Nuclear Magnetic Resonance Studies on Partially Deuteriated Transition Metal–Methyl Derivatives

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Nuclear magnetic resonance studies on [W(η-C_5Me_4Et)$(CH_2D)_4$][PF_6] show a strong temperature dependence of the isotope shift [δ(CH_3) − δ(CH_2D)] indicating the presence of a monoagostic methyl group. The magnitude and sign of the geminal coupling constant ^2J(H–D) [and ^2J(H–H)] and the isotope shift, together with the temperature dependence of this shift, have been recorded for [Ti(CH_2D)Cl_3], [Ti(CH_2D)Cl_3(dmpe)] (dmpe = $Me_2PCH_2CH_2PMe_2$), [Ta$(CH_2D)_nCl_{5-n}$] (n = 1–3), [M(η-C_5H_5)$_2$$(CH_2D)_2$] (M = Ti, Zr or Hf), [M(η-C_5H_5)$_2$(CH_2D)(thf)][BPh_4] (M = Ti or Zr, thf = tetrahydrofuran), [Ti(η-C_5H_5)$_2$(CH_2D)F], [Zr(η-C_5H_5)$_2$(CH_2D)(MeCN)$_2$][BPh_4], [Ti(η-C_5H_5)$(CH_2D)_3$], [M(η-C_5Me_4Et)$(CH_2D)_3$] (M = Ti, Zr or Hf) and [Y(η-C_5Me_5)$_2$(CH_2D)(thf)]. The isotope shifts for all these complexes are essentially temperature independent. A convenient synthesis of Li(CH_2D) is described.

The chemistry of compounds with agostic M⇽H–C bonds has been reviewed.[1–3] Whilst there are many examples of β-agostic alkyl groups there are relatively few simple α-agostic alkyls. However, α-agostic bonds have recently been implicated in intermediates or transition states in the carbon–carbon bond-forming step in Ziegler–Natta catalysis.[4] Therefore, we have set out to seek further evidence for agostic methyl groups in early transition-metal alkyl derivatives.

The presence of α-agostic bonds in M–CHRR′ groups is relatively easy to detect by, for example, ^1J(C–H) coupling constants and the M–C_α–C_β angle, even when the agostic and terminal hydrogens for R or R′ = H are undergoing exchange. It has, however, proved difficult to establish agostic bonding spectroscopically in simple methyl groups, partly because there is no example of an agostic methyl group which is static on the NMR time-scale.[3] For such rapidly exchanging agostic alkyl groups the NMR technique of isotopic perturbation of resonance (IPR), originally described by Saunders,[5a] and first applied to agostic systems by Shapley,[5b] provides perhaps the most reliable positive spectroscopic evidence.

In the IPR method the effect of partial deuteriation on the magnitudes of the ^{1}H chemical shift and on the values of ^1J(C–H) for the methyl group is determined. The basis of the technique is as follows; the zero-point energy difference between a C–H and a C–D bond is greater for a terminal than an agostic bond. Thus in an agostic CH_2D group there is a thermodynamic preference for the deuterium to occupy a terminal position. This changes the average environment of the ^{1}H nuclei under observation, and a change in the chemical shift to higher field results. As the temperature is lowered the population of agostic C–D bonds falls, accentuating the change in chemical shift.[3] Further, partially deuteriated agostic methyl groups may show a decrease in the value of the coupling constant ^1J(C–H) in the sequence $CH_3 > CH_2D > CHD_2$, and the coupling constants of the partially deuteriated complexes are also temperature dependent.

In summary, the presence of an agostic bond in a partially deuteriated methyl group is indicated by a marked change in the ^{1}H NMR chemical shift, in the order (lowest field) $\delta(CH_3) > \delta(CH_2D) > \delta(CHD_2)$ (highest field), and the chemical shifts are temperature dependent. It should be noted that there are secondary isotope shifts associated with deuteriated methyl groups in organic methyl compounds,[6] but such shifts are typically an order of magnitude smaller than those due to IPR.

We also investigated the possibility of using the magnitude and relative sign of the geminal ^2J(H–H) coupling constant of metal–methyl groups as a probe for α-agostic bonding. The relative sign of ^2J(H–H) for 18-electron metal methyls such as [Fe(η-C_5H_5)(CO)$_2$(CH_3)] has been determined to be negative.[7] In addition, the formally eight-electron compound [Ti(CH_3)Cl_3], which electron diffraction has shown to have an undistorted methyl group,[8] also has a negative geminal coupling constant ^2J(H–H).[9] Extended-Hückel calculations indicate that increasingly acute M–C–H angles, a possible result of α-agostic metal–methyl interaction, should lead to a more positive value of the geminal coupling constant.[10]

The origin of the term 'relative' for the sign of geminal coupling constants is as follows. Since known geminal coupling constants for hydrogens attached to both sp^2 and sp^3 carbons cover the approximate range 0–20 Hz,[11] it is possible that these values may be either positive or negative (note that the coupling constants of substituted ethylenes are typically close to zero). However, since the values of ^1J(C–H) coupling constants cover, at an extreme, the range 60–200 Hz, these values are all assumed to have the same sign; the sign of ^1J(C–H) has been determined to be positive for CH_3CN.[12] Using heteronuclear spin tickling and, more recently, two-dimensional NMR (see below) techniques, it is possible to determine the sign of ^2J(H–D) relative to that of ^1J(C–D). Since the ^{1}H, ^{2}D and ^{13}C nuclei all have positive magnetogyric ratios (γ), the sign of ^2J(H–H) is the same as that of ^2J(H–D), and the sign of ^1J(C–H) is the same as that of ^1J(C–D).

Results and Discussion

A rapid and convenient preparation of CH_2DCl, which avoids the use of ketene,[13] has been developed. The tin deuteride $SnBu^n_3D$ was prepared by the treatment of $SnBu^n_3Cl$ with $LiAlD_4$. The hydrostannolysis reaction of CH_2BrCl with $SnBu^n_3D$ gives pure CH_2DCl in high yield.[14] The analogous reaction between $CHBr_2Cl$ and 2 equivalents of $SnBu^n_3D$ gives CHD_2Cl.[15] The methylation reactions were carried out using Mg(CH_2D)Cl or halide-free Li(CH_2D) prepared by treatment of CH_2DCl with lithium in diethyl ether.[15]

The early transition metal–methyl compounds and the partially deuteriated methyl analogues studied in this work are given in Table 1, together with the chemical shift and coupling constant data.

Table 1 NMR data for the CH_2D complexes (J in Hz)

Compound	Solvent	$\delta(^1H)$[a]	$^2J(H\text{–}D)$	$^2J(H\text{–}H)$	$\Delta\delta_1$[b]	$\delta(^{13}C)$	$^1J(C\text{–}H)$
1 $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4][PF_6]$[c]	CD_2Cl_2	1.53	−1.75	−11.42	0.137 at 243 K (0.185 at 183 K)[d]	78.7	128
2 $[Ti(CH_2D)Cl_3]$	CD_2Cl_2	2.93	−1.73	−11.27	0.0414	118.2[e]	130
3 $[Ti(CH_2D)Cl_3(dmpe)]$	CD_2Cl_2	2.25[f]	—	—	0.057[f] (0.070 at 173 K)	87.1	131[g]
4 $[Ta(CH_2D)Cl_4]$	CD_2Cl_2	2.51	−2.18	−14.1	0.032 (0.038 at 203 K)	—	—
5 $[Ta(CH_2D)_2Cl_3]$	CD_2Cl_2	2.20	−2.06	−13.15	0.046 (0.055 at 203 K)	—	—
6 $[Ta(CH_2D)_3Cl_2]$	CD_2Cl_2	1.77	−2.13	−13.54	0.036 (0.039 at 203 K)	—	—
7 $[Ti(\eta\text{-}C_5H_5)_2(CH_2D)_2]$	C_6D_6	0.01	−1.47	−9.59	0.064	45.7	123
8 $[Zr(\eta\text{-}C_5H_5)_2(CH_2D)_2]$	$C_6D_5CD_3$	−0.17	−1.75	−11.39	0.043 (0.050 at 203 K)	29.8	116
9 $[Hf(\eta\text{-}C_5H_5)_2(CH_2D)_2]$	$C_6D_5CD_3$	−0.36	−1.80	−11.72	0.042 (0.049 at 203 K)	36.1	114
10 $[Ti(\eta\text{-}C_5H_5)_2(CH_2D)F]$	$CDCl_3$	0.90	−1.40	−9.12	0.037 (0.040 at 233 K)	42.0	128
11 $[Ti(\eta\text{-}C_5H_5)_2(CH_2D)(thf)]^+$	CD_2Cl_2	1.36	−1.28	−8.30	0.061	66.2	131
12 $[Zr(\eta\text{-}C_5H_5)_2(CH_2D)(thf)]^+$	CD_2Cl_2	0.72[f]	±1.67[h]	±10.89[f,h]	0.050	—	—
13 $[Zr(\eta\text{-}C_5H_5)_2(CH_2D)(MeCN)_2]^+$	CD_3CN	1.22	−1.81	−11.83	0.018	31.0	129
14 $[Ti(\eta\text{-}C_5H_5)(CH_2D)_3]$[i]	$C_6D_5CD_3$	1.30	−1.59	−10.35	0.042 (0.045 at 203 K)	69.7	—
15 $[Ti(\eta\text{-}C_5Me_4Et)(CH_2D)_3]$	$C_6D_5CD_3$	0.96	−1.64	−10.68	0.036 (0.038 at 203 K)	60.7	119
16 $[Zr(\eta\text{-}C_5Me_4Et)(CH_2D)_3]$	C_6D_6	0.23	−1.93	−12.57	0.037	45.5	113
17 $[Hf(\eta\text{-}C_5Me_4Et)(CH_2D)_3]$	C_6D_6	0.02	−1.98	−12.90	0.037	57.6	113
18 $[Y(\eta\text{-}C_5Me_5)_2(CH_2D)(thf)]$	C_6D_6	−0.74	−1.57	−10.24	0.037 (0.036 at 203 K)[j]	20.6	108

[a] The chemical shift of the CH_3 compound at 293 K. [b] The isotope shift, $\Delta\delta_1 = \delta(CH_3) - \delta(CH_2D)$ at 293 K unless indicated otherwise; values at lower temperature given in parentheses. [c] Data for equatorial methyl groups only; for the axial methyl group, $\delta(CH_3) = 3.31$, $\delta(CH_3) = 180.0$ and $^1J(C\text{–}H) = 126$ Hz, all at 243 K. [d] Value measured from a mixture of $[W(\eta\text{-}C_5Me_4Et)(CH_3)_4][PF_6]$ and $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4][PF_6]$. [e] At 200 K. [f] At 233 K. [g] Data from ref. 16. [h] Sign not determined. [i] Thermally sensitive, all data at 273 K, except $\Delta\delta_1$ at low temperature. [j] In $C_6D_5CD_3$.

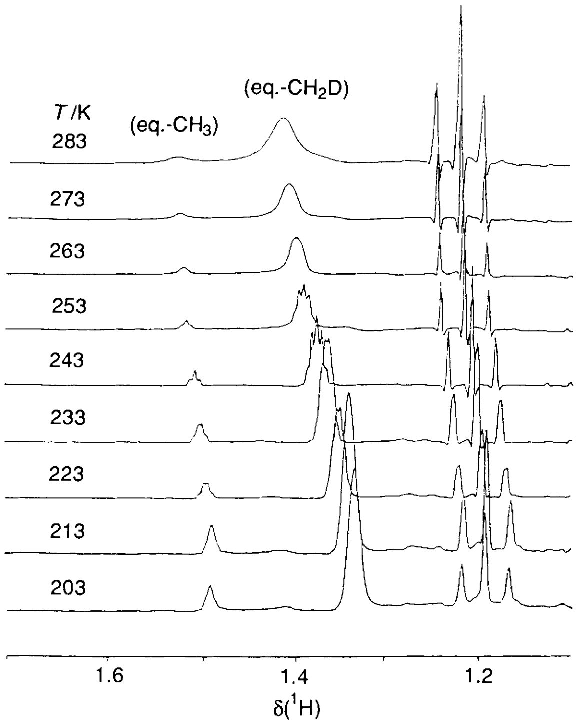


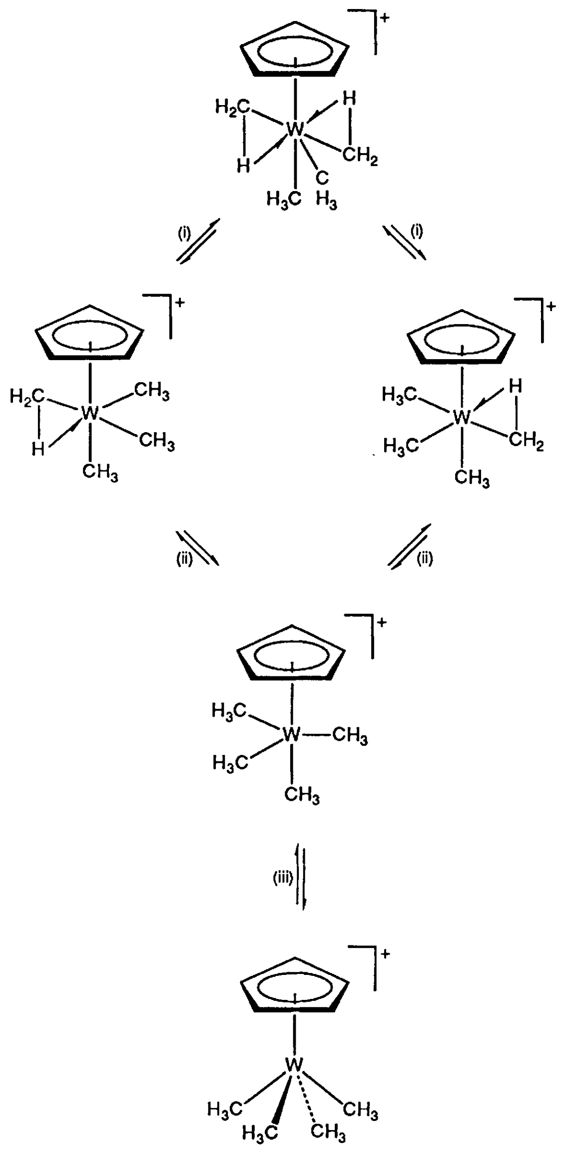
Fig. 1 Variable-temperature ^1H NMR spectrum of partially deuteriated $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4][PF_6]$ in CD_2Cl_2, showing the temperature dependence of the chemical shift of the equatorial methyl groups

IPR Studies.—The NMR data in Table 1 show that the only methyl derivative to exhibit substantial changes on partial deuteriation is the tungsten compound $[W(\eta\text{-}C_5Me_4R)(CH_3)_4][PF_6]$ **1** (R = Et). The compounds $[W(\eta\text{-}C_5Me_4R)(CH_3)_4][PF_6]$ **1** (R = Me or Et) were first described by Schrock and co-workers.[16,17] The crystal structure of **1** (R = Me) suggested a trigonal-bipyramidal geometry, rather than that of a square-based pyramid (or four-legged piano-stool) normally found for compounds of formulation $M(\eta\text{-}C_5R_5)X_4$.[17] Owing to disorder, however, the structural determination did not accurately resolve the positions of the methyl groups.

The variable-temperature ^1H NMR spectra of **1** (R = Et) show that the axial and equatorial methyl groups undergo exchange with a rate constant comparable to the frequency separation of the resonances.[17] Thus, at 300 MHz a single resonance is observed at 313 K, whilst two resonances in the intensity ratio 1:3 are observed below 283 K.

The partial variable-temperature ^1H NMR spectra of a partially deuteriated methyl derivative of **1** (R = Et) are shown in Fig. 1. Since the deuterium isotope purity of $LiAlD_4$ is 98% there is *ca.* 8% probability for the isotopomer $[W(\eta\text{-}C_5Me_4Et)(CH_3)(CH_2D)_3]^+$, but the probability of the isotopomer containing two CH_3 groups is negligible. The peak labelled equatorial CH_3 in Fig. 1 is thus due to the species $[W(\eta\text{-}C_5Me_4Et)(eq\text{-}CH_3)(eq\text{-}CH_2D)_2(ax\text{-}CH_2D)]^+$, whereas that labelled equatorial CH_2D is due to $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4]^+$. The most noticeable feature of the NMR spectra is that there is a temperature-dependent isotope shift (> 0.1 ppm) for the equatorial-methyl resonance. In contrast, the axial-methyl resonance behaves normally (data not shown), with a very small, and temperature-independent, isotope shift. The data strongly suggest that the axial methyl group is undistorted, but there is agostic bonding in the equatorial plane.

An important point which arises in the isotope shift experiments is how the rapid exchange between agostic and non-agostic equatorial methyl groups affects the observed shifts. The correct isotope shift value is *not* that measured from Fig. 1, but rather by comparing the equatorial-methyl chemical shifts of a *mixture* of $[W(\eta\text{-}C_5Me_4Et)(CH_3)_4]^+$ and $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4]^+$. In addition, if only one of the equatorial methyl groups is agostic, then the experimentally observed, exchange-averaged, isotope shift is one-third of the actual value of the shift had the system been static on the NMR time-scale. The isotope shift for **1** (R = Et) thus determined from such a mixture was 0.137 ppm at 243 K, increasing to 0.185 ppm at 183 K. In the crystal structure of **1** (R = Me) two of the equatorial C–W–C angles are greater than the third. This is most likely to be a result of disorder of an agostic methyl group such that the agostic hydrogen is either side of the mirror plane in the complex. We therefore conclude that only one of the equatorial methyl groups is agostic, so that the actual isotope shifts are 0.137 × 3 = 0.411 ppm at 243 K and 0.555 ppm at 183 K. These values are comparable with those observed by Calvert and Shapley[5b] in the original experiment on $[Os_3H(CO)_{10}(CH_2D)]$. Furthermore, agostic bonding readily accounts



Scheme 1 Possible mechanisms for the observed dynamic processes for complex **1** (R = Et): (i) associative and (ii) dissociative pathways for agostic methyl–methyl exchange and (iii) dissociative pathway for axial equatorial methyl exchange

for the apparent trigonal-bipyramidal rather than square-pyramidal geometry about the tungsten centre. The possible mechanisms for the dynamic processes observed for **1** (R = Et) are shown in Scheme 1.

It is possible to obtain chemical shift values for the equatorial methyl hydrogens[5] of **1** (R = Et) from a variable-temperature NMR experiment such as that shown in Fig. 1. In analysing the data, it is necessary, however, to take into account the fact that the $\delta(CH_3)$ chemical shift observed is due to the isotopomer $[W(\eta\text{-}C_5Me_4Et)(eq\text{-}CH_3)(eq\text{-}CH_2D)_2(ax\text{-}CH_2D)]^+$, whilst the $\delta(CH_2D)$ chemical shift is due to $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4]^+$. The expressions used for these chemical shifts in terms of δ_t (the chemical shift of a terminal C–H), δ_b (the chemical shift of a bridging $C\text{–}H_b\rightharpoonup M$ hydrogen) and ΔE (the zero-point derived energy preference for deuterium to be in a terminal position) are given in the Experimental section. The solution of these expressions is complicated by the fact that either δ_t and/or δ_b is temperature dependent, as can be demonstrated by the fact that the chemical shift of the equatorial methyl group in $[W(\eta\text{-}C_5Me_4Et)(CH_3)_4]^+$ moves to higher field as the temperature is lowered. From the data at temperatures below 283 K, where exchange of the equatorial and axial methyl groups is in the limit of slow exchange, we extract the values $\delta_t = 3.4 \pm 1$, $\delta_b = -11.1 \pm 1$ and $\Delta E = 0.84 \pm 0.2$ kJ mol^{-1} for the agostic methyl group, the chemical shifts being those at 273 K.

The ^{13}C NMR spectrum of complex **1** (R = Et) at 243 K shows only one exchange-averaged resonance for the three equatorial methyl groups. The observed ^1J(C–H) coupling constant of 128 Hz is an average of the values for agostic and non-agostic methyl groups. This value is in the region normally observed for simple sp^3-hybridised methyl groups and so, as is often the case in rapidly exchanging agostic methyls, gives no indication of an agostic interaction.

The infrared spectrum of solid $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4][PF_6]$ shows a broad band centred at 2900 cm^{-1}, assigned to all the overlapping ν(C–H), with the associated ν(C–D) being a single sharp resonance at 2166 cm^{-1}. There is no evidence for a band assignable to an agostic $C\text{–}H\rightharpoonup M$ group, which would be expected to lie in the region 2300–2800 cm^{-1}. However, frequently such bands are not observed.[3]

The neutral pentamethyl compound $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4(CHD_2)]$ was obtained by treatment of **1** (R = Et) with $Li(CHD_2)$.[17] Treatment of this compound with $HBF_4\cdot Et_2O$ gives the cation $[W(\eta\text{-}C_5Me_4Et)(methyl)_4]^+$, in which CH_3, CH_2D and CHD_2 groups are present. The chemical shifts observed for the CH_3 and CH_2D groups in this experiment differ from those for **1** (R = Et) since, for example, the CH_2D resonance is due to approximately 20% $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4]^+$ and 80% $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_3(CHD_2)]^+$, and the latter cation occurs with the CHD_2 group in either axial or equatorial sites. The variable-temperature ^1H NMR spectra also show an IPR effect in support of the presence of an agostic methyl group.

All of the compounds **2**–**18** show a small but significant isotope shift on deuteriation, but none shows a significant temperature dependence. These shifts are therefore most likely to be due to a second-order isotope effect, where the redistribution of vibrational energy levels on deuteriation causes minor changes in the electronic nature of the methyl group, and not from an agostic interaction. This second-order effect has been discussed in detail elsewhere.[6,18]

The absence of IPR effects on partial deuteriation is not definitive evidence for the *absence* of an agostic bond.[3,5] Thus, the neutron structure of $[Ti(CH_3)Cl_3(dmpe)]$[19] (dmpe = $Me_2PCH_2CH_2PMe_2$) shows that the methyl group is distorted but that the methyl C–H bond lengths are closely similar. The variable-temperature ^1H NMR spectra of $[Ti(CH_2D)Cl_3(dmpe)]$ and the CH_3 analogue show no significant isotopic perturbation.[19] The absence of effects on deuteriation arises because the IPR method depends on there being a difference between the zero-point energies (and hence bond lengths) of the agostic and non-agostic bonds.

The apparent absence of agostic methyl groups in several of the compounds **2**–**18** can be understood. For example, the cation $[Zr(\eta\text{-}C_5H_5)_2(CH_2D)(MeCN)_2]^+$ **13** already has an 18-electron metal centre. The crystal structure determination for the compound $[Zr(\eta\text{-}C_5H_5)_2(CH_2D)(thf)][BPh_4]$ **12** shows a planar oxygen atom, allowing the possibility that the tetrahydrofuran (thf) ligand is acting as a four-electron donor, which would give the zirconium centre an 18-electron configuration.[20,*] Further, the fluoride ligand can often be considered as a three-electron donor, in which case the compound $[Ti(\eta\text{-}C_5H_5)_2(CH_2D)F]$ **10** can also achieve an 18-electron configuration.

Geminal Coupling Constants in Metal–Methyl Groups.—The data in Table 1 give the magnitude and relative sign of the geminal coupling constant ^2J(H–D) [and ^2J(H–H)] for the

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[*] There are examples where a thf ligand with planar oxygen does not act as a four-electron donor, *e.g.* see ref. 21. We thank a referee for bringing this to our attention.

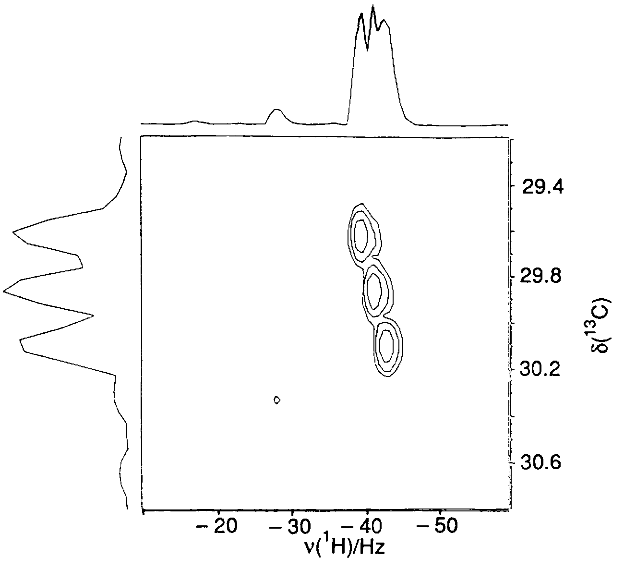

Fig. 2 The inverse-mode two-dimensional ^{1}H–^{13}C heteronuclear shift-correlation spectrum of [Zr(η-C_5H_5)$_2$(CH_2D)$_2$] **8** in C_6D_6, showing the negative slope of the triplet cross-peaks indicating the opposite signs of the ^{1}J(C–H) and ^{2}J(H–H) coupling constants. The sign of ^{1}J(C–H) is taken as positive

Table 2 Temperature dependence of the isotope shift for [W(η-C_5Me_4Et)(CH_3)$_4$][PF_6] **1** (R = Et)*

	δ(CH_3) − δ(CH_2D)	
T/K	axial	equatorial
243	0.028	0.137
223	0.028	0.159
203	0.028	0.168
183	0.028	0.185

* Measured from a mixture of [W(η-C_5Me_4Et)(CH_3)$_4$][PF_6] and [W(η-C_5Me_4Et)(CH_2D)$_4$][PF_6] in CD_2Cl_2 and reported in ppm

methyl compounds **1**–**18**. The relative signs of ^{2}J(H–D) and ^{1}J(C–D) for CH_2D (or CHD_2) groups were determined from heteronuclear spin-tickling experiments and from the ^{13}C–^{1}H heteronuclear shift correlation spectra by observation of the orientation of the cross-peaks between the 1:1:1 deuterium-coupled triplets in the ^{1}H and ^{13}C projections. In cases where it was required to carry out measurements below ambient temperatures we used the proton-detected (inverse mode) version of this experiment.[22] This method has been employed by Benn and co-workers[23–25] to establish relative signs of ^{1}J(M–P) and ^{2}J(P–H) (M = Fe, Os, W, *etc.*) in some metal–tertiary phosphine–hydride complexes. A typical, inverse-mode, two-dimensional NMR spectrum, that of [Zr(η-C_5H_5)$_2$(CH_2D)$_2$] **8**, is shown in Fig. 2. The slant of the triplet clearly indicates a negative value of ^{2}J(H–H), a conclusion supported by heteronuclear spin-tickling.

The values of ^{2}J(H–H) for compounds **1**–**18** are all negative and show no remarkable deviation from the range of values (7.9–12.2 Hz) previously observed for 18-electron transition metal–methyl compounds.[7] The relative sign of this coupling constant was measured for one of the compounds, [Fe(η-C_5H_5)(CO)$_2$(CH_3)], and found to be negative.[7] We note that the magnitude of ^{1}J(C–H) becomes smaller (less positive) as that of ^{2}J(H–H) becomes larger (more negative). Values of coupling constants in transition metal–methyl compounds have been discussed in terms of σ and π bonding between the metal and the methyl ligand, according to the original studies of Pople and Bothner-By.[26] Consideration of the values of ^{2}J(H–H) in Table 1 does not, however, identify any clear distinction between σ and π contributions in the metal–methyl bonds.

The gas-phase structure determination of [Ti(η-C_5Me_5)(CH_3)$_3$], a close analogue of [Ti(η-C_5Me_4Et)(CH_3)$_3$] **15** shows a less-than-tetrahedral average Ti–C–H angle of 103.8° suggesting the presence of agostic methyl group(s).[27] If only one of the metal–methyl groups is agostic, the Ti–C–H angle for this methyl must be very small (and consequently the H–C–H angle is large) to give an average Ti–C–H angle of 103.8°. However, due to rapid exchange, an average value of the ^{2}J(H–H) coupling constant for the three titanium–methyl groups is observed, and this does not show the positive deviation that might be expected for a flattened methyl group.[10] In fact the value is more negative than that for [Ti(η-C_5H_5)$_2$(CH_2D)F] **10**, which can be considered an 18-electron compound if the fluoride acts as a three-electron donor.

The crystal structure determination of [Y(η-C_5Me_5)$_2$(CH_3)(thf)][28] **18** showed some disorder and did not allow accurate location of the methyl hydrogens. However, there was some evidence for a tilting of the methyl group, possibly arising from an α-agostic interaction. The ^{1}H NMR spectrum for the Y–CH_2D analogue shows the η-C_5Me_5 resonance as a doublet, due to coupling to the ^{89}Y nucleus ($I = \frac{1}{2}$, 100%), and the CH_2D resonance as an apparent 1:2:2:1 quartet since ^{2}J(Y–H) ≈ ^{2}J(H–D). The ^{1}H–^{13}C shift correlation spectrum shows the relative sign of ^{2}J(H–D) to be negative, and the signs of ^{1}J(Y–C) and ^{2}J(Y–H) to be opposite. It is important to note, however, that if the tilting of the methyl group in **18** occurs only about the Y–C axis without flattening and further distortion of this group, then no IPR effect or change in ^{2}J(H–H) is expected. Such a tilting without distortion of a metal–methyl group has been found in [Ti(CH_3)Cl_3(dmpe)].[19] We were unable to determine either the sign or the magnitude of the ^{2}J(H–D) coupling constant in the Ti(CH_2D) derivative due to viscosity broadening at the low temperature required.

The fact that no positive deviation of ^{2}J(H–H) has been observed for the compounds studied, including **1**, **14**, **15** and **18** where there is other evidence for the presence of agostic methyl groups, may arise from a number of factors. First, when there is more than one metal–methyl group and there is rapid exchange, an average value of the coupling constant is observed and the positive deviation may be masked. Secondly, the agostic methyl group may be tilted without any change in the H–C–H angles. Finally, the positive deviation of the coupling constant ^{2}J(H–H) due to agostic bonding may be present but the magnitude is too small to be detectable. Hence it can only be concluded that the absence of the effect does not indicate the absence of agostic bonding.

Conclusion

We have shown that compound **1** contains a rare example of an agostic methyl group and this indicates the presence in the cation of a strongly electrophilic tungsten metal centre. The preference for an equatorial agostic methyl rather than an agostic axial methyl can arise from the expected location of the appropriate metal acceptor orbital in the equatorial plane.

It appears that the magnitude and sign of the geminal coupling constant of an M–CH_2D group is not a good probe for α-agostic bonding. Finally, we note that structure determinations by X-ray and electron diffraction are less reliable than those from neutron diffraction for detection of hydrogen positions, and even with neutron diffraction it is desirable that measurements should be carried out at low temperatures.

Experimental

All preparations, manipulations and reactions, unless otherwise stated, were carried out under an inert atmosphere of dinitrogen (<10 ppm oxygen, <20 ppm water) using standard Schlenktube techniques, or in an inert-atmosphere box. Dinitrogen was purified by passage through a column containing BTS catalyst and 5 Å molecular sieves.

Solvents were pre-dried over activated molecular sieves and then distilled from potassium [tetrahydrofuran (thf), 1,2-dimethoxyethane (dme)], sodium [toluene, light petroleum (b.p. 100–120 °C)], sodium–potassium alloy [light petroleum (b.p. 40–60 °C unless otherwise stated), diethyl ether, pentane], or phosphorus pentaoxide (dichloromethane), under an inert atmosphere of dinitrogen before use. Deuteriated solvents for NMR samples were used as received (Aldrich), or after drying over Na/K alloy.

The NMR spectra were recorded on a Brüker AM-300 spectrometer [^{1}H (300), ^{13}C (75.43), ^{19}F (282.24 MHz)]. Spectra were referenced internally using the residual solvent (^{1}H and ^{13}C) resonances relative to tetramethylsilane (δ 0), or externally relative to $CFCl_3$ (^{19}F). All chemical shifts are quoted in δ, high-field shifts being taken as negative, and coupling constants are in Hz. Samples were either prepared under nitrogen in screw-capped tubes (Wilmad), or under vacuum in sealed soda-glass NMR tubes. Two-dimensional NMR experiments were carried out using standard Brüker software, and processed using an ASPECT 3000 computer. The proton-detected inverse-mode experiments were carried out with broad-band ^{13}C decoupling, using a Brüker BFX-5 decoupler. Elemental analyses were performed by the Analysis Department in this laboratory. Infrared spectra were recorded as CsI or KBr pellets on a Mattson Polaris FT-IR interferometer.

The monodeuteriomethyl analogues of the known protiomethyl compounds $[M(\eta\text{-}C_5H_5)_2(CH_2D)_2]$ (M = Ti,[29] Zr[30] or Hf[31]), $[Y(\eta\text{-}C_5Me_5)_2(CH_2D)(thf)]$,[28] $[Ti(\eta\text{-}C_5H_5)(CH_2D)_3]$,[32] $[Zr(\eta\text{-}C_5H_5)_2(CH_2D)(MeCN)_2][BPh_4]$,[33] $[Zr(\eta\text{-}C_5H_5)_2(CH_2D)(thf)][BPh_4]$[20] and $[Ti(\eta\text{-}C_5H_5)_2(CH_2D)(thf)][BPh_4]$[34] were prepared using $Li(CH_2D)$ instead of $Li(CH_3)$. The method described by Schrock and Sharp[35] for the small-scale preparation of $[TaMe_3Cl_2]$ was used for the preparation of the mixture of $[Ta(CH_2D)_nCl_{5-n}]$. Slightly modified procedures, whereby $Si(C_5Me_4Et)Me_3$ instead of $Si(C_5Me_5)Me_3$ were used to prepare $[M(\eta\text{-}C_5Me_4Et)Cl_3]$ (M = Ti, Zr or Hf),[36] then these were treated with $Li(CH_2D)$ to give $[M(\eta\text{-}C_5Me_4Et)(CH_2D)_3]$ (M = Ti,[37] Zr[38] or Hf[39]). The method of Schrock and co-workers[16] was used to prepare $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4][PF_6]$, using $Mg(CH_2D)Cl$ prepared from CH_2DCl; $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4(CHD_2)]$ was also prepared by the method of Schrock and co-workers,[16] using $Li(CHD_2)$.

Preparations.—CH_2DCl. A flask (300 cm^3) containing $SnBu^n{}_3D$ (46.7 g, 0.16 mol) and a magnetic stirrer was attached to a vacuum manifold, possessing a manometer, with a total volume of 2 l. The flask was evacuated and cooled to −196 °C. A second, smaller, round-bottom flask containing CH_2BrCl (20 g, 0.155 mol) was attached, cooled to −196 °C, and evacuated. The CH_2BrCl was warmed to 20 °C and condensed onto the frozen $SnBu^n{}_3D$. The mixture was carefully melted and warmed slowly to about −20 °C. At this temperature an exothermic reaction commences, and it was necessary to ensure that the volatile products could expand into sufficient evacuated volume. Once the reaction had moderated, the flask was warmed to 20 °C for 1 h. The resulting volatiles were fractionated through traps at 0 °C (ice–water), then −78 °C (solid CO_2–acetone) and finally trapped at −196 °C (liquid nitrogen). Any unreacted CH_2BrCl was collected in the −78 °C trap, whilst the product condensed as a white solid in the −196 °C trap. This solid was melted and the product transferred into a storage bulb (5000 cm^3). The yield was not determined [but see the preparation of $Li(CH_2D)$ below].

The compound CHD_2Cl was prepared in an analogous fashion by the reaction of $SnBu^n{}_3D$ (2 equivalents) with $CHBr_2Cl$.

$Li(CH_2D)$. In an atmosphere of argon, a lithium dispersion [10 g of a 30% (w/w) dispersion in mineral oil, *ca* 1 mol] was placed in a reaction vessel (300 cm^3) equipped with a magnetic stirrer, and was washed with light petroleum (b.p. 40–60 °C, 2 × 100 cm^3). The metal was then dried *in vacuo*. Diethyl ether (150 cm^3) was added, the flask attached to a vacuum line and the suspension frozen at −196 °C. The flask was evacuated and CH_2DCl was condensed from the storage bulb into a small flask and held at *ca.* −30 °C. A portion (*ca.* 2 cm^3) of the CH_2DCl was condensed onto the frozen lithium suspension, and then allowed to warm slowly to room temperature. After stirring at 20 °C for 20 min the reaction flask was cooled to −196 °C and a second portion of CH_2DCl added. The procedure was repeated until no further CH_2DCl remained. After the suspension had been stirred at *ca.* 20 °C for 10 h the resulting solution was filtered under argon. A portion of the $Li(CH_2D)$ solution was titrated against a 1.06 mol dm^{-3} solution of *m*-cresol in toluene using 2,2′-bipyridine as an indicator, giving an overall yield of *ca.* 150 cm^3 of a 0.86 mol dm^{-3} solution (80% based on 46.7 g of $SnBu^n{}_3D$). The $Li(CHD_2)$ was prepared in an identical fashion.

$[Ti(CH_2D)Cl_3]$. A one-piece apparatus consisting of a bulb (20 cm^3) with a Rotaflo tap side-arm and a second side-arm containing (in sequence) a right-angle bend, a glass frit, Pyrex-to-soda glass graded seal and 5 mm soda-glass NMR tube was used for this preparation. The reaction bulb was quickly (in the dark and at as low a temperature as possible) charged with $[Ti(\eta\text{-}C_5H_5)_2(CH_2D)_2]$ (0.21 g, 1.05 mmol) and a magnetic follower. The reaction bulb was then wrapped in aluminium foil and cooled to −80 °C. A solution of $TiCl_4$ (0.38 g, 2.1 mmol) in CD_2Cl_2 (0.4 cm^3) was added through the tap side-arm. The apparatus was allowed to warm to 20 °C and the contents stirred in the dark for 1 h. The bulb was then cooled to −196 °C and the apparatus evacuated. The volatiles were condensed into the NMR tube by cooling it in liquid nitrogen and gently warming the reaction bulb. The NMR tube was then sealed under dynamic vacuum and carefully warmed to melt the frozen solution. The ^{1}H NMR spectrum at 253 K showed this to be essentially pure $[Ti(CH_2D)Cl_3]$.

$[Ti(\eta\text{-}C_5H_5)_2(CH_2D)F]$. The compound $[Ti(\eta\text{-}C_5H_5)_2(CH_2D)_2]$ (0.268 g, 0.86 mmol) was dissolved in acetonitrile (15 cm^3) in a plastic beaker open to air. A slight excess of aqueous HF (0.05 cm^3 of a 22.5 mol dm^{-3} solution) was added and the mixture was stirred for 2 h, during which time the orange solution lightened slightly in colour and a colourless gas was evolved. The solvent was removed under reduced pressure to yield the product as a yellow-orange microcrystalline solid. Yield 0.242 g (90%).

Analysis of the IPR Data for $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4]^+$.—Using the method originally described by Calvert and Shapley,[5b] equations (1) and (2) can be derived. It is assumed

For the equatorial $\delta(CH_3)$ of $[W(\eta\text{-}C_5Me_4Et)(CH_3)(CH_2D)_3]^+$

$$\delta(CH_3) = (6\delta_t + 2A\delta_t + \delta_b)/(7 + 2A) \qquad (1)$$

For the ^{1}H-$\delta(CH_2D)$ of $[W(\eta\text{-}C_5Me_4Et)(CH_2D)_4]^+$

$$\delta(CH_2D) = (5\delta_t + 3A\delta_t + \delta_b)/(6 + 3A) \qquad (2)$$

that the rate of axial–equatorial exchange is negligible at the relevant temperatures and, therefore, only the three equatorial methyl groups need be considered. Here δ_t is the ^{1}H chemical shift of a terminal (non-agostic) C–H, δ_b is the ^{1}H chemical shift of a bridging (agostic) C–H, A is the Boltzmann term $\exp(-\Delta E/RT)$ and ΔE is the energy preference for a C–H to be bridging and a C–D to be terminal.

Attempts to fit the observed data using these equations, or to fit Δδ to the appropriate differences, were not successful. This mainly arises from the fact that the inherent temperature dependence of either δ_t and/or δ_b is greater than that due to the Shapley effect. The data were finally analysed by iterating for the variables ΔE, δ_t and δ_b.

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