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Hydrogen shifts in $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$; a density functional study

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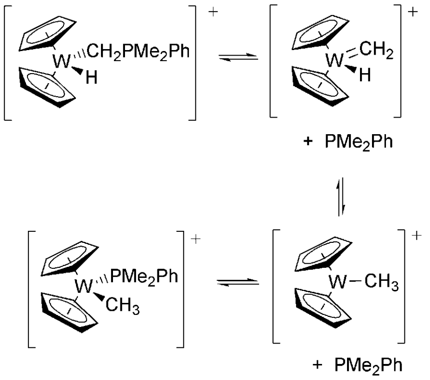
1,2-Hydrogen shifts in $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$ have been shown to proceed *via* a hydridocarbene intermediate and an agostic methyl complex. The energy difference between the two is estimated as 42 kJ mol^{-1} with the hydridocarbene being the more stable. Calculations on the two phosphine adducts $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PH_3)]^+$ and $[W(\eta\text{-}C_5H_5)_2(CH_3)(PH_3)]^+$ confirm the latter to be the thermodynamic product of the reaction.

Introduction

Although α-, β- and γ-elimination pathways are mechanistically feasible for many unsaturated transition metal alkyl compounds, the observation of α elimination has been somewhat limited. It is widely acknowledged that alkyls with accessible β-hydrogens will preferentially undergo β elimination,[1] although there are exceptions to this generalisation. Notably, elimination *via* α pathways has been observed for systems where steric factors hinder β elimination[2] and indeed the kinetics of α elimination may be faster than that of β elimination.[3]

Naturally, α elimination is widely observed in systems where there are no β-carbons.[4] One of the most intensively studied systems has been that of the bis(cyclopentadienyl)methyltungsten cation. The cation $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+$ has been shown to undergo thermal isomerisation to $[W(\eta\text{-}C_5H_5)_2(CH_3)(PMe_2Ph)]^+$ on prolonged heating, and a 1,2 hydrogen shift was suggested to explain the isomerism (Scheme 1).[5]

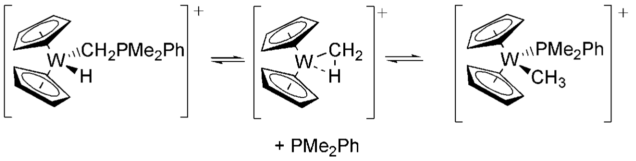


Scheme 1

It was suggested that the equilibrium between $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$ and the hydridocarbene species $[W(\eta\text{-}C_5H_5)_2(H)CH_2]^+$ was facile, and that the latter was the more stable of the two species. This was confirmed by Hoffmann and co-workers[6] who postulated a small activation energy for the rearrangement step.

The compound $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+$ was formed from $[W(\eta\text{-}C_5H_5)_2(CH_3)(C_2H_4)]^+$ and PMe_2Ph, which initially forms the adduct $[W(\eta\text{-}C_5H_5)_2(CH_3)(CH_2CH_2PMe_2Ph)]^+$. This then eliminates C_2H_4 to form $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+$. Deuterium labelling studies have shown that the carbon in $[W(\eta\text{-}C_5H_5)_2(H)(\mathbf{C}H_2PMe_2Ph)]^+$ is the methyl carbon from $[W(\eta\text{-}C_5H_5)_2(\mathbf{C}H_3)(C_2H_4)]^+$. This suggested that $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+$ is formed as the kinetic product from the bis(cyclopentadienyl) methyl tungsten cation *via* Scheme 1. The thermodynamic product $[W(\eta\text{-}C_5H_5)_2(CH_3)(PMe_2Ph)]^+$ is only produced on further heating. It is thus likely that both $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$ and $[W(\eta\text{-}C_5H_5)_2(H)(CH_2)]^+$ are common intermediates in the formation of $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+$ from $[W(\eta\text{-}C_5H_5)_2(CH_3)(C_2H_4)]^+$ and $[W(\eta\text{-}C_5H_5)_2(CH_3)(PMe_2Ph)]^+$ from $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+$.

The discovery of agostic bonding in the early 1980s[7] cast some doubt over the mechanism of this reaction and the nature of the intermediates involved. It became apparent that hydrogen transfer from metal to ligand often occurs *via* an agostic structure, and indeed that the latter may be the ground state of such a system. Further kinetic studies were thus undertaken to test for this.[8] They showed the rate of reaction to be strongly dependent on temperature, but essentially independent of the concentration of free tertiary phosphine. This suggests that the attack of tertiary phosphine to form $[W(\eta\text{-}C_5H_5)_2(CH_3)(PMe_2Ph)]^+$ is not the rate determining step. An inverse kinetic isotope effect is observed on replacement of the hydride ligand by deuterium. This implicates formation of a C–H bond from the W–H bond in the rate-determining step of the reaction, due to the smaller difference in zero point energies for W–H and W–D than for C–H and C–D. Two schemes have been suggested for the reaction. One is Scheme 1, which involves an equilibrium between the carbene hydride species formed on loss of tertiary phosphine and the bis(cyclopentadienyl)methyl tungsten cation. The kinetic data rule out a slow equilibrium for this step. However, a fast equilibrium would be in accordance with the small activation barrier postulated by Hoffmann. The alternative scheme involves formation of an agostic methyl cation directly from $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+$ (Scheme 2).



Scheme 2

In light of the uncertainty of the mechanism of this fundamental organometallic reaction, this work calculates the ground state energies of all the postulated species. The pathways involved are examined in order to understand the potential energy surface of this system, and hence elucidate the most feasible mechanism for the isomerisation.

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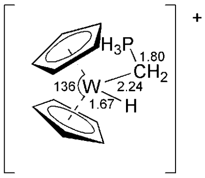
Computational methods

Calculations were performed using density functional methods of the Amsterdam Density Functional Package (versions 2.3 and 2000.2).[9,10] They employed type IV basis sets with triple ζ accuracy sets of Slater type orbitals, with a single polarisation function added; 2p on H, 3d on C, and 4d on P. The cores of the atoms were frozen up to 4f for W, 1s for C, 2p for P and treated relativistically using the "Dirac" utility. The generalised gradient approximation (GGA non-local) method was employed, using Vosko, Wilk and Nusair's[11] local exchange correlation with non-local exchange corrections by Becke,[12] non-local correlation corrections by Perdew.[13] The valence calculations were quasi-relativistic using the Pauli formalism. Linear transit runs were carried out fixing one internuclear distance to successive values as a reaction coordinate and optimising the other structural parameters. Full frequency calculations were performed to verify that local minima resulted from geometry optimisations. These could take up to 300 h cpu time. Some initial attempts resulted in very small imaginary freqencies (<30 cm^{-1}) for ring rotations. For transition states the frequency calculations were carried out on the metal and reacting groups with frozen rings in order to save cpu time. Scheme 1 was analysed by optimising $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PH_3)]^+$, $[W(\eta\text{-}C_5H_5)_2(H)(CH_2)]^+$ and $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$ without symmetry constraints. A linear transit run was performed between the last two species. A geometry optimisation was also performed on $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$ in the triplet state to check the nature of the methyl species. Scheme 2 was analysed by performing a linear transit run between $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PH_3)]^+$ and $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$ and PH_3. The calculations carried out are summarized in Table 1.

Results and discussion

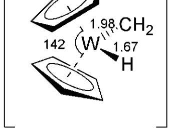
Scheme 1

The species $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PH_3)]^+$ was used as a model for $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PMe_2Ph)]^+$ to save computational time. A geometry optimisation yielded structure **1**.



1

The hydridocarbene structure depicted in Scheme 1 may be accessed from $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PH_3)]^+$ by direct loss of PH_3. A linear transit run showed the barrier to phosphine dissociation to be approximately 33 kJ mol^{-1}. Geometry optimisations on the hydridocarbene species readily converged to give two possible structures both of which were shown to be local minima by frequency calculations. One had the open face of the tungstenocene unit formed by four carbons (**2**). The other (**3**) had the open face formed by two carbons. Despite the latter's marginally longer W–H and W–C bond lengths, it was the lower lying by 0.180 eV (17.4 kJ mol^{-1}), due to smaller steric interactions with the ring (the ancillary ligands in **3** are staggered with respect to ring C–H bonds, whilst those in **2** are eclipsed). It should be noted that the two structures are simply interconverted by rotation of the cyclopentadienyl rings. The combined energy of **3** and PH_3 lies 0.18 eV (17 kJ mol^{-1}) above **1**.



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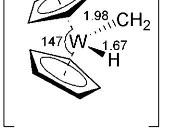

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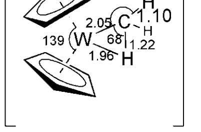

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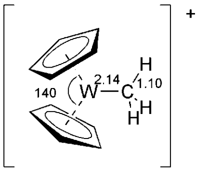
Table 1 Calculations performed on bis(cyclopentadienyl)methyl tungsten cations

Compound	Calculation type	Spin state
$[W(\eta\text{-}C_5H_5)_2(H)(CH_2PH_3)]^+$, **1**	GO	Singlet
$[W(\eta\text{-}C_5H_5)_2(H)(CH_2)]^+$, **2** and **3**	GO, F	Singlet
$[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$, **4**	GO, F	Singlet
$[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$, **5**	GO (W–C–H equal)	Singlet
$[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$, **6**	GO	Triplet
$[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$, **7**	TS, F	Singlet
$[W(\eta\text{-}C_5H_5)_2(CH_3)(PH_3))]^+$, **8**	GO	Singlet
$[W(\eta\text{-}C_5H_5)_2(H)(CH_2PH_3)]^+$, **9**	TS, F	Singlet
PH_3	GO	Singlet
$[W(\eta\text{-}C_5H_5)_2(H)(CH_2)]^+$	LT (C···H 2.63–1.19 Å)	Singlet
$[W(\eta\text{-}C_5H_5)_2(H)(CH_2)]^+$	LT (C···H 2.63–1.19 Å)	Triplet
$[W(\eta\text{-}C_5H_5)_2(H)(CH_2PH_3)]^+$	LT (C···H 2.45–1.19 Å)	Singlet
$[W(\eta\text{-}C_5H_5)_2(H)(CH_2PH_3)]^+$	LT (C···P 1.80 – 2.60 Å)	Singlet

GO = Geometry optimisation, F = frequency calculation, LT = linear transit run, TS = transition state optimisation.

Geometry optimisations on $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$ revealed an agostic methyl cation (**4**), as indicated by the differing C–H bond lengths and W–C–H angles. The methyl group projects out of the open face of the metallocene unit which is formed by four carbons. Structure **4** lies 42 kJ mol^{-1} above **3**. A frequency calculation on structure **4** showed it to be a local minimum. A further geometry optimisation on the same species, in which the W–C–H angles were constrained to be equal, identified a non-agostic methyl cation that was 0.26 eV (25 kJ mol^{-1}) higher in energy (**5**). This suggests an agostic methyl species is more likely to be formed in the reaction than the non-agostic methyl compound postulated in Scheme 1. Such an agostic stabilisation of the methyl cation has previously been suggested to explain the stereochemical stability of chiral tungstenocene methyl complexes.[14] The results found for the cationic tungsten system are in contrast to those found for neutral $[Sc(\eta\text{-}C_5H_5)_2(CH_3)]$ where the methyl group is undistorted.[15]



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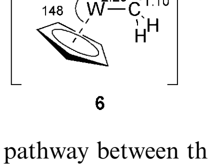
Geometry optimisation of $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$ in the triplet state yielded structure **6**, which lies 0.09 eV (9 kJ mol^{-1}) above the singlet **4**. This triplet species is non-agostic.



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The α elimination pathway between the hydridocarbene and agostic methyl cations was investigated by performing linear transit runs, utilising the carbon–hydrido distance as a reaction coordinate, in both singlet and triplet spin states. The energy rises from the hydrido carbene, **3**, reaching a transition state, **7**, where the hydrogen is neither bonded to the metal nor the carbon. Structure **7** was confirmed as a transition state by a frequency calculation. It gave one imaginary frequency of 847*i*

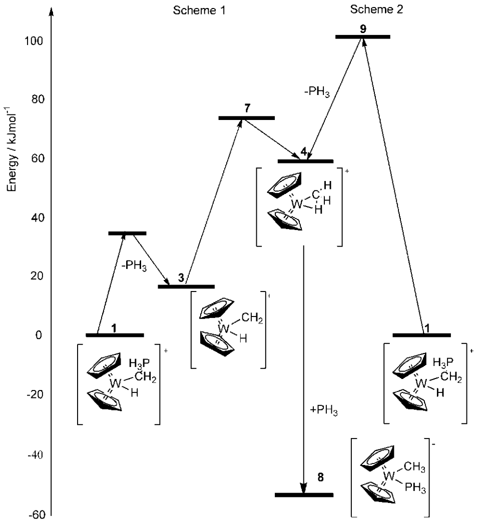
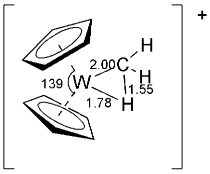


Fig. 1 Energetics of 1,2 hydrogen shifts in the $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$–$PH_3$ system.



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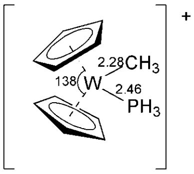
cm^{-1} ($i = \sqrt{-1}$). The motion corresponded to movement of the H along the reaction coordinate.

As C–H bonding interactions are introduced, the energy drops to form the agostic methyl cation, **4**. The reaction pathway has an activation energy of 0.59 eV (57 kJ mol^{-1}) for conversion from $[W(\eta\text{-}C_5H_5)_2(H)(CH_2)]^+$ into $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$. This gives an overall activation energy of 0.77 eV (74 kJ mol^{-1}) for conversion of $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PH_3)]^+$ into the agostic $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$ *via* Scheme 1.

The triplet surface rose sharply in energy from that of structure **6** as the C–H distance was increased. Given the closeness in energy of the singlet and triplet structures, **4** and **6** respectively, it is unclear as to how important conversion into the triplet state is within the overall scheme.

Optimisation of $[W(\eta\text{-}C_5H_5)_2(CH_3)(PH_3)]^+$ yielded structure **8**, which lies 1.17 eV (113.0 kJ mol^{-1}) below the agostic methyl structure **4**. This large energy difference provides the thermodynamic driving force for the isomerisation reaction by trapping the methyl cation.



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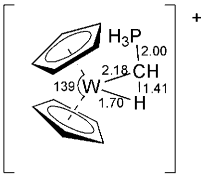
Scheme 2

A linear transit run was performed to model the reaction pathway between $[W(\eta\text{-}C_5H_5)_2(H)(CH_2PH_3)]^+$ **1** and $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$ **4**, with the hydrido ligand acting as a nucleophile expelling PH_3 in an S_N2 type reaction. Again the carbon–hydrido distance was utilised as a reaction coordinate. This too showed a reaction profile with a single transition state, **9**, which had an imaginary frequency of 266*i* cm^{-1} ($i = \sqrt{-1}$).



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The calculation predicted an activation energy for Scheme 2 of 1.06 eV (102 kJ mol^{-1}). The agostic methyl intermediate, **4**, is trapped by PH_3 as in Scheme 1.

The activation energies calculated for Schemes 1 and 2 of 74 and 102 kJ mol^{-1} respectively suggest a marginal preference for isomerisation *via* Scheme 1. A comparison of the two schemes is shown in Fig. 1.

Conclusion

The activation energies for Schemes 1 and 2 of 74 and 102 kJ mol^{-1} respectively show a preference for Scheme 1, which includes a hydridocarbene intermediate. Both schemes involve the species $[W(\eta\text{-}C_5H_5)_2(CH_3)]^+$, which is agostic in character.

Acknowledgements

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