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α-Hydrogen migration reactions in tungsten(VI) cyclopentadienyl alkylidyne complexes

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Abstract

$W(CAd)(OCMe_3)_3$ (Ad = 1-adamantyl) can be prepared by treating $W_2(OCMe_3)_6$ with 1-adamantanecarbonitrile and converted into $W(CAd)(triflate)(OCMe_3)_2(dme)$ by treating it with $Me_3Si(triflate)$ (dme = 1,2-dimethoxyethane). $W(CAd)(triflate)(OCMe_3)_2(dme)$ reacts with NaCp to yield $CpW(CAd)(OCMe_3)_2$. $CpW(CAd)(OCMe_3)_2$ can be converted into $CpW(CAd)Cl_2$ in dichloromethane by treating it with Me_3SiCl. Alkylation of $CpW(CAd)Cl_2$ yields $CpW(CAd)(CH_2CMe_3)Cl$ or $CpW(CAd)R_2$ complexes ($R = CH_2CMe_3$, CH_2Ph, or CH_3). Both $CpW(CAd)(CH_2CMe_3)Cl$ and $CpW(CAd)(CH_2CMe_3)_2$ tautomerize to give mixtures containing $CpW(CCMe_3)(CH_2Ad)Cl$ and $CpW(CCMe_3)(CH_2CMe_3)(CH_2Ad)$, respectively. An X-ray study of $CpW(CAd)(CH_2CMe_3)_2$ is consistent with some α agostic interaction of a neopentyl proton in each neopentyl ligand with the metal. In contrast, $CpW(CAd)(NMe_2)(CH_2CMe_3)$ shows no evidence of tautomerizing to $CpW(CCMe_3)(NMe_2)(CH_2Ad)$ at room temperature over the course of two weeks, while $CpW(CAd)(NHCMe_3)Cl$ tautomerizes to two rotameric forms of $CpW(NCMe_3)(CHAd)Cl$.

Keywords: Migration reactions; α-Hydrogen; Tungsten

1. Introduction

In a d^0 complex containing at least two alkyl ligands an α-hydrogen in one alkyl ligand can sometimes be 'abstracted' by a neighboring alkyl to give an alkane and an alkylidene complex [1–3]. It has long been known that neopentyl complexes are most prone to α abstraction, with trimethylsilylmethyl, benzyl, and (especially) methyl being progressively less so. It was also noted in early studies that α abstraction is faster in sterically crowded environments, e.g. coordination of additional ligands such as phosphines can induce or accelerate α-hydrogen abstraction reactions. Recently it has been shown that α abstraction and β abstraction can compete in $[(Me_3SiNCH_2CH_2)_3]Ta(alkyl)_2$ species [4], that the rate of α abstraction can be enhanced by increasing the size of the alkyls in the apical 'pocket' of triamidoamine complexes [4], and that α abstraction to give an alkylidene can be forced to be virtually the only sterically tenable process by increasing the size of the silyl substituent in $[(R_3SiNCH_2CH_2)_3]Ta(alkyl)_2$ species from R = Me to R = Et [5]. The evidence suggests that in a more crowded 'pocket', the β agostic interaction that precedes β abstraction in the alkyl becomes sterically disfavored, while the α agostic interaction that precedes α abstraction at the same time is encouraged. (A lack of 'steric pressure' of this type is part of the explanation as to why formation of methylene complexes from methyl complexes is generally slow [2].) The process of α abstraction in a dialkyl complex to give an alkylidene complex can be viewed as one that involves activation of an α-hydrogen through some agostic interaction [6] with the metal, making it susceptible to migration as a 'proton' to a neighboring nucleophilic α carbon atom. Abstraction of an alkylidene's α-hydrogen by an alkyl group to give an alkylidyne ligand is

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also relatively well-known [7] and most likely involves an activation of the alkylidene's α-hydrogen through an α agostic interaction with the metal. Formation of alkane has always been thought to be irreversible, although there is now evidence for CH activation by a non-d^0 tungsten alkylidene complex [8] and by '$(Me_3CCH_2)_2Ti=CHCMe_3$' [9].

In contrast, there are few documented examples of migration of an α-hydrogen in a d^0 alkyl complex to an alkylidene ligand (a literally or approximately degenerate process) or to an alkylidyne ligand (to give a bis(alkylidene) complex). In the first category is α H/D scrambling in $Ta(CDCMe_3)(CH_2CMe_3)_3$ [10], which takes place with a rate constant of ca. 3.5×10^{-5} s^{-1} at 348 K. In the latter category is the reaction in which $W(CSiMe_3)(CH_2CMe_3)_3$ produces an equilibrium mixture of $W(CSiMe_3)(CH_2CMe_3)_3$ and $W(CCMe_3)(CH_2CMe_3)_2(CH_2SiMe_3)$ (Eq. (1)) upon heating in solution [11]; at 352 K the average rate constant (forward and reverse reactions) is ca. 1.7×10^{-5} s^{-1}. The 'bis(alkylidene)' complex, $W(CHSiMe_3)(CHCMe_3)(CH_2CMe_3)_2$, is the proposed intermediate in this reaction. Stable 'd^0' bisalkylidene complexes are extremely rare, the only examples being tantalum complexes such as $Ta(CHCMe_3)_2(PMe_3)_2Cl$ or $CpTa(CHCMe_3)_2(PMe_3)$ [12–14].

$$W(CSiMe_3)(CH_2CMe_3)_3 \overset{\Delta}{\rightleftharpoons} W(CCMe_3)(CH_2SiMe_3)(CH_2CMe_3)_2 \quad (1)$$

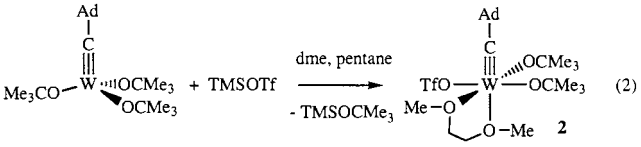
We became interested in the possibility of observing migration of an α proton from an alkyl to an adamantylidyne ligand in tungsten 'd^0' complexes. An attractive feature of the adamantyl group is that it is electronically and sterically more similar to a *t*-butyl group than is a trimethylsilyl group. (In order for α proton scrambling to be observed in $W(CSiMe_3)(CH_2CMe_3)_3$ an α proton must migrate to a silyl-substituted alkylidyne ligand and from a silyl-substituted alkyl ligand.) As in the case of α-hydrogen migration in $W(CSiMe_3)(CH_2CMe_3)_3$, the consequence of α-hydrogen migration to an adamantylidyne ligand should be readily observable. In order to explore the possibility of observing a bisalkylidene intermediate related to $CpTa(CHCMe_3)_2(PMe_3)$, we chose to prepare monocyclopentadienyl alkylidyne complexes of the type $CpW(CR)(CH_2R')_2$. Another interest in complexes of this type is that the Cp(RC)W core is analogous in electron count and structure to Cp_2M (M in group 4) [15,16], Cp(RN)M (M in group 5) [17–21], and $(RN)_2M$ (M in group 6) [22–27] cores. (An extensive discussion of these analogies and some of the structural consequences thereof has been published by Gibson [28].) The results of these investigations are reported here.

2. Results

2.1. Synthesis of $CpW(CR)X_2$

The most facile synthesis of 'd^0' tungsten alkylidyne complexes is the reaction between internal alkynes or nitriles [29,30] and readily prepared $W_2(OCMe_3)_6$ [31–33]. When a nitrile is employed the resulting $(Me_3CO)_3W{\equiv}CR$ and $(Me_3CO)_3W{\equiv}N$ products usually can be separated readily, as the alkylidyne is soluble in pentane, while the nitride product (a polymer in the solid state [34]) is not. $W_2(OCMe_3)_6$ reacts smoothly with 1-adamantanecarbonitrile in pentane to give a mixture of $W(CAd)(OCMe_3)_3$ (Ad = 1-adamantyl) (**1**) and $W(N)(OCMe_3)_3$. $W(CAd)(OCMe_3)_3$ is readily separated from $W(N)(OCMe_3)_3$ by filtration and crystallizes from the reaction mixture as colorless cubes in good yield.

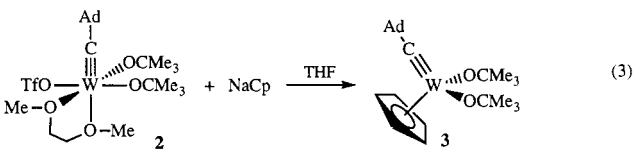
Attempts to displace a *t*-butoxide ligand in **1** with a cyclopentadienyl ligand using NaCp under a variety of conditions were not successful. However, a much more reactive monotriflate species (**2**) can be prepared as shown in Eq. (2). Complex **2** precipitates from the reaction mixture as yellow microcrystals and can be isolated in 85–95% yield by filtration.



(2)

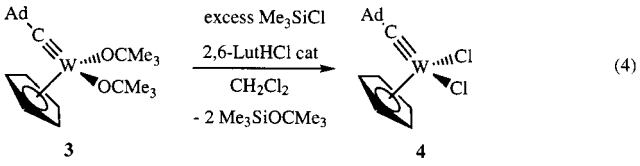
Complex **2** exhibits broad, inequivalent *t*-butoxide resonances in room temperature ^{1}H-NMR spectra (in benzene-d_6) as a consequence of dissociation of dimethoxyethane on the ^{1}H-NMR time scale. The reaction between an alkylidyne complex and trimethylsilyl triflate should be compared with reactions between $W(CCMe_3)(OCMe_3)_3$ and two equivalents of acids HX (e.g. X = Br, acetate, OC_6F_5) to give complexes of the type $W(CHCMe_3)(OCMe_3)_2X_2$ [35].

Sodium cyclopentadienide reacts with **2** in THF at -40°C to give $CpW(CAd)(OCMe_3)_2$ (**3**), which can be isolated in high yield as yellow crystals from pentane (Eq. (3)). In contrast, reactions between cyclopentadienyl sources and $W(CCMe_3)(dme)Cl_3$ or $[NEt_4][W(CCMe_3)Cl_4]$ do not afford known $CpW(CCMe_3)Cl_2$ [36,37]. The presence of the two *t*-butoxide ligands prevents side reactions such as reduction of the metal or formation of dimeric species.



(3)

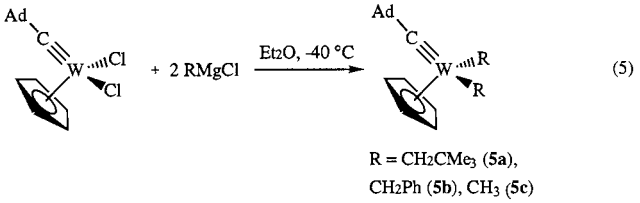
Complex **3** can be converted into $CpW(CAd)Cl_2$ (**4**) in dichloromethane in the presence of five equivalents of Me_3SiCl and a catalytic amount of 2,6-lutidinium chloride (Eq. (4)). The reaction proceeds in 80–85% yield and **4** crystallizes readily from ether/pentane solutions as brilliant purple shards. Compound **4** also could be prepared by dissolving **3** in neat trimethylsilyl chloride, but this procedure proved irreproducible. Addition of two equivalents of HCl to **3** in ether also gave **4** in good yield, but an unidentified impurity thwarted ready isolation of **4** in this case.



(4)

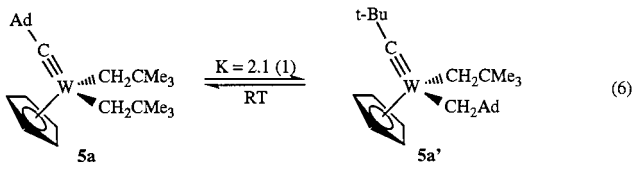
2.2. Synthesis of alkyl derivatives containing the CpW(CAd) core

Addition of Grignard reagents to **4** in ether at −40°C smoothly yields the dialkyl complexes shown in Eq. (5). Careful addition of one equivalent of neopentyl Grignard to **4** produced the mononeopentyl complex, $WCp(CAd)(CH_2CMe_3)Cl$ (**6**). Complex **5b** is isolated as bright yellow crystals from a mixture of ether and dichloromethane while complexes **5a**, **5c**, and **6** are isolated as deep red crystals from pentane at −40°C (70–80% yield).

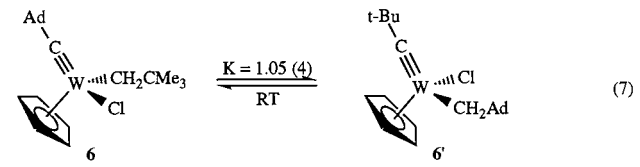


(5)

Compounds **5a** and **6** partially tautomerize over a period of days in benzene-d_6 at room temperature by a double α-H shift (Eqs. (6–7)). At room temperature equilibrium ($K_{eq} = 2.1(1)$) is reached between **5a** and **5a′** after ca. 24 h, whereas the analogous equilibration of **6** with **6′** occurs considerably more slowly, reaching completion ($K_{eq} = 1.05(4)$) only after 1–2 weeks at room temperature.



(6)



(7)

If we assume that 24 h is at least five half-lives, then $t_{1/2}$ is ca. 4 h, or the rate constant for scrambling is ca. 5×10^{-5} s^{-1} for **5a**. The final equilibrium value in each case is what one would expect on a statistical basis (2 and 1, respectively) if one assumes there is no significant difference between an adamantyl and a *t*-butyl group in alkyl or alkylidyne ligands in systems of this type. Addition of a slight excess of 2,6-lutidinium chloride in dichloromethane to the equilibrium mixtures produces corresponding mixtures of $CpW(CAd)Cl_2$ and $CpW(CCMe_3)Cl_2$, according to ^{1}H-NMR spectroscopy. In contrast, **5b** and **5c** decompose to give many products over a period of 36 h, according to NMR spectra, probably as a consequence of intermolecular processes that compete with intramolecular processes when the alkyl ($CH_2C_6H_5$ or CH_3) is small relative to neopentyl or adamantyl.

NMR data for compounds **5a**, **5a′**, **6**, and **6′** are dramatically different from NMR data for **5b** and **5c** (Table 1). In **5b,** for example, although two different methylene protons are observed at ca. 1.5 and 2.4 ppm, the values for J_{WH} and J_{CH} are similar for the two methylene protons. In contrast, each symmetry independent WCH_2R group in compounds **5a**, **5a′**, **6**, and **6′** displays two sets of ^{1}H resonances due to chemically inequivalent methylene protons centered around δ 3.5 and −1.0 ppm, and the differences in the magnitude of $^2J_{WH}$ within a pair of geminal C*H* resonances is substantial (Fig. 1). The second order nature of the methylene proton resonances in **5a** is apparent (AA′BB′ pattern overlaying an AA′BB′X pattern where X = ^{183}W, ca. 14% abundant.) In each case the upfield resonance appears to be most strongly coupled to ^{183}W with $^2J_{WH}$ ranging from 12.0 to 13.0 Hz, whereas each corresponding downfield resonance exhibits a $^2J_{WH}$ estimated to be less than ca. 4 Hz. The ^{13}C resonance for the C_α carbon atoms in the neopentyl and adamantyl complexes also are consistently ca. 50 ppm further downfield from the C_α carbon resonances in **5b** and **5c** and the geminal α-hydrogens in each symmetry independent WCH_2R group are coupled to their corresponding alkyl α-C atom to a different extent. Each WCH_2R ^{13}C resonance shows a four line pattern resulting from one $^1J_{CH}$ of ca. 120 Hz and one $^1J_{CH}$ of ca. 100 Hz. Selective $^{13}C\{^1H\}$-NMR decoupling experiments allow assignment of the high and low $^1J_{CH}$ values to the downfield and upfield ^{1}H resonances, respectively, in several cases.

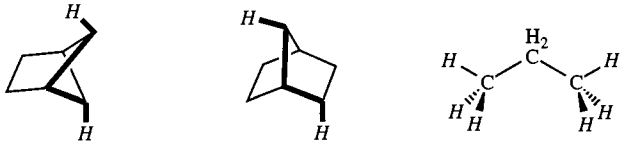
The $^4J_{HH}$ (2.6 Hz) in the upfield WCH_2CMe_3 and WCH_2Ad resonances (Fig. 1) in the mixed alkyl tautomer **5a′** is unusually large. For comparison, a related $^4J_{HH}$ of 3.1 Hz has been observed in the zirconocene silylamide complex $Cp_2Zr(H)[N(^tBu)(SiMe_2H)]$ that has been shown crystallographically to possess a β agostic Si–H bond [38]. In organic molecules proton-proton couplings through four σ-bonds generally are

Table 1
C_α- and H_α-NMR parameters or complexes **5**–**7** (in benzene-d_6 unless noted otherwise)

Complex	δ ^{1}H (ppm)	$^2J_{WH}$ (Hz)	δ ^{13}C (ppm)	$^1J_{CH}$ (Hz)
CpW(CAd)(CH_2Ph)$_2$[a] (**5b**)	2.422	4.8	32.37	134.1[b]
	1.484	8.1		137.1[b]
CpW(CAd)(CH_3)$_2$ (**5c**)	1.133	5.8	40.25	121.9
CpW(CAd)(CH_2CMe_3)$_2$ (**5a**)	3.528[c]	<4	90.67	121.0
	1.147[c]	12.6		98.8
CpW($CCMe_3$)(CH_2CMe_3)(CH_2Ad) (**5a′**)	3.557[d]	<4	94.98[g]	120.2
	−1.502[d,e]	12.0		99.6
	0.886[e,f]	12.9	87.78[g]	101.2
	3.299[f]	<4		119.3
CpW(CAd)(CH_2CMe_3)Cl (**6**)	4.790	4.1	98.08	125.2
	−0.454	13.0		98.4
CpW($CCMe_3$)(CH_2Ad)Cl (**6′**)	4.715	4.4	100.58	125.0
	−0.631	12.9		97.1
CpW(CAd)(CH_2CMe_3)(NMe_2) (**7**)	1.69	11.7	48.60	113.6[h]
	1.53	8.7		115.9[h]

[a] Recorded in dichloromethane-d_2.
[b] Arbitrary assignment.
[c] $^4J_{HH}$ = 2.1 Hz.
[d] $^2J_{HH}$ = 11.7 Hz.
[e] $^4J_{HH}$ = 2.6 Hz.
[f] $^2J_{HH}$ = 12.4 Hz.
[g] Arbitrary correlation of ^{13}C resonance with ^{1}H resonances. $^1J_{CH}$ values assigned to downfield and upfield ^{1}H resonances in analogy with compounds **5a** and **5a′**.
[h] Arbitrary assignment of $^1J_{CH}$ values.

large only in bicyclic systems in which the H–C–C–C–H linkage is locked in a 'W' configuration[39–41] such as those shown below [42–44].



The NMR data for **5a**, **5a′**, **6**, and **6′** are consistent with two interpretations. One is that one or more protons in the neopentyl or adamantyl complexes is (are) interacting with the metal in an agostic fashion. Upfield shifted α-C*H* resonances have been correlated with agostic structures [6], although the chemical shift anisotropy of the W-alkylidyne triple bond may also contribute to the disparity in chemical shifts between the geminal hydrogen resonances [45]. A low $^1J_{C\alpha H\alpha}$ coupling constant is not in itself a rigorous criterion for the identification of α agostic interactions, but the low and high ranges for $^1J_{CH}$ values is at least consistent with α agostic interactions [46–48]. Agostic interactions between CH_α and the metal in alkylidene complexes has also been documented [1,3]. In general the C_α resonance shifts downfield and the H_α resonance shifts upfield as the alkylidene becomes more distorted toward what might be viewed as an incipient alkylidyne hydride complex. We would expect α agostic interactions in **5b** and **5c** to be minimal, as α agostic interactions are believed to be encouraged (in part) by steric crowding in the alkyl complex by the alkyl itself, which leads to an opening of the M–C_α–C_β angle and (presumably) a closing of the M–C_α–H_α angle.

The second interpretation is that the bulky alkyl ligands in **5a**, **5a′**, **6**, and **6′** have a preferred orientation (as a consequence of steric crowding) that circumstantially leads to the observed characteristics for the methylene group in proton and carbon NMR spectra. In contrast, the benzyl groups in **5b** would be expected to be more freely rotating and the two protons therefore more similar than in neopentyl or adamantyl complexes. However, the steric hindrance that would lead to limited rotation probably would also lead to an opening of the W–C_α–C_β angle and to a bending of one or both α protons toward the metal. Limited rotation and α agostic interactions in fact should be synergistic and inseparable. Therefore we can only say that the steric demands in the system lead to limited rotation, or to an α agostic interaction, or (most likely) to both simultaneously.

An X-ray study of **5a** (Fig. 2; Tables 2 and 3) reveals an overall structure that is consistent with a crowded coordination sphere, a limited ability of the neopentyl

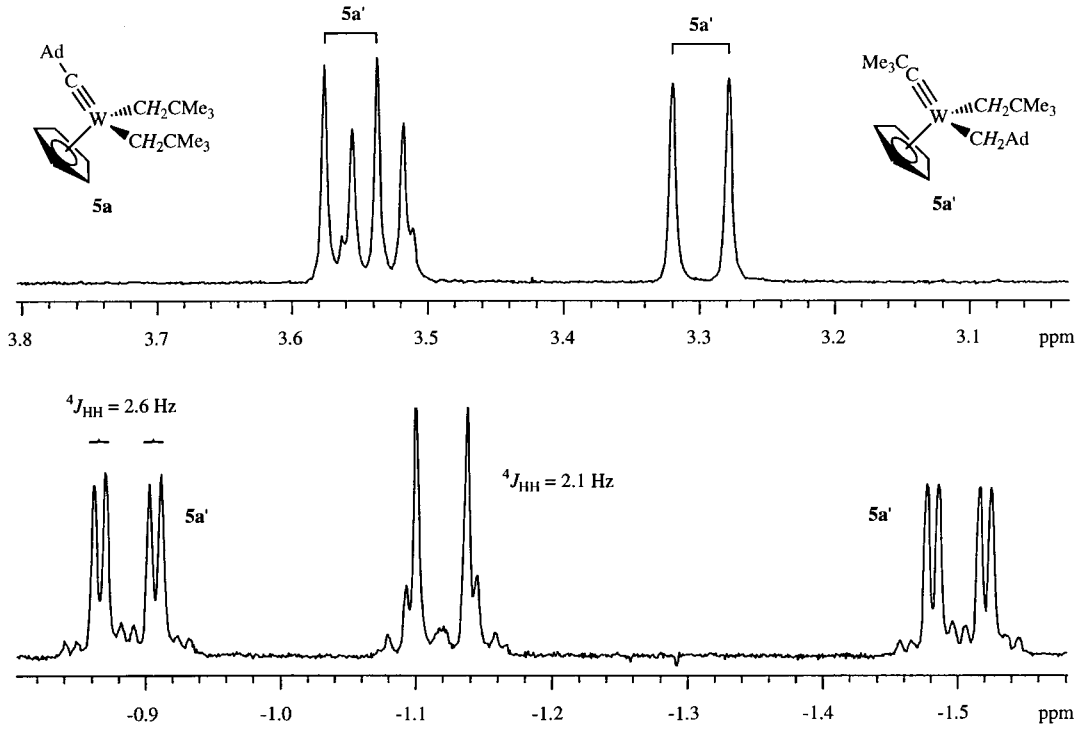


Fig. 1. A partial ^{1}H-NMR (300 MHz) spectrum of an equilibrium mixture of **5a** and **5a′** showing the downfield (top) and upfield (bottom) methylene resonances.

ligands to rotate, and (we will argue) an α agostic interaction of some magnitude. The two neopentyl ligands are related by a crystallographic mirror plane passing through the alkylidyne C_α–W–Cp(centroid) plane. The C(1)–W–Cp(centroid) angle (121.5(5)°; Table 2) is considerably larger than the angle between the two neopentyl ligands (C(3)–W–C(3′) = 106.2(4)°), as might be expected for a complex that is formally analogous to a metallocene in bonding parameters. However, the disparity is not as great as found in a typical metallocene (ca. 135° and 95°, respectively). The W-alkylidyne linkage is nearly linear (< W–C(1)–C(2) = 166.2(6)°) with a normal [7] W≡C distance of 1.746(9) Å. The deviation from linearity can be ascribed to repulsion between the adamantyl group and the neopentyl ligands. Although the cyclopentadienyl ring is clearly bound in an η^5 manner, some slippage is apparent with W–C distances ranging from 2.328(7) Å (W–C(5)) to 2.512(10) Å (W–C(7)). This asymmetry may reflect the influence of the triply bound alkylidyne ligand, as the longest distance is to the Cp carbon atom (C(7)) roughly *trans* to the W-alkylidyne linkage (C(1)–W–C(7) = 149°).

Although the α-H atoms were not located in a difference map, they were refined by placing them in idealized positions, fixing the C(3)–H(3A) and C(3)–H(3B) distances at 0.96 Å, and then allowing the orientations of these C–H bonds to refine freely, a technique that has been employed in similar circumstances in order to support an argument concerning an α agostic interaction [19]. Although the uncertainty in these distances is understandably large, the resulting W…H(3A) and W…H(3B) contacts of 2.42(7) and 2.61(7) Å suggest that one of the neopentyl α-H atoms in **5a** (H(3A)) lies closer to the tungsten center than the other. The α-H atom (H(3A)) nearest to W also makes the smallest W–C(3)–H(3) angle (93(4)° versus 109(4)°) and rests just above the C(3)–W–C(3′) plane. As located, protons H(3A) and H(3B) are 3.19 Å from the adamantylidyne carbon atom.

The W–C(3) distance (2.159(7) Å) lies toward the low end of the range (2.096(5)–2.258(8) Å) found in other crystallographically characterized four- and five-coordinate tungsten neopentyl complexes [11,49–51]. Of note, however, is the wide W–C(3)–C(4) angle of 134.8(4)°, which is outside of the range in the neopentyl complexes referenced above (122–131°). Similar Nb–C_α–C_β angles (131.2(2), 132.5(3)°), however, have been found in $CpNb(NAr)(CH_2CMe_3)_2$ (Ar = 2,6-diisopropylphenyl) in which an α agostic interaction was proposed [19]. The *t*-butyl group is directed toward the alkylidyne ligand by 38.5° (the dihedral angle between the C(3)–W–C(3′) and W–C(3)–C(4) planes). Therefore H(3A) should be located nearest to tungsten, should be directed there by orientation of the neopentyl group, and should lie almost in the C(3)–W–C(3′) plane. If one takes the analogy between the d^0 CpW(-CAd) and Cp_2M (M in group 4) fragments seriously

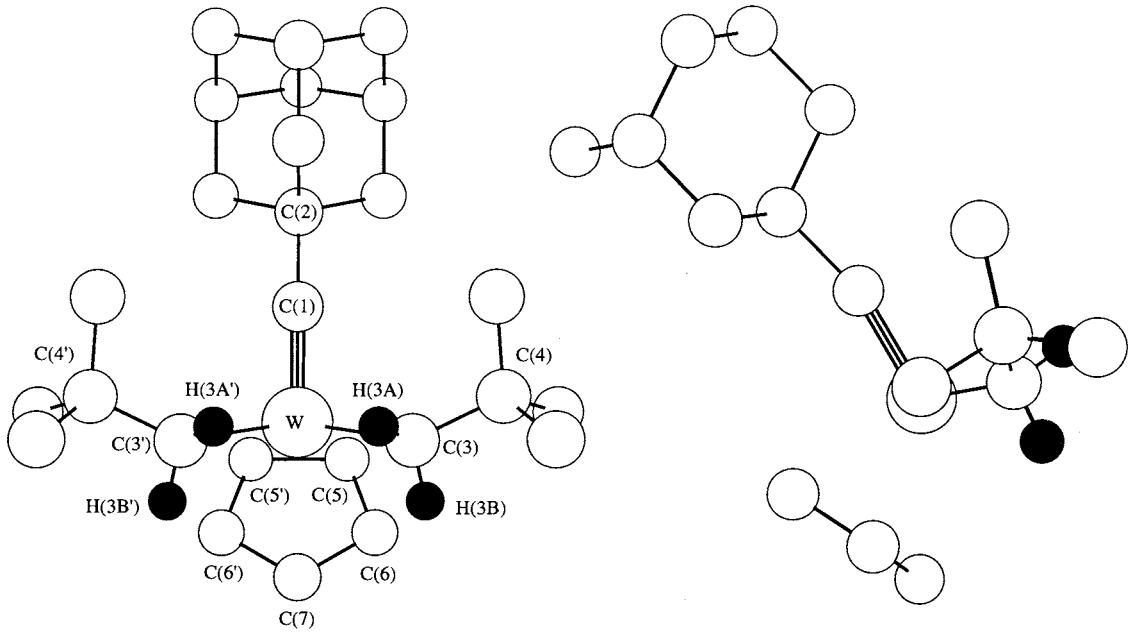
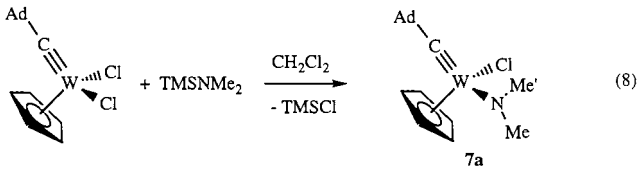


Fig. 2. Two views of the structure of **5a**. (Only the methylene protons in the two neopentyl ligands are shown.)

[15], an unoccupied orbital with A_1 symmetry is available approximately in the C(3)–W–C(3′) plane and is the only one that could accept electron density from the two suitably oriented α-CH bonds. The resulting 'double α agostic' interaction would be consistent with the X-ray structure and with all NMR parameters as discussed above. In the simple MO description shown in Fig. 3, the lowest energy MO would be totally bonding, while the next highest occupied MO would contain a node at W. The highest energy MO that has antibonding character would not be occupied.

2.3. The preparation of amido and imido complexes

The reaction between $CpW(CAd)Cl_2$ and Me_3SiNMe_2 produces yellow crystalline $CpW(CAd)(NMe_2)Cl$ (**7a**) in good yield (Eq. (8)).



(8)

Table 2
Selected bond lengths (Å) and angles (°) for $CpW(CAd)(CH_2CMe_3)_2$ (**5a**)

Distances			
W–C(1)	1.746(9)	W–C(3)	2.159(7)
W–C(5)	2.328(7)	C(3)–H(3A)	0.98(7)
W–C(6)	2.444(7)	C(3)–H(3B)	0.93(7)
W–C(7)	2.512(10)	W…H(3A)	2.42(7)
W-centroid	2.098(8)	W…H(3B)	2.61(7)
Angles			
W–C(1)–C(2)	166.2(6)		
C(3)–W–C(3′)	106.2(4)	W–C(3)–C(4)	134.8(4)
C(1)–W-centroid	121.5(5)	W–C(3)–H(3A)	93(4)
C(1)–W–C(3)	102.1(2)	W–C(3)–H(3B)	109(4)
C(3)–W-centroid	111.8(5)		

Table 3
Crystallographic data, collection parameters, and refinements for $CpW(CAd)(CH_2CMe_3)_2$ (**5a**)

Empirical formula	$C_{26}H_{42}W$
Formula weight	538.47
Diffractometer	Siemens SMART/CCD
Crystal color, morphology	Red, plate
Crystal dimensions (mm)	$0.18 \times 0.24 \times 0.24$
Crystal system	Monoclinic
a (Å)	15.7061(8)
b (Å)	12.4619(7)
c (Å)	12.1803(6)
α (°)	90
β (°)	97.5680(10)
γ (°)	90
V (Å^3)	2363.3(2)
Space group	$C2$
Z	2
D_{calc} (g cm^{-3})	1.513
F_{000}	1088
μ(Mo–K$_\alpha$) (mm^{-1})	4.896
Scan type	ω scans
Temperature (K)	293(2)
Total number of unique reflections	1797
No. of variables	140
R [I > 2σ(I)]	0.0375
R_w [I > 2σ(I)]	0.0906
Goodness-of-fit	1.011

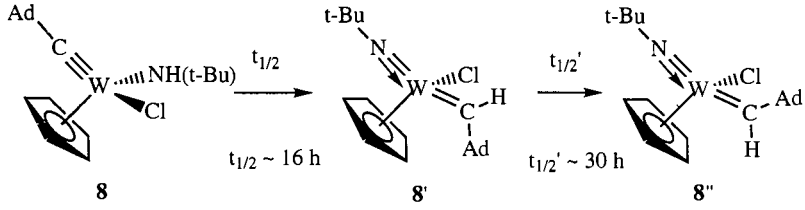
^{1}H-NMR spectra of **7a** at room temperature in toluene-d_8 display two well-separated methyl resonances for the dimethylamido group (Me and Me′), as expected if the lone pair on the amido ligand is donated into an orbital with B_2 symmetry (in the C_{2v} symmetric Cp_2HfR_2 relative [15]) that lies in the Cl–W–N plane [28]. Heating an NMR sample of **7a** to 110°C caused the Me and Me′ resonances to broaden only slightly. We would not expect the dimethylamido ligand to rotate about the W–N bond rapidly on the NMR time scale, since a π bond effectively would have to be fully broken in the process (if the cyclopentadienyl ligand remains η^5), i.e. there is no orbital that can stabilize the rotated NMe_2 ligand in the absence of significant distortion of the $(\eta^5\text{-}C_5H_5)W{\equiv}CAd$ framework.

Treatment of **7a** with neopentyllithium in ether yields orange-yellow crystalline $CpW(CAd)(NMe_2)(CH_2\text{-}CMe_3)$ (**7b**). In **7b** two sharp and well-separated methyl resonances also are observed for the NMe_2 ligand, as expected. We also noticed that characteristics of α agostic interactions are not present in ^{1}H- and ^{13}C-NMR spectra of **7b** (Table 1). Most informative are the $^1J_{CH}$ values of 113 and 115 Hz recorded for the diastereotopic methylene protons. These similar values are in the expected range for normal sp^3 CH bonds, and contrast with the $^1J_{CH}$ values centered around 100 and 120 Hz for complexes **5a**, **5a′**, **6**, and **6′**. This result is sensible from an electronic point of view since one might expect α agostic interactions to be 'blocked' in **7b**, i.e. π donation from the dimethylamido ligand involves the orbital that we proposed is used for an α agostic interaction in **5a**, **5a′**, **6**, or **6′**. Compound **7b** shows no evidence of tautomerizing to $CpW(C\text{-}CMe_3)(NMe_2)(CH_2Ad)$ at room temperature over the course of 2 weeks (Eq. (9)), consistent with the 18 electron count if amido π donation is included.

(9)

Reaction of $CpW(CAd)Cl_2$ with *N*-*t*-butylaminotrimethylsilane in dichloromethane gave $CpW(CAd)(NH\text{-}t\text{-}Bu)Cl$ (**8**) as yellow crystals in high yield. The NH proton is observed as a broad singlet at 9.40 ppm in the proton NMR spectrum and an N–H stretch is observed at 3249 cm^{-1} in the IR spectrum. In theory two rotameric forms of the amido complex could be formed, since formation of the W–N pseudo double bond employing an orbital that lies in the N–W–Cl plane, and therefore the *t*-butyl group would be oriented either toward the cyclopentadienyl ring or away from it. Only one rotamer was observed and we cannot say which rotamer that is.

Solutions of **8** are not stable towards migration of the amido α-H to the alkylidyne α-carbon atom. After standing a solution of **8** for 24 h at room temperature in dichloromethane-d_2 the major species that is present is what we propose to be $CpW(NCMe_3)(CHAd)Cl$ (**8′**). A second product (**8″**) is also observed at this point and becomes the sole product after 9 days at room temperature. It is also an alkylidene, but its NMR characteristics differ from those for **8′** (Table 4). We propose that **8′** and **8″** are W=C rotamers that differ in the relative orientation of the 1-adamantyl alkylidene substituent (Eq. (10)).



(10)

They are analogous to the known compound, $CpW(NPh)(CH\text{-}t\text{-}Bu)Cl$ [52], only one rotamer of which was observed. Formation of rotamers is best viewed in terms of the analogy between the Cp(RN)M core and the Cp_2M core [28], and in terms of the bonding found in $Cp_2Ta(CHR)(CH_2R)$ complexes [1]. Formation of the first rotamer formed by transfer of the amido H_α to the adamantylidyne C_α would place the 1-adamantyl group of the alkylidene *syn* to the Cp ring. Therefore we believe that **8′** is the *syn* rotamer, as shown in Eq. (10). This is not likely to be the favored orientation of the alkylidene, as the 1-adamantyl group is directed toward the cyclopentadienyl ring. Therefore the final product (**8″**) is believed to be that in which the 1-adamantyl group points

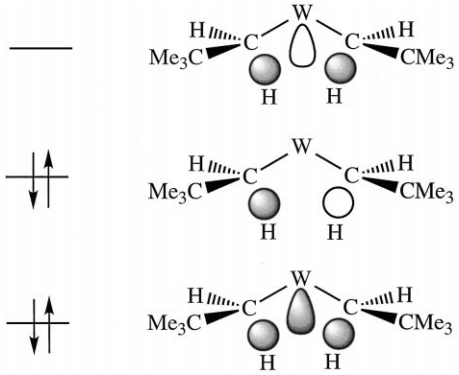


Fig. 3. A simple MO description of the 'double agostic' interaction.

Table 4
Selected NMR parameters for complexes **8**, **8′** and **8″** (in CD_2Cl_2)

Complex	δ ^{1}H (Cp)	δ ^{1}H (α-H)	δ ^{13}C (α-C)	$^1J_{CH}$ (Hz)
CpW(CAd)(N*H*CMe$_3$)Cl (**8**)	6.08	9.39	303.5	
syn-CpW(NCMe$_3$)(C*H*Ad)Cl (**8′**)	6.12	11.15[a]	264.7	131.3
anti-CpW(NCMe$_3$)(C*H*Ad)Cl (**8″**)	6.05	10.40[b]	274.1	123.5

[a] $^2J_{WH} = 14.1$ Hz.
[b] $^2J_{WH} < 4$ Hz.

away from the cyclopentadienyl ring (*anti* rotamer). Consistent with this assignment is the fact that irradiation of the Cp resonance in the proton NMR spectrum of **8″** results in an NOE enhancement of the alkylidene's H_α resonance. Note that the *syn* and *anti* notations here are different than those for tungsten and molybdenum complexes of the type M(CHR)(NR′)(OR″)$_2$, where the imido ligand is employed as the reference for assigning *syn* and *anti* alkylidene orientations [53,54]. Since the imido ligand is pseudo triply bound to tungsten, and the CpW(N–*t*-Bu) fragment is metallocene-like, one would not expect any agostic interaction involving the α proton of the alkylidene ligand, and no evidence for an α agostic interaction is observed. Similar arguments were put forward in order to explain the lack of agostic interactions in 18 electron compounds of the type $Cp_2Ta(CHR)X$ [55], which are related to **8** and **8′** via the analogy between Cp_2M and Cp(RN)M cores.

Migration of an amido ligand's H_a to a neopentylidyne C_a atom was the first method developed for synthesizing imido neopentylidene complexes [2]. Therefore it is not surprising to find that **8** is converted into **8′** and ultimately **8″** by a 'proton migration' reaction. However, it was noted at that time that the process appeared to be catalyzed by external base (e.g. NEt_3). Therefore, in the absence of detailed studies, we cannot exclude the possibility that this particular 'migration' reaction actually is catalyzed by external base, e.g. by traces of *t*-BuNH_2. All evidence in the literature so far suggests that π donation from a primary amido ligand takes precedence over any α agostic C–H interaction a primary amido ligand, and that proton migration from a nitrogen to a carbon ligand is fundamentally different from proton migration from a carbon to a carbon ligand.

3. Discussion and conclusions

The data presented here suggest that there is a strong correlation between an agostic CH_α interaction and the tendency for a neopentyl or adamantyl proton to migrate to a neighboring alkylidyne ligand to give what we must presume is a bisalkylidene intermediate and then a new alkylidyne complex. Proton migration in CpW(CAd)(CH_2CMe_3)X compounds occurs considerably faster when X = CH_2CMe_3 than when X = Cl, even after considering also the expected rate enhancement due to a statistical factor of two, primarily (we propose) because the chloride is so much less demanding sterically than the neopentyl ligand. However, a constrained orientation of an alkyl group in a crowded environment is an inseparable part of the phenomenon, and the fraction of its contribution to the whole cannot be quantified. The lack of tautomerization in **5b** and **5c** is consistent with the lack of any α agostic interactions and with observed rates of α abstraction in d^0 alkyl complexes to give alkylidenes that rapidly decline in the order $CH_2CMe_3 > CH_2Ph \gg Me$. The extent to which the agostic interaction could exist in the absence of accompanying steric factors that reinforce it in general should depend heavily upon the energy of the acceptor orbital and its ability to accept electron density from a CH bond. In fact, at this stage no definitive evidence has been obtained for an α agostic interaction in a methyl ligand. Even in $[W(\eta^5\text{-}C_5Me_5)Me_4]^+$, which is known to be deprotonated readily to give intermediate, unstable $W(\eta^5\text{-}C_5Me_5)Me_3(CH_2)$ [56], a solid state NMR study has revealed no evidence for an α agostic interaction [57].

The reason why bisalkylidene intermediates such as CpW(CHAd)($CHCMe_3$)Cl are not lower in energy than the observed alkyl alkylidyne complexes is not obvious. Both hypothetical CpW(CHAd)($CHCMe_3$)Cl and known $CpTa(CHCMe_3)_2(PMe_3)$ are 16 electron species, as are CpW(CAd)(CH_2CMe_3)Cl and hypothetical $CpTa(CCMe_3)(CH_2CMe_3)(PMe_3)$. It should be noted, however, that bisneopentylidene complexes such as $CpTa(CHCMe_3)_2(PMe_3)$ have not been thoroughly studied. In particular it was noted that the two neopentylidene ligands in $CpTa(CHCMe_3)_2(PMe_3)$ become equivalent at 60–80°C in proton and carbon NMR spectra [12], but the nature of the equilibration was not examined in detail. At that time equilibration was ascribed to rotation of the neopentylidene ligands to give an intermediate with mirror symmetry. Although $CpTa(CCMe_3)(PMe_3)_2Cl$ was known, and it was known to react with $LiCH_2CMe_3$ to give $CpTa(CHCMe_3)_2(PMe_3)$ via proposed 'CpTa(C-CMe_3)(PMe_3)$_2$(CH_2CMe_3)' the possibility of equilibration of the neopentyl groups via intermediate

$CpTa(CCMe_3)(CH_2CMe_3)(PMe_3)$ was not considered. Neopentylidene ligands in complexes such a trigonal bipyramidal $Ta(CHCMe_3)_2(PMe_3)_2X$ ($X = Cl$, CH_2CMe_3, etc.) [13] also equilibrate readily, but on the basis of the reaction of $Ta(CHCMe_3)_2(PMe_3)_2(CD_2CMe_3)$ with acetone to give ca. two equivalents of $Me_2C{=}CHCMe_3$-d_0 alkylidene equilibration was ascribed to alkylidene ligand rotation. There would seem to be a significant possibility that neopentylidene ligands equilibrate in some circumstances, if not in all circumstances, via α proton migration from one neopentylidene ligand to another to form a neopentyl neopentylidyne intermediate. Therefore the energy difference between $CpTa(CCMe_3)(CH_2CMe_3)(PMe_3)$ and $CpTa(CHCMe_3)_2(PMe_3)$ may not be large. The tantalum systems clearly warrant further study before any definitive conclusions can be drawn. In any case tantalum bisneopentylidene complexes are the lower energy species. We speculate that the efficiency of an α agostic interaction in at least one of the neopentylidene ligands in $CpTa(CHCMe_3)_2(PMe_3)$ is the reason why $CpTa(CHCMe_3)_2(PMe_3)$ is stabilized relative to $CpTa(CCMe_3)(CH_2CMe_3)(PMe_3)$. The recently reported rearrangement of a tantalum ethylene complex to its ethylidene tautomer [4,58] also was rationalized in terms of a strong α agostic interaction and the resulting 18 electron count. We further speculate that (for example) $CpW(CAd)(CH_2CMe_3)Cl$ is lower in energy than $CpW(CHAd)(CHCMe_3)Cl$ because of the inherent strength of the W≡C bond but perhaps primarily because of a weaker α agostic interaction in one of the alkylidene ligands in 16 electron $CpW(CHAd)(CHCMe_3)Cl$ than in a 16 electron tantalum bisalkylidene complex.

The original goal was to observe a proton migration analogous to that proposed for conversion of $W(CSiMe_3)(CH_2CMe_3)_3$ to $W(CCMe_3)(CH_2CMe_3)_2(CH_2SiMe_3)$ [11]. In this context it is worth noting that α proton scrambling in $CpW(CAd)(CH_2CMe_3)_2$ (ca. 5×10^{-5} s^{-1} at 298 K) appears to be significantly faster than α proton migration in $W(CSiMe_3)(CH_2CMe_3)_3$ (ca. 1.7×10^{-5} s^{-1} at 352 K) or α proton migration in $Ta(CDCMe_3)(CH_2CMe_3)_3$ (ca. 3.5×10^{-5} s^{-1} at 348 K). In view of these results and the uncertainty concerning the mechanism of neopentylidene ligand equilibration in $CpTa(CHCMe_3)_2(PMe_3)$, we may not any longer be justified in saying that α proton migration from an alkyl ligand to an alkylidyne ligand in 'd^0' systems is necessarily inherently 'slow'. At the same time it should be pointed out that α-hydrogen migration in the $CpW(CAd)(CH_2CMe_3)X$ systems conceivably could involve migration of H_α first to the cyclopentadienyl ligand and then to the alkylidyne's C_α, although this possibility is not thought to be very likely. In any case detailed kinetic studies of both tungsten alkyl alkylidyne complexes and tantalum bisneopentylidene complexes will be necessary before firm conclusions can be reached.

4. Experimental section

4.1. General procedures

All experiments were performed under nitrogen in a Vacuum Atmospheres drybox or under argon using standard Schlenk techniques. All solvents were purified by standard techniques while deuterated NMR solvents were dried and stored over activated 4 Å molecular sieves before use.

$W_2(OCMe_3)_6$ was prepared by adding $Na[W_2Cl_7(THF)_5]$ [33] (prepared in situ in THF from WCl_4 and sodium [32]) to a THF solution of six equivalents of $LiOCMe_3$ (prepared from Li metal and *t*-butanol in hexane). 1-Adamantanecarbonitrile, trimethylsilyl triflate, *N*,*N*-dimethylaminotrimethylsilane, and *N*-*t*-butylaminotrimethylsilane were purchased commercially and used as received. Solutions of benzylmagnesium chloride and methylmagnesium chloride were purchased from Aldrich and titrated before use. Neopentylmagnesium chloride [59] and neopentyllithium [60] were prepared as described in the literature.

Proton spectra were referenced internally by the residual solvent proton signal relative to tetramethylsilane. Carbon spectra were referenced internally relative to the ^{13}C signal of the NMR solvent relative to tetramethylsilane. All spectra were run in C_6D_6, except where noted otherwise. All coupling constants are reported in Hz; those found in Tables 1 and 4 are not reported below. IR spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses (C, H, N) were performed in our laboratories using a Perkin-Elmer PE2400 microanalyzer or by Oneida Research Services, Whitesboro, New York.

4.2. $W(CAd)(OCMe_3)_3$ (1)

1-Adamantanecarbonitrile (2.91 g, 18.08 mmol) was added to a solution of $W_2(OCMe_3)_6$ (14.58 g, 18.08 mmol) in pentane (175 ml. The deep red color of $W_2(OCMe_3)_6$ soon faded as a voluminous white precipitate formed. The mixture was stirred overnight and the $[W(N)(OCMe_3)_3]_x$ collected by filtration. The filtrate was concentrated in vacuo and cooled to -40°C to afford 8.0 g (80%) of colorless $W(CAd)(OCMe_3)_3$ in three crops. An analytical sample was obtained by double recrystallization from pentane: ^1H-NMR δ 2.08 (br, 6, Ad), 2.00 (br, 3, Ad), 1.62 (br, q 6, Ad), 1.503 (s, 27, $OCMe_3$); $^{13}C\{^1H\}$-NMR δ 272.1 ($J_{CW} = 294.1$, *C*Ad), 79.0 ($OCMe_3$), 52.7 (C*Ad*), 47.0 (Ad), 37.3 (Ad),

33.0 (OCMe_3), 29.9 (Ad). Anal. Calc. for $C_{23}H_{42}O_3W$: C, 50.19; H, 7.69. Found C, 50.03; H, 7.70.

4.3. W(CAd)(OCMe$_3$)$_2$(OTf)(dme) (2)

Trimethylsilyl triflate (2.92 g, 13.2 mmol) was added dropwise to a solution of **1** (7.24 g, 3.87 mmol) and dimethoxyethane (3.62 g) in pentane (125 ml) at −40°C. Bright yellow microcrystals began to appear after addition began. The mixture was stood for 1 h at –40°C and the microcrystals were collected by filtration and washed with pentane (3 × 15 ml); yield 9.03 g (96%). The product is thermally sensitive and should be stored below room temperature or used immediately: ^{1}H-NMR δ 3.98 (s, 3, MeOCH$_2$), 3.57 (br, 1, MeOCH_2), 3.08 (s, 3, MeOCH$_2$), 3.02 (br, 1, MeOCH_2), 2.96 (br, 1, MeOCH_2), 2.04 (br, 9, OCMe_3), 1.99 (br, 3, Ad), 1.60 (br, 9, OCMe_3), 1.53 (br, 6, Ad), 1.49 (br, 6, Ad); ^{13}C{^{1}H}-NMR δ 288.1 (J_{CW} = 273.5, CAd), 120.6 (J_{CF} = 318.4, O_3SCF_3), 80.13 (br, OCMe$_3$), 80.08 (br, OCMe$_3$), 75.2 (MeOCH_2), 73.4 (MeOCH_2), 69.5 (MeOCH$_2$), 59.2 (MeOCH$_2$), 52.2 (J_{CW} = 40.0, CAd), 46.6 (Ad), 37.1 (Ad), 33.1 (br, OCMe_3), 32.9 (br, OCMe_3), 29.7 (Ad). An analytical sample was recrystallized from toluene at −40°C. Anal. Calc. for $C_{24}H_{43}F_3O_7SW$: C, 40.23; H, 6.05. Found: C, 40.27; H, 6.27.

4.4. CpW(CAd)(OCMe$_3$)$_2$ (3)

A solution of NaCp in THF (4.6 ml, 2.0 M, 9.1 mmol) was added to a solution of **2** (6.50g, 9.11 mmol) in THF (70 ml) at −40°C. The resulting light orange solution was stirred overnight at room temperature. The volatiles were removed in vacuo and the residue was extracted with pentane (100 ml). The mixture was filtered and the solvent was removed from the filtrate in vacuo to give a yellow solid. This solid was recrystallized from pentane to yielded 4.88 g (99%) of the product: ^{1}H-NMR δ 6.071 (s, 5, Cp), 1.97 (br, 3, Ad), 1.83 (d, 6, Ad), 1.60 (br, 6, Ad), 1.41 (s, 18, OCMe_3); ^{13}C{^{1}H}-NMR δ 285.2 (J_{CW} = 277.2, CAd), 105.7 (Cp), 76.7 (OCMe$_3$), 51.8 (J_{CW} = 43.5, CAd), 46.6 (Ad), 37.4 (Ad), 32.8 (OCMe_3), 29.9 (Ad). An analytical sample was prepared by recrystallizing a sample from pentane. Anal. Calc. for $C_{24}H_{38}O_2W$: C, 53.15; H, 7.06. Found: C, 53.42; H, 7.24.

4.5. CpW(CAd)Cl$_2$ (4)

A solution of 2,6-lutidinium chloride (0.500 g, 3.48 mmol) and trimethysilyl chloride (3.00 g, 27.6 mmol) in dichloromethane (20 ml) was added to **3** (3.00g, 5.53 mmol) in dichloromethane (15 ml). The solution immediately turned deep red and slowly became purple over a period of ca. 4 h. After 12 h the volatile solvents were removed in vacuo from the intensely purple solution, and the resulting purple solid was extracted with a 50/50 mixture of ether and pentane (125 ml). Purple crystals formed upon concentrating the solution to ca. 10 ml. The solution was stood overnight at −40°C and 2.10 g (81%) of purple product was collected: ^{1}H-NMR δ 5.72 (s, 5, Cp), 1.92 (br, 3, Ad), 1.62 (br d, 6, Ad), 1.47 (br t, 6, Ad); ^{13}C{^{1}H}-NMR δ 328.6 (J_{CW} = 233.4, CAd), 106.1 (Cp), 51.3 (J_{CW} = 32.9, CAd), 44.7 (Ad), 36.6 (Ad), 29.0 (Ad). An analytical sample was recrystallized from ether/dichloromethane at −40°C. Anal. Calc. for $C_{16}H_{20}Cl_2W$: C, 41.14; H, 4.32. Found: C, 41.17; H, 4.42.

4.6. CpW(CAd)(CH$_2$CMe$_3$)$_2$ (5a)

Neopentylmagnesium chloride (0.259 ml, 2.97 M in ether, 0.768 mmol) was added to a solution of **4** (0.175 g, 0.375 mmol) in ether (10 ml) at −40°C. The solution immediately turned cherry red and became turbid. The mixture was stirred at room temperature for 1h and dioxane (0.070 ml, 0.82 mmol) was added and the suspension was filtered through Celite. The filtrate was concentrated to dryness and the solid was extracted with pentane (10 ml). The mixture was filtered again and the volatile components were once again removed in vacuo to afford a red powder which was recrystallized from pentane at −40°C to afford 0.143 g (71%) of small red crystals in two crops: ^{1}H-NMR δ 5.40 (s, 5, Cp), 3.54 ($J_{AB} + J_{AB'}$ = 11.3, 2, CH_2CMe$_3$), 1.99 (br, 9, Ad), 1.64 (br, 6 Ad), 1.30 (s, 18, CMe_3), −1.14 ($J_{BB'} = {}^4J_{HH}$ = 2.1, $^2J_{WH}$ = 12.6, 2, CH_2CMe$_3$); ^{13}C-NMR δ 300.4 (CAd), 100.19 (Cp), 90.67 (J_{CW} = 94.9, CH$_2$CMe$_3$), 51.98 (CAd), 45.18, 37.18 (Ad), 35.32 (CMe$_3$), 34.37 (CMe_3), 29.52 (Ad). Anal. Calc. for $C_{26}H_{42}W$: C, 58.00; H, 7.86. Found: C, 57.74; H, 7.73.

4.7. CpW(CAd)(CH$_2$Ph)$_2$ (5b)

Benzylmagnesium chloride (0.593 ml, 1.11 M in ether, 0.658 mmol) was added to a chilled (−40°C) solution of **4** (0.150 g, 0.321 mmol) in ether (10 ml). The solution immediately turned yellow. After 1 h dioxane (0.057 ml, 0.66 mmol) was added and the volatile components were removed in vacuo. The residue was extracted with toluene (25 ml) and the extract was filtered through Celite. The filtrate was concentrated to ca. 1.5 ml and stood at −40°C to afford 0.147 g (79%) of yellow crystals: ^{1}H-NMR (CD_2Cl_2) δ 7.27 (t, 1, Ph$_p$), 7.05 (d, 2, Ph$_o$), 6.96 (t, 2, Ph$_m$), 5.51 (s, 5, Cp), 2.42 (d, $^2J_{HH}$ = 7.5, $^2J_{WH}$ = 4.8, 2, CH_2Ph,), 1.94 (br, 3, Ad), 1.69 (d, 6, Ad), 1.63 (t, 6, Ad), 1.48 (d, $^2J_{HH}$ = 7.5, $^2J_{WH}$ = 8.1, 2, CH_2Ph); ^{13}C-NMR δ 294.5 (WCAd), 135.6 (C$_i$), 131.4, (C$_o$), 127.5 (C$_p$), 125.6 (C$_m$), 97.7 (Cp), 53.2 (CAd), 42.9 (Ad), 37.2 (Ad), 32.4 (J_{CW} = 63.3, CH$_2$Ph), 29.2 (Ad). An analyti-

cal sample was recrystallized from ether/dichloromethane at −40°C. Anal. Calc. for $C_{30}H_{34}W$: C, 62.29; H, 5.92. Found: C, 62.41; H, 5.86.

4.8. *CpW(CAd)Me$_2$ (**5c**)*

A solution of methylmagnesium chloride (0.228 ml, 2.89 M in THF, 0.658 mmol) was added to a solution of CpW(CAd)Cl_2 (0.150 g, 0.321 mmol) in THF (3 ml) at −40°C. After standing the solution for ca. 10 min at −40°C, dioxane (0.070 ml, 0.82 mmol) was added and the solvents were removed in vacuo. The residue was was extracted with pentane (10 ml) and the extract was filtered and taken to dryness in vacuo. The resulting red powder was recrystallized from ether/pentane at −40°C to yield 0.099 g (72%) of red crystals in two crops: ^{1}H-NMR δ 5.42 (s, 5, Cp), 2.03 (br, 3, Ad), 1.89 (d, 6, Ad), 1.67 (br, 6, Ad), 1.13 (s, 6, *Me*,); ^{13}C-NMR δ 300.4 ($J_{CW} = 240$, *C*Ad), 100.14 (Cp), 50.79 (C*Ad*), 44.72 (Ad), 40.25 ($J_{CW} = 93$, W–*C*H$_3$), 37.25, 29.37 (Ad). Anal. Calc. for $C_{18}H_{26}W$: C, 50.72; H, 6.14. Found: C, 50.97; H, 5.97.

4.9. *CpW(CAd)(CH$_2$CMe$_3$)Cl (**6**)*

Neopentylmagnesium chloride (0.108 ml, 2.97 M in ether, 0.321 mmol) was added to a stirred solution of **4** (0.150 g, 0.321 mmol) in ether (10 ml) at −40°C. The solution turned red immediately and became turbid. The solution was stood at room temperature for 15 min and dioxane (0.028 ml, 0.32 mmol) was added. The volatile components were removed in vacuo and the residue was extracted with pentane (10 ml). THe extract was filtered and concentrated to dryness. The resulting red powder was recrystallized from pentane at −40°C to yield 0.123 g (76%) of red microcrystals in two crops: ^{1}H-NMR δ 5.52 (s, 5, Cp), 4.79 (d, $^2J_{HH} = 10.3$, $^2J_{WH} = 4.1$, 1, C*H*$_2$CMe$_3$), 1.95 (br, 3, Ad), 1.81 (br, 6, Ad), 1.56 (br, 6, Ad), 1.18 (s, 9, CH$_2$C*Me*$_3$), −0.45 (d, $^2J_{HH} = 10.3$, $^2J_{WH} = 13.0$, 1, C*H*$_2$CMe$_3$); ^{13}C-NMR δ 313.6 ($J_{CW} = 242$, *C*Ad), 101.80 (Cp), 98.08 ($J_{CW} = 93.8$, *C*H$_2$CMe$_3$), 51.74 (C*Ad*), 45.04 (Ad), 36.88 (Ad), 36.49 (C*C*Me$_3$), 33.51 (CH$_2$C*Me*$_3$), 29.25 (Ad). Anal. Calc. for $C_{21}H_{31}ClW$: C, 50.17; H, 6.21. Found: C, 50.24; H, 6.01.

4.10. Conversion of ***5a*** to a mixture containing *CpW(CCMe$_3$)(CH$_2$CMe$_3$)(CH$_2$Ad) (**5a′**)*

A solution of **5a** (0.050 g, 0.093 mmol) in benzene-d_6 (0.60 ml) and a small amount of C_6H_6 was added as an internal standard. The solution was transferred to a Teflon-sealed NMR tube and monitored periodically over 2.5 days. After 48 h an equilibrium mixture of **5a** and **5a′** was reached; the ratio was 1:2.1. After 55 h, the solution was added to a solution of 2,6-lutidinium chloride (0.030 g, 0.21 mmol) in dichloromethane (3 ml). The mixture was stood overnight and the volatile components were removed in vacuo the next day. The resulting residue was extracted with ether and filtered through Celite to remove unreacted 2,6-lutidinium chloride. The sample was taken to dryness in vacuo and dissolved in benzene-d_6. A 2.0 to 1 ratio of CpW(CCMe$_3$)Cl_2 and CpW(CAd)Cl_2 was measured by integrating the Cp resonances at δ 5.63 and 5.69 ppm, respectively.

^{1}H-NMR (**5a′**) δ 5.37 (s, 5, Cp), 3.56 (d, $^2J_{HH} = 11.7$, 1, C*H*$_2$), 3.28 (d, $^2J_{HH} = 12.3$, 1, C*H*$_2$), 2.11 (m, 3, Ad), (br d of t, 3, Ad), 1.77 (t, 6 Ad), 1.623 (br d of t, 3, Ad), 1.35 (C*Me*$_3$), 1.273 (C*Me*$_3$), −0.88 (dd, $^2J_{HH} = 12.3$ Hz, $^4J_{HH} = 2.6$, 1, C*H*$_2$), −1.50 (dd, $^2J_{HH} = 11.7$, $^4J_{HH} = 2.6$, 1, C*H*$_2$); ^{13}C-NMR δ 299.62 (*C*Ad), 100.39 (Cp), 94.98 ($J_{CW} = 93.5$, *C*H$_2$), 87.78 ($J_{CW} = 95.6$, *C*H$_2$), 49.74 (C*Ad*), 47.21 (CAd), 37.84 (Ad), 35.57, 33.48 (C*Me*$_3$), 30.42 (Ad).

4.11. Conversion of ***6*** to a mixture containing *CpW(CCMe$_3$)(CH$_2$Ad)Cl (**6′**)*

6 (0.072 g, 0.093 mmol) was dissolved in benzene-d_6 (0.60 ml) and a small amount of C_6H_6 was added as an internal standard. The solution was transferred to a Teflon-sealed NMR tube and monitored periodically over 3 weeks while standing at room temperature. After 14 days an equilibrium mixture of **6** and **6′** was reached in the ratio of 1:1.05 with minimal sample decomposition. After 3 weeks the mixture was quenched with 2,6-lutidinium chloride as described for the mixture of **5a** and **5a′** to give a 1.0:1 ratio of CpW(CCMe$_3$)Cl_2 and CpW(CAd)Cl_2.

^{1}H-NMR (**6′**) δ 5.50 (s, 5, Cp), 4.72 (d, $^2J_{HH} = 9.9$ Hz, $^2J_{WH} = 4.4$ Hz, 1, C*H*$_2$Ad), 2.05 (br, 3, Ad), 1.80 (br d of m, 6, Ad), 1.71 (br, 6, Ad), 1.41 (br d of m, 3 Ad), 1.23 (s, 9, CC*Me*$_3$), −0.63 (d, $^2J_{HH} = 9.9$, $^2J_{WH} = 12.8$, 1, C*H*$_2$Ad); ^{13}C-NMR δ 312.8 ($J_{CW} = 242$, *C*Ad), 101.89 (Cp), 100.58 (*C*H$_2$Ad), 49.35 (C*Ad*), 46.15 (Ad), 38.62 (C*C*Me$_3$), 37.37 (Ad), 32.99 (CH$_2$C*Me*$_3$), 29.96 (Ad).

4.12. *CpW(CAd)(NMe$_2$)Cl (**7a**)*

Me$_3$SiNMe$_2$ (60 μl, 0.37 mmol) was added to a solution of **4** (0.160 g, 0.343 mmol) at −40°C in dichloromethane (5 ml). The solution turned from brilliant purple to light yellow over a period of 15 min. The mixture was stirred for 1h and the volatile components were removed in vacuo. The residue was extracted with ether (10 ml) and the extracts were filtered and the filtrate was concentrated and cooling to −40°C to afford 0.142 g (87%) of yellow crystals: ^{1}H-NMR δ 5.73 (s, 5, Cp), 4.25 (s, 3, N*Me*$_2$), 3.04 (s, 3, N*Me*$_2$), 1.93 (br, 3, Ad), 1.78 (d, 6, Ad), 1.57 (t, 6, Ad); ^{13}C{^{1}H}-NMR

δ 302.3 ($J_{CW} = 257.7$, *C*Ad), 102.2 (Cp), 71.1 (N*Me*$_2$), 57.1 (N*Me*$_2$), 52.5 ($J_{CW} = 36.4$, C*Ad*), 44.2 (Ad), 37.0 (Ad), 29.0 (Ad). An analytical sample was recrystallized from ether at -40 °C. Anal. Calc. for $C_{18}H_{26}NClW$: C, 45.45; H, 5.51; N, 2.94. Found: C, 45.50; H, 5.37; N, 2.72.

4.13. CpW(CAd)(NMe$_2$)(CH$_2$CMe$_3$) (7b)

Neopentyllithium (0.012 g, 0.15 mmol) in ether (1 ml) was added with stirring to a solution of **7a** (0.060 g, 0.13 mmol) in ether (3 ml) at −40°C. The solution became cloudy immediately. The mixture was stood for 6 h at −40°C and then taken to dryness in vacuo. Dichloromethane was added in order to destroy any excess neopentyllithium. The residue was extracted with pentane and the extract was filtered. The extracts were taken to dryness in vacuo. The residue was recrystallized from pentane at −40°C to afford 0.045 g (70%) of orange crystals: ^{1}H-NMR (CD_2Cl_2) δ 5.78 (s, 5, Cp), 4.10 (s, 3, N*Me*$_2$), 3.16 (s, 3, N*Me*$_2$), 1.96 (br, 3, Ad), 1.77 (d, 6, Ad), 1.69 (AB, $^2J_{WH} = 11.7$ Hz, 1, C*H*$_2$CMe$_3$), 1.63 (t, 6, Ad), 1.53 (AB, $^2J_{WH} = 8.7$ Hz, 1, C*H*$_2$CMe$_3$), 1.02 (s, 9, CH$_2$C*Me*$_3$); ^{13}C{^{1}H}-NMR δ 291.7 ($J_{CW} = 254.7$ Hz, *C*Ad), 100.63 (Cp), 71.00 (N*Me*$_2$), 56.27 (N*Me*$_2$), 52.27 (C*Ad*), 48.60 ($J_{CW} =$ 118.6, *C*H$_2$CMe$_3$), 45.15, 37.46 (Ad), 35.52 (CH$_2$*C*Me$_3$), 35.11 (CH$_2$C*Me*$_3$), 29.63 (Ad). Anal. Calc. for $C_{23}H_{37}NW$: C, 54.02; H, 7.29; N, 2.74. Found: C, 54.18; H, 7.51; N, 2.62.

4.14. CpW(CAd)(NH–t-Bu)Cl (8)

Me$_3$SiNH(*t*-Bu) (0.195 g, 1.46 mmol) was added to a solution of **4** (0.500 g, 1.07 mmol) in dichloromethane (15 ml). After 30 min the volatiles were removed from the solution in vacuo. The residue was extracted with ether, and the extracts were filtered, concentrated in vacuo and cooled to yield 0.463 g (88%) of yellow crystals: ^{1}H-NMR (CD_2Cl_2) δ 9.40 (br, 1, N*H*), 6.077 (s, 5, Cp), 2.00 (br, 3, Ad), 1.79 (d, 6, Ad), 1.64 (t, 6, Ad), 1.39 (s, 9, NH–*t-Bu*); ^{13}C-NMR δ 303.54 (*C*Ad), 103.01 (Cp), 59.53 (N*C*Me$_3$), 52.72 (C*Ad*), 44.49 (Ad), 37.05 (C*Me*$_3$), 33.97, 29.36 (Ad); IR (Nujol/KBr) 3249 ν(NH) cm^{-1}. Anal. Calc. for $C_{20}H_{30}NClW$: C, 47.68; H, 6.00; N, 2.78. Found: C, 48.04; H, 6.05; N, 2.67.

4.15. anti-CpW(NCMe$_3$)(CHAd)Cl (8″)

A saturated solution of **8** in dichloromethane-d_2 (ca. 0.020 g in 0.60 ml) was allowed to stand in a Teflon-sealed NMR tube for 11 days. After 3 days ^{1}H resonances for **8** had completely disappeared and a mixture of **8′** and **8″** had formed. After 10 days only **8″** was present and < 5% of the sample had decomposed as measured by a CH_2Cl_2 internal standard: ^{1}H-NMR δ 5.50 (s, 5, Cp), 4.72 (d, $^2J_{HH} = 9.9$ Hz, $^2J_{WH} = 4.4$ Hz, 1, C*H*$_2$Ad), 2.05 (br, 3, Ad), 1.80 (br d of m, 6, Ad), 1.71 (br, 6, Ad), 1.41 (br d of m, 3 Ad), 1.23 (s, 9, CC*Me*$_3$), −0.63 (d, $^2J_{HH} = 9.9$, $^2J_{WH} = 12.8$, 1, C*H*$_2$Ad); ^{13}C–NMR δ 274.1 ($J_{CW} = 154.7$ in $CDCl_3$), *C*Ad), 103.82 (Cp), 69.81 (N*C*Me$_3$), 46.65 (Ad), 45.82 (C*Ad*), 37.40 (Ad), 31.77 (C*Me*$_3$), 30.23 (Ad).

Complete NMR data for *syn*-CpW(NCMe$_3$)(CHAd)Cl **(8′)** could not be obtained. Selected data can be found in Table 4.

5. Supporting information available

Crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters, for **5a**.

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