*. IR data (Nujol mull, KBr plates, cm^{-1}): 1080 [C—O—C] (not separated from $[Cp^*W(=O)_2]_2O$).

$C_5Me_4{=}CH_2$. ^1H NMR data (400 MHz, C_6D_6): δ 1.68, br, 2 (CH_3)$_\alpha$; δ 1.84, q, partially resolved, $^5J_{H-H} = 1$, 2 (CH_3)β; δ 5.33, septet, partially resolved, $^5J_{H-H} = 1$, (CH_2). ^{13}C NMR data (100 MHz, C_6D_6): δ 9.4, q, $^1J_{C-H} = 128.2$ (CH_3); δ 11.1, q, $^1J_{C-H} = 128.2$ (CH_3); δ 109.8, t, $^1J_{C-H} = 157$, (CH_2); δ 155.4, s, $1C_{ipso}$; δ 123.7, s, 2*C*; δ 138.7, s, 2*C*.

Photochemical decomposition of $(\eta^5\text{-}C_5Me_5)W(=O)_2(OC_5Me_5)$

A solution of $(\eta^5\text{-}C_5Me_5)W(=O)_2(OC_5Me_5)$ (*ca* 15 mg) in C_6D_6 (*ca* 0.5 cm^3) in a Pyrex NMR tube was photolysed with a medium pressure mercury lamp for 12 h. The products were observed to be cleanly $[Cp^*W(=O)_2]_2O$ and $C_5Me_4{=}CH_2$ by ^1H NMR spectroscopy.

CONCLUSIONS

A variety of derivatives of permethyltungstenocene, including $Cp^*_2WH_2$, $Cp^*_2W(H)Cl$, $Cp^*_2W(CH_3)_2$, $Cp^*_2W(CH_3)Cl$, $Cp^*_2W(R)H$ (R = CH_3, CH_2Ph), $Cp^*_2W(\eta^2\text{-}CH_2O)$ and $Cp^*_2W{=}O$ have been synthesized starting from $Cp^*_2WCl_2$. The dihydride derivative, $Cp^*_2WH_2$, is readily protonated via attack at the W—H bonds, and not the d^2 tungsten centre, to give $[Cp^*_2WH_3]^+$. An interesting example of charge or SHOMO control, rather than HOMO control, leads to preferentially central protonation, via a trihydrogen ($\eta^3\text{-}H_3$) cation. The central and lateral hydride ligands of $[Cp^*_2WH_3]^+$ exchange sites by an intramolecular mechanism in preference to a deprotonation/protonation mechanism. The oxo derivative, $Cp^*_2W{=}O$, exhibits facile oxo exchange with labelled $H_2{}^*O$ via a 1,2-addition–elimination mechanism. Furthermore, $Cp^*_2W{=}O$ is both easily reduced, e.g. giving $Cp^*_2WH_2$ with either H_2, Me_3SiH or $LiAlH_4$, and easily oxidized giving $[Cp^*_2W(=O)CH_3][I]$ with CH_3I, $(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)W(=O)_2$ with H_2O_2 or Me_3CO_2H, and $(\eta^5\text{-}C_5Me_5)W(=O)_2(OC_2Me_5)$ with O_2. This diversity of chemical reactivity of tungsten oxo-derivatives augurs well for their potential relevance to selective catalytic oxidation of hydrocarbons.

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