

## CARBON–HYDROGEN–TRANSITION METAL BONDS

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### Summary

Evidence that carbon–hydrogen bonds may act as ligands to transition metal centres forming covalent C–H–M systems in which, formally, the C–H group donates two electrons to the metal is reviewed and consequences are discussed.

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### Introduction

Carbon–hydrogen bonds, especially those of saturated ( $sp^3$ ) carbon centres, are normally regarded as being chemically inert. Generally, the C–H group is not thought of as a potential ligand which can have a structural role or play an energetically significant part in ground states or in reaction intermediates.

In this article we review recent observations which show that there are in fact many circumstances in which a carbon–hydrogen group will interact with a transition metal centre with formation of a two-electron three-centre bond and that the extent of the interaction is such as to have a marked effect on the molecular and electronic structure and hence reactivity of the molecule.

We propose the term “agostic” which will be used to discuss the various manifestations of covalent interactions between carbon–hydrogen groups and transition metal centres in organometallic compounds\*. The word agostic will be used to refer specifically to situations in which a hydrogen atom is covalently bonded simultaneously to both a carbon atom and to a transition metal atom. The agostic C–H–M bond is similar to the familiar and long known bridging hydrogen systems which occur in B–H–B, M–H–M, and B–H–M groups. The C–H–M bonds are a recent observation but as will be discussed below, they are probably very much more common than hitherto suspected. Since carbon–hydrogen bonds are a ubiquitous feature of organometallic compounds we have found it useful to define

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\* The word agostic is derived from the Greek word  $\alpha\gamma\omicron\sigma\tau\acute{\omega}$  which occurs in Homer and translates as to clasp or hold to oneself.

the new term agostic which serves to emphasise and describe the phenomena and to differentiate between terminal hydridoalkyl (C–M–H) systems.

## Background studies

Many years ago it was found that *ortho*-hydrogens of certain aryl-phosphine ligands were orientated in a manner such that some weak interaction between the metal and the hydrogen was indicated. Examples include the compounds  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  [1] and *trans*- $\text{Pd}(\text{PPhMe}_2)_2\text{I}_2$  [2] and the cation  $[\text{Rh}(\text{PPh}_3)_3]^+$  [3], whose structures are represented in Fig. 1.

Trofimenko observed unusual low field shifts for the ethyl hydrogens in the  $^1\text{H}$  NMR spectrum of  $\text{Ni}[\text{Et}_2\text{B}(\text{pz})_2]_2$  ( $\text{pz}$  = pyrazole) [4], and suggested that the hydrogens were held close to the nickel centre. In 1972 Maitlis reported the crystal structure of the compound  $\text{Pd}(\text{PPh}_3)_2(\text{CMeCMeCMeCHMe})\text{Br}$  (**1**) [5] which is shown in Fig. 2. The Pd–C(HMe) distance of 2.3 Å is less than the expected sum of the Van der Waals radii (ca. 3.1 Å) and it was proposed that there was a direct Pd–H–C interaction. This was supported by the observation of spin–spin coupling between the proposed bridging hydrogen and the two equivalent  $^{31}\text{P}$  nuclei ( $J(\text{P–H})$  1.4 Hz).

The compound  $\text{Mo}(\text{Et}_2\text{B}(\text{pz})_2)(2\text{-RC}_3\text{H}_4)(\text{CO})_2$  (**2**, R = Ph) also showed an anomalous  $^1\text{H}$  NMR of the methylene hydrogens of one ethyl group of the pyrazolyl ligand and the crystal structure (Fig. 2) again showed a short Mo–C distance leading to the proposal of an direct Mo–H–C interaction [6,7,8].

The first neutron diffraction study of an agostic C–H–M system which definitively showed the position of the agostic hydrogen was that of the compound  $\{\text{Fe}[\text{P}(\text{OMe})_3]_3(\eta^3\text{-C}_8\text{H}_{13})\}\text{BF}_4$  (**3**) (Fig. 2) [9].

In very recent years and increasingly the presence of agostic hydrogens has been shown both by NMR and by crystal structure determinations and this work is discussed in detail below.

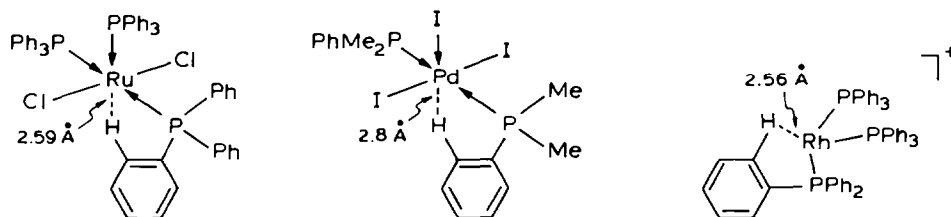
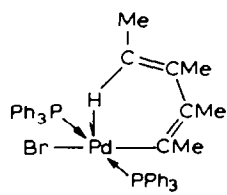
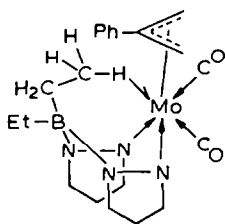


Fig. 1. The structures of compounds which gave early indications for the formation of C–H–M interactions.

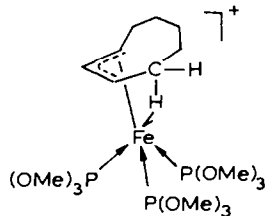
Fig. 2. The structures of some of the compounds in Table 1. In drawing these compounds the two-electron three-centred bond is represented by the “half-arrow” convention, i.e. C–H–M [17]. This is our preferred representation since it serves to distinguish two-electron from four-electron bridging systems, e.g. Al–Cl → Al in  $[\text{AlCl}_3]_2$ , but at the same time provides an indication that the two electrons in the C–H bond are formally donated to the metal centre, i.e. the C–H group acts as a two-electron ligand to the metal centre.



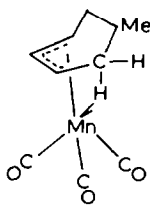
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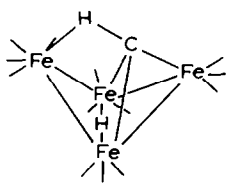
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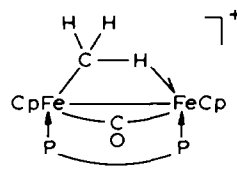
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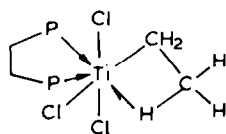
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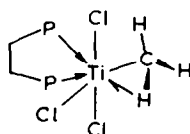
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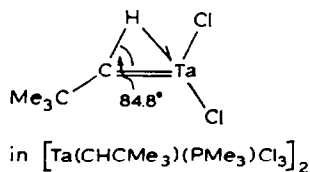
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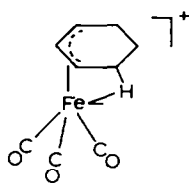
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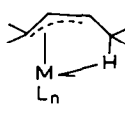
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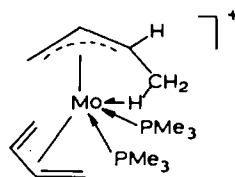
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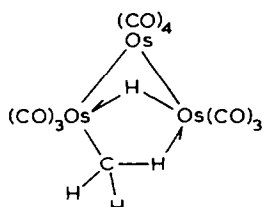
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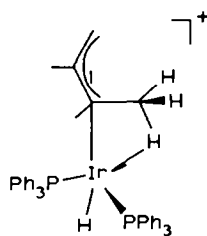
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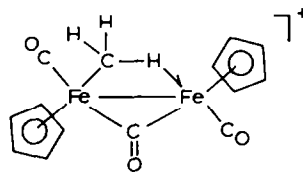
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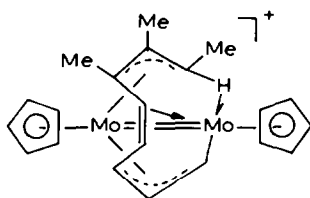
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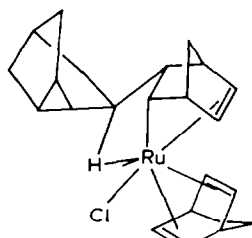
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(24)



(23)



(25)

## I. Evidence for C-H→M bonds

## (i) Crystal structure determinations

Table 1 summarises the crystal structure data available on agostic C-H→M systems and the structures of some of the compounds are represented in Fig. 2. As noted above, the early crystal structure determinations did not observe the agostic hydrogen directly but evidence for interaction between the C-H group and the metal centre was inferred from close M-C distances. The neutron diffraction data shows that the bridging C-H bond distance is ca. 5–10% longer than for normal non-bridging analogous C-H bonds. The M-H bond distances of the agostic group also appear to be longer (ca. 15–20%) than normal M-H bonds.

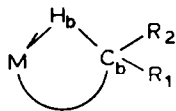
## (ii) Nuclear magnetic resonance data

The C-H→M bridged system may be represented generally as follows:

TABLE 1  
CRYSTAL STRUCTURE NMR AND INFRARED DATA FOR SOME BRIDGING C-H→M SYSTEMS

Compound	Distances		
	M-H	C-H	M-C
(1) Pd(CMeCMeCMeCH <sub>2</sub> -μ-H)(PPh <sub>3</sub> ) <sub>2</sub> Br			2.3
(2) Mo(Et <sub>2</sub> B(pz) <sub>2</sub> )(2-RC <sub>3</sub> H <sub>4</sub> )(CO) <sub>2</sub>	R = Ph 2.27(8)	0.97(8)	3.06
(3) Fe(P(OMe) <sub>3</sub> ) <sub>3</sub> ((η <sup>3</sup> -octenyl))BF <sub>4</sub> <sup>a</sup>	1.874(3)	1.164(3)	2.384(4)
(4) Mn(η <sup>3</sup> -C <sub>6</sub> H <sub>5</sub> R)(CO) <sub>3</sub> <sup>a</sup>	R = Me 1.84(1)	1.19(1)	2.34(1)
(5) Fe <sub>4</sub> H(μ <sup>2</sup> -CH)(CO) <sub>12</sub> <sup>a</sup>	1.80(4)	1.18(4)	1.926(5)
(6) Fe <sub>2</sub> (CH <sub>2</sub> -μ-H)(μ-CO)(μ-dppm)(η-Cp <sub>2</sub> )PF <sub>6</sub>	1.64(4)	1.06(4)	2.101(3)
	1.78(3)	0.83(4)	2.118(3)
(7) Ti(CH <sub>2</sub> CH <sub>2</sub> -μ-H)Cl <sub>3</sub> (dmpe)	2.29	1.02	2.516(10)
(8) Ti(CH <sub>2</sub> -μ-H)Cl <sub>3</sub> (dmpe)	2.03(4)	1.00(2)	2.149(5)
(9) [Ta(CHMe <sub>3</sub> )Cl <sub>3</sub> (PMe <sub>3</sub> ) <sub>2</sub> ] <sup>a</sup>	2.119	1.131	1.898
(10) [Ta(η-C <sub>5</sub> Me <sub>5</sub> )(CHMe <sub>3</sub> )(η <sup>2</sup> -C <sub>2</sub> H <sub>4</sub> )(PMe <sub>3</sub> )] <sup>a</sup>	2.043	1.135	1.946
(11) [Ta(CH <sub>2</sub> CMe <sub>3</sub> ) <sub>3</sub> (CHCMe <sub>3</sub> )Cl <sub>2</sub>			
(12) [Ta(η-C <sub>5</sub> H <sub>5</sub> )(CHCMe <sub>3</sub> )Cl <sub>2</sub>			
(13) [W(CHCMe <sub>3</sub> )(H)Cl <sub>3</sub> (PMe <sub>3</sub> ) <sub>2</sub> ]			
(14) [Fe(η <sup>3</sup> -cyclohexenyl)Fe(CO) <sub>3</sub> ]OSO <sub>2</sub> F			
(15) [Fe(η <sup>3</sup> -butenyl)Fe(CO) <sub>3</sub> ]OSO <sub>2</sub> F			
(16) [Fe(η <sup>3</sup> -butenyl)Fe(P(OMe) <sub>3</sub> ) <sub>3</sub> ]BPh <sub>4</sub>			
(17) [Fe(η <sup>3</sup> -cycloheptenyl)Fe(P(OMe) <sub>3</sub> ) <sub>3</sub> ]BPh <sub>4</sub>			
(18) [Mn(η <sup>3</sup> -cyclohexenyl)(CO) <sub>2</sub> (POMe <sub>3</sub> )] <sup>a</sup>			
(19) [Mo(η <sup>3</sup> -C <sub>3</sub> H <sub>4</sub> CH <sub>2</sub> -μ-H)(η-C <sub>4</sub> H <sub>6</sub> )(PMe <sub>3</sub> ) <sub>2</sub> ]BF <sub>4</sub>			
(20) [Os <sub>3</sub> (CO) <sub>10</sub> (CH <sub>3</sub> )H]			
(21) [Ir(η <sup>3</sup> -C <sub>6</sub> H <sub>11</sub> )(Ph <sub>3</sub> P) <sub>2</sub> H]			
(22) [Ru(η <sup>3</sup> -C <sub>12</sub> H <sub>17</sub> )(dippe)PMe <sub>2</sub> Ph] <sup>a</sup>			
(23) [(η-C <sub>3</sub> H <sub>5</sub> )Mo(C <sub>11</sub> H <sub>15</sub> )Mo(η-C <sub>5</sub> H <sub>5</sub> )]X	1.88(8)	0.89(7)	2.196(5)
(24) [η-CpFe(CO)(μ-CH <sub>3</sub> )(μ-CO)Fe(CO)η-Cp] <sup>+</sup>			
(25) Ru(C <sub>14</sub> H <sub>17</sub> )(C <sub>7</sub> H <sub>8</sub> )Cl			

<sup>a</sup> Neutron diffraction data, η-Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>.



The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra can be diagnostic of the presence of such systems. In particular, the value of  $J(^{13}\text{C}^{\text{b}}-\text{H}^{\text{b}})$  is lower than for non-bridged C-H groups, the agostic hydrogen  $\text{H}^{\text{b}}$  and  $^{13}\text{C}^{\text{b}}$  often show high field shifts and, in fluxional systems, there is a strong dependence of the average  $^1\text{H}$  (and  $^2\text{H}$ ) chemical shifts upon partial deuteration at the bridging carbon. Many agostic alkyls are fluxional at room temperature but static spectra can be obtained at lower temperatures (typically  $-90^\circ\text{C}$ ). If static spectra cannot be obtained then partial deuteration of the agostic alkyl will normally be required for full characterisation of the compound.

Static		Fluxional		$\nu(\text{C}-\text{H})$ ( $\text{cm}^{-1}$ )	References
$(^{13}\text{C}-\text{H})$ ( $\text{cm}^{-1}$ )	$\delta(\text{H})$ (ppm)	$J(^{13}\text{C}-\text{H})_{\text{ave.}}$ ( $\text{cm}^{-1}$ )	$\delta(\text{H})_{\text{ave.}}$ (ppm)		
			R = H -2.4 -6.5	2704,2664	5 6,7,8 9 11,12,13
R = H	85	-13.0			
R = H	85	-12.5			
	103	-1.3			14
			114		15
					16
			2.7		17
			2.3		18
	101	5.3		2605	19
	74				20
	90	1.9			21
	84	6.4		2510	22
	84	1.4		2395	10
ca.	83				10,23
	74				9
ca.	100	-15.0	129		9
	80	-15.8			9
	86	-13			24
		-9.4			25
			121		26
					27
					28
					29
		-9.4			30
			121		31
		-3.7		2586	

### Static systems

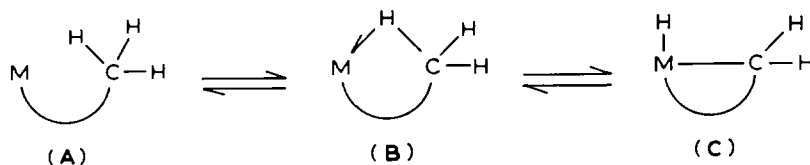
The most reliable indication of the presence of a C–H–M bridged system is the substantially diminished value of  $J(^{13}\text{C}^{\text{b}}\text{--H}^{\text{b}})$  (75–100 Hz) which arises from the reduced C–H bond order in the two-electron, three-centre C–H–M bond. These low values were first reported by Brookhart and Whitesides for the compound  $[\text{Fe}(\eta^3\text{-C}_6\text{H}_9)(\text{CO})_3]^+$  (**14**, **15**) [10]. Reported values of  $J(^{13}\text{C}\text{--H}(\text{agostic}))$  are given in Table 1, and are all substantially lower than typical values for normal saturated ( $sp^3$ ) C–H bonds (120–130 Hz). The coupling constant data also allows distinction between the C–H–M system and the C–M–H alkyl-hydride group since  $J(^{13}\text{C}\text{--H})$  for the H–M–C system are normally less than ca. 10 Hz.

The bridging hydrogen of the C–H–M systems for  $d^n$ ,  $n > 0$  normally exhibit high field chemical shifts with negative  $\delta$  values, up to ca. –16 ppm in some systems (Table 1). Since these chemical shifts are comparable with those of terminal M–H systems care must be taken to avoid confusion. Typical  $\delta$  values for agostic hydrogens are given in Table 1. For those  $d^n$  compounds where  $n = 0$  high field shifts ( $-\delta$  values) for the agostic hydrogen are not observed, e.g. in  $\text{TiRCl}_3(\text{dppe})$ , R = Me or Et (**7**, **8**) [16,17] and in the agostic alkylidene compounds of tantalum and tungsten (**9–13**) [18–22]. However in the latter shifts for the agostic hydrogens generally lie to higher fields than terminal hydrogens in 18-electron alkylidene complexes which exhibit normal values for  $J(^{13}\text{C}\text{--H})$  [32].

### Fluxional systems

When a spectrum of the static species cannot be acquired then only average values are obtainable for  $J(\text{C}\text{--H})$  and chemical shifts.

The problem that arises is to distinguish between the following possible isomeric ground state structures and this is illustrated for a methyl system, viz.:



The average value of  $J(^{13}\text{C}\text{--H})$  expected for **A** is the normal  $J(\text{C}\text{--H})$  value of 120–130 Hz. For **C** a value  $J(\text{C}\text{--H})_{\text{ave.}}$  of 80–90 Hz is expected i.e.  $(J(\text{H}\text{--M}\text{--C}) = 0\text{--}10 + 2J(\text{C}\text{--H}) = 120\text{--}130)/3$  Hz. However for **B**, even though  $J(\text{C}\text{--H}_{\text{agostic}}) = 80\text{--}100$  Hz, the values of  $J(\text{C}\text{--H})_{\text{ave.}}$  can be ca. 120 Hz (i.e. the same as for **A**) because as the C–H–M bridge forms there is an increase of  $J(\text{C}\text{--H}_{\text{non-bridging}})$  up to ca. 140 Hz. This arises from an increase in  $s$ -character in the non-bridging C–H bonds. Thus the value of  $J(\text{C}\text{--H})_{\text{ave.}}$  for **C** is  $(J(\text{C}\text{--H}\text{--M}) 80\text{--}100 + 2(J(\text{C}\text{--H}_{\text{non-bridging}}) 140)/3)$  Hz = ca. 120 Hz.

The average  $^1\text{H}$  chemical shift  $\delta_{\text{ave.}}$  for the fluxional agostic methyl group of **B** and **C** will (for  $d^n > 0$ ) be expected at  $\delta < 0$  and at higher field than that for the methyl group of **A**. This can lead to incorrect assignment of the **B** structure as an alkyl hydride. However, since the  $\delta$  values for agostic hydrogens and terminal M–H hydrogens are quite variable the  $\delta_{\text{ave.}}$  value is a poor criterion for distinguishing between **B** and **C** and, in  $d^0$  compounds, for distinguishing amongst the three isomers **B**, **C**, and **A**.

A third and important NMR method for identifying agostic C–H systems is that of partial deuteration first developed by Shapley [26] and applied to the osmium compound  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3)\text{H}]$  (**20**) (Fig. 1). He noted that in the  $\text{CH}_2\text{D}$  and  $\text{CHD}_2$  systems the  $^1\text{H}$  chemical shift and  $J(^{13}\text{C}-\text{H})$  values fall in the order  $\delta(\text{CH}_3) > \delta(\text{CH}_2\text{D}) > \delta(\text{CHD}_2)$  and  $J(^{13}\text{C}-\text{H})$  for  $\text{CH}_3 > J(^{13}\text{C}-\text{H})$  for  $\text{CH}_2\text{D} > J(^{13}\text{C}-\text{H})$  for  $\text{CHD}_2$ . In addition both the chemical shift and  $J(^{13}\text{C}-\text{H})$  value of the partially deuterated species (but not the  $\text{CH}_3$  species) are strongly temperature dependent. This arises because there is a thermodynamic preference for hydrogen rather than deuterium to occupy the bridging position. The fundamental reason for this preference is the smaller zero point energy difference between H and D in the C–H–M and C–D–M bonds relative to the differences in the “terminal” C–H and C–D bonds and the consequent preference of deuterium to occupy the terminal sites leaving hydrogen to occupy the bridging site. This isotopic perturbation effect has now been widely used and is exhibited by compounds **4**, **6**, **16**, **19–21**, and **24**.

Observation of this effect clearly distinguishes between agostic systems **B** and a non-interacting methyl group **A**, but it does not distinguish between the **B** and the alkyl-hydrido case **C** since applying similar arguments  $^1\text{H}$  will preferentially occupy the terminal M–H site in a partially deuterated system.

In summary, a fluxional agostic methyl group is clearly indicated if both the  $J(^{13}\text{C}-\text{H})$  value falls to ca. 110 Hz (rules out **C**) and isotopic perturbation of the  $J(^{13}\text{C}-\text{H})$  and  $^1\text{H}$  chemical shift is observed (rules out **A**). Further support is added in  $d^n$  ( $n > 0$ ) systems if the average  $^1\text{H}$  chemical shift occurs at  $\delta_{\text{ave.}} < 0$ .

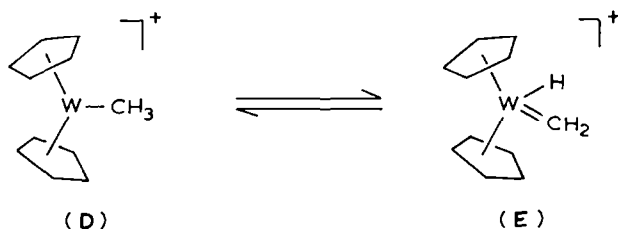
### (iii) Infrared data

The stretching frequency of the agostic C–H system has been reported for some of the compounds and the available data is given in Table 1. This shows that agostic C–H groups have bands in the region  $\nu(\text{C}-\text{H})$  ca.  $2700\text{--}2350\text{ cm}^{-1}$  which is lower than for normal C–H stretches. This lowering may be associated with the observed increase in length of the agostic C–H bonds.

## II. Examples of compounds containing agostic C–H–M groups

### (i) Agostic Alkyls

In Oxford we had been interested in reversible 1,2-hydrogen shifts in alkyl-transition-metal compounds and had obtained evidence for this reaction occurring in di- $\eta$ -cyclopentadienyltungsten compounds. The 1,2-shift equilibrium was proposed to occur between the 16-electron methyl cation **D** and the 18-electron carbene-hydride **E** [33], viz.:



In regard to this reaction we had noted that Schrock had synthesised some

interesting highly distorted carbenetantalum compounds such as  $[\text{Ta}(=\text{CHCMe}_3)(\text{PMe}_3)\text{Cl}_3]_2$  (**9**) in which a hydrogen of the carbene ligand was occupying a bridging position between the tantalum and the carbenoid carbon [18,32]. These are discussed below. We envisaged that similar distortions might occur for alkyl-transition-metal compounds, especially where suitable empty orbitals on the metal centre were available.

We set out to obtain evidence for this by the synthesis and determination of the crystal structures of the compounds  $\text{TiRCl}_3(\text{dmpe})$ , where  $\text{R} = \text{Me}$  (**8**) and  $\text{Et}$  (**7**). These compounds were selected for several reasons. Titanium (A.N. 22) has relatively few electrons for a transition metal and therefore X-ray diffraction is more likely to reveal nearby hydrogens. The titanium centre is highly electron deficient having a formal electron count (ignoring the agostic hydrogen) of 12 electrons. The overall symmetries of the molecules are low thus minimising the chance of molecular disorder in the crystals. Since compounds such as  $\text{TiMe}_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$  are known there was little likelihood that the titanium centres in **7** and **8** would be sterically overcrowded.

The structures of the compounds **7** and **8** are shown in Fig. 2. The Ti-C-C angle of the Ti-Et group of **7** is only  $86^\circ$  and clearly indicates that the titanium centre is interacting with a  $\beta$ -hydrogen of the ethyl group with formation of a C-H-Ti bond. The methyl group of **8** has a remarkable structure. One hydrogen is severely distorted from the expected  $\text{C}_{3v}$  position of a normal methyl hydrogen so that the M-C-H angle is  $70^\circ$ . The other two hydrogens appear to be in effectively normal positions so that the three hydrogens are almost co-planar with the methyl carbon atom. In view of the chemical analogy between the two compounds **7** and **8** it seems reasonable to maintain an essentially common description of the bonding such that the M-C bonds are, to the first approximation, regarded as being separate from the bridging C-H-M bonding as shown in Fig. 2.

*The occurrence of agostic alkylmetal groups.* Apart from the agostic C-H-Ti systems, the molecules  $\text{TiRCl}_3(\text{dmpe})$ ,  $\text{R} = \text{Me}, \text{Et}$ , contain no very special features so we have proposed that agostic alkyl ligands will occur in other compounds containing sterically unsaturated metal centres with suitable empty orbitals [17].

The minimal requirement is that the metal centre should have an empty orbital to receive the two electrons of the C-H bond. It is to be presumed that this orbital will be essentially of *d*-character for transition metal compounds. The orbital should be a very good acceptor and the energy and disposition should approach that of the C-H bonding electrons as far as possible.

If there is an unoccupied valency orbital then the metal atom cannot have achieved a maximum coordination number. Nonetheless it is probably the case that the formation of agostic alkyl groups will be favoured by coordination numbers of six or less.

It is to be expected that an agostic hydrogen can be displaced from the metal centre by another donor group. This raises the question of competition with an agostic hydrogen from lone-pairs on ligands such as halogen. It is found that in  $\text{TiMeCl}_3(\text{dmpe})$  those lone-pair electrons of the three chlorine ligands which have suitable symmetry to overlap with the titanium orbitals do not successfully compete with the agostic C-H electron pair.

This point can be exemplified by consideration of the problem of counting electrons in  $\text{TiCl}_4$ . If we ignore the chlorine lone-pair electrons then the formal



electron count of the titanium is eight. However, the eight lone pairs on the four chlorine ligands combine in  $T_d$  symmetry to form occupied  $e_2$ ,  $t_1$  and  $t_2$  combinations. The ten electrons in the  $e_2$  and  $t_1$  MOs are of suitable symmetry to overlap with the appropriate symmetry combinations of the titanium centre. If these ten electrons are thought of as donating sufficiently strongly to the metal then  $\text{TiCl}_4$  may be described as an 18-electron molecule. If the C–H bond pairs of the  $\text{CH}_3$  group are taken as essentially equivalent to the lone-pair electrons of a Cl ligand and

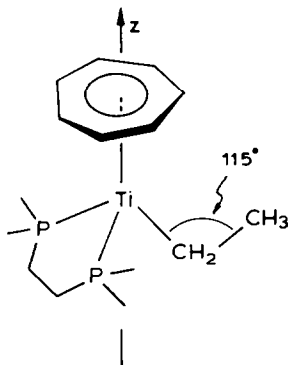


Fig. 3. Crystal structure of  $\text{Ti}(\eta\text{-C}_7\text{H}_7)(\text{dmpe})\text{Et}$ .

if  $\text{TiMeCl}_3$  is to have an eighteen electron count on the above basis, then we expect  $\text{TiMeCl}_3$  to have a bridging Ti–H–C system and not a simple ethane-like structure.

Simple analogy coupled with the observations above suggest that agostic alkyl compounds will occur in many compounds of the type  $\text{MR}_n\text{X}_x$ , where R = Me, Et, etc. and X = halogen.

Similarly, compounds with a < 16-electron environment of the general class  $\text{MR}_x\text{X}_y\text{L}_z$ , where R = alkyl, X = halogen and L =  $\text{PR}_3$ ,  $\text{R}_3\text{N}$ , etc. and for which  $x + y + z = 6$  or less, would be expected to show agostic hydrogens. Compounds such as  $\text{V}(\eta\text{-C}_5\text{H}_5)_2\text{R}$  may well have agostic hydrogens. In this context we note that there is presently no evidence to distinguish between the proposed cations  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{CH}_3]^+$ ,  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(=\text{CH}_2)\text{H}]^+$  and the agostic analogue  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{-CH}_2\text{-}\mu\text{-H}]^+$ .

We also note that it is necessary to distinguish between non-agostic and agostic alkylmetals for the purposes of discussion of “the metal–carbon bond energies” of alkylmetal systems. The bond dissociation energy for an agostic alkyl group comprises both the metal–carbon  $\sigma$ -bond and the contribution from the C–H–M bond.

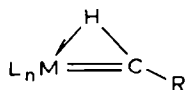
The requirement of a 16-electron centre is a necessary but not sufficient condition for the occurrence of an agostic hydrogen. This is illustrated by the 16-electron compound  $\text{Ti}(\eta\text{-C}_7\text{H}_7)(\text{dmpe})\text{Et}$  (**26**) whose crystal structure is represented in Fig. 3 (along with the Cartesian axes) [34].

The structure shows that there is no evidence for interaction between the ethyl hydrogens and the titanium. Consideration of the likely bonding in compound **26** suggests that the lowest unoccupied molecular orbital (LUMO), namely, that which would be used in the formation of a Ti–H–C bridge will be of essentially  $d_{z^2}$  character and will lie along the z-axis. Therefore it is not suitably disposed to act as an acceptor orbital. It would be necessary for compound **26** to adopt a “bent”

configuration in order to present a suitably directed empty orbital to the C–H electrons. Further, this  $a_1$  orbital would be expected to lie at substantially higher energy than the C–H electrons. Thus the absence of an agostic hydrogen in **26** can be understood in these terms.

(ii) *Agostic alkylidene compounds*

There are more than a dozen examples of compounds containing the system:



They have been prepared by Schrock and examples are shown in Table 1 and Fig. 3. The bonding of the alkylidene group in these compounds has been discussed in terms of a tilting of the plane of the CHR group via interaction between the metal atom and the alkylidene lone pair [35] and also in terms of a C–H–M two-electron, three-centred bond, in a manner analogous to that of agostic alkyl systems [18].

(iii) *Polyenyl compounds*

Numerous systems have been characterised in which there is a C–H–M bridge between a metal centre and a C–H group of the terminal carbon substituent of polyenyl ligands (Table 1 and Fig. 2). The structure, dynamics and potential chemistry of these systems are well-illustrated by the cyclohexenylmanganese tricarbonyl complex  $\text{Mn}(\eta\text{-C}_6\text{H}_9)(\text{CO})_3$  (**4**), as shown in Fig. 4 [11,12,13].

Whilst the bridged structure **P** is the ground state, dynamic NMR measurements indicate the  $\eta$ -allylic **Q** and diene hydride **R** isomers are in equilibrium with the bridged structure with  $\Delta G^\ddagger$ 's of 8.3 and 15.5 kcal/mol respectively. The agostic hydrogen of **P** is acidic and the compound can be readily deprotonated giving the diene anion **S**. This reacts with carbon electrophiles to effect C–C bond formation and net electrophilic substitution of the agostic hydrogen. The bridging hydrogen can be readily displaced by donor ligands such as tertiary phosphines and carbon

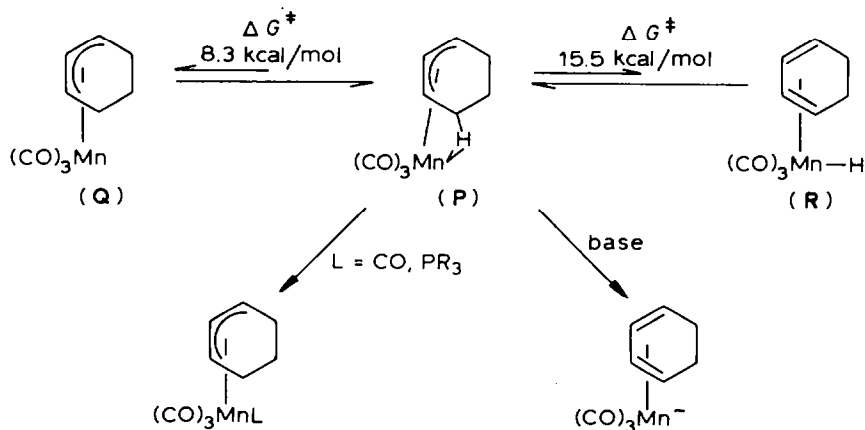


Fig. 4. Some chemistry of the agostic  $\eta^3$ -cyclohexenylmanganese tricarbonyl complex.

monoxide forming  $\eta$ -allylic derivatives. Preliminary results suggest the C–H homolytic bond strength is reduced and the agostic hydrogen can be transferred to activated olefins as a hydrogen atom [11]. These experiments show that substantial chemistry can be carried out on agostic systems as a result of the weakened C–H bond and the enhanced reactivity of the agostic hydrogen.

*(iv) Bi- and poly-nuclear compounds*

Agostic C–H bonds have been observed in a number of bi- and poly-nuclear compounds. Examples are shown in Fig. 2. The first of these was in the osmium compound  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3)\text{H}]$  (**20**) and was detected by elegant  $^1\text{H}$  NMR studies on partially deuteriated derivatives the essence of which are described in Section I ii.

In these systems the alkyl group is attached to one metal and the C–H–M bond forms with the second metal of the dimer so they are somewhat analogous to the bonding in **7** rather than in the methylmetal compound **8** in which both the carbon and the hydrogen are interacting with the same metal.

*(v) The mechanism of olefin polymerisation by Ziegler–Natta catalysts*

The traditional mechanism for the carbon–carbon bond forming step in Ziegler–Natta polymerisation of olefins, proposed by Cossee [36], proceeds by a simple alkyl migration to the coordinated olefin, as shown in Fig. 5. There is no direct involvement of the C–H bonds of the alkyl chain in this mechanism. In marked contrast, it has been proposed that prior to the formation of the carbon–carbon bond the alkyl group undergoes a 1,2-hydrogen shift giving a metallacarbene intermediate [37], see Fig. 5. This mechanism provided an explanation for control of the stereochemistry of the polymerisation of propene since substituents could lie either *cis* or *trans* with respect to the metallacyclobutane ring.

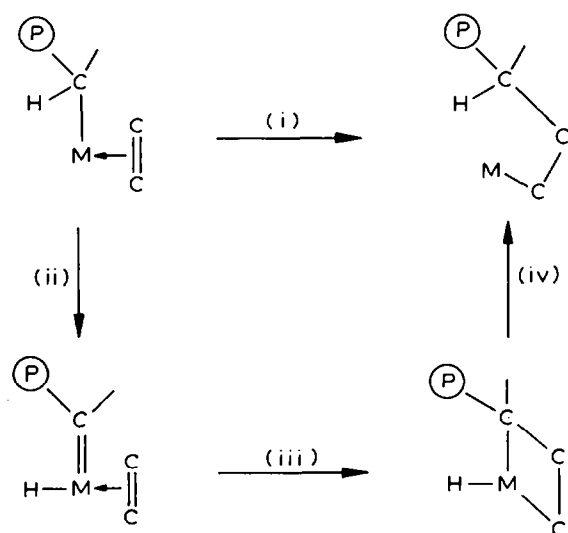


Fig. 5. (i) Carbon–carbon bond forming step by methyl migration (Cossee). (ii) 1,2-Hydrogen shift forming an alkyldene hydride. (iii) Carbon–carbon bond forming step by metallacycle formation. (iv) Reductive elimination step. Encircled P represents the growing polymer chain.

Further, the mechanism implies a close connection between olefin polymerisation and olefin metathesis.

A detailed study of the kinetics of polymerisation of ethylene and tetradeuterioethylene showed that there was only a very small isotope effect on the rates of propagation ( $k_p^h/k_p^d = 1.04 \pm 0.03$ ). These data strongly support a mechanism that does not involve hydrogen migration in a rate determining step [38].

An elegant study on the insertion of a variety of olefins into the lanthanum-carbon bonds of  $M(\eta\text{-C}_5\text{Me}_5)_2\text{CH}_3 \cdot \text{ether}$  ( $M = \text{Yb}$  or  $\text{Lu}$ ) shows the olefin insertion proceeds smoothly under mild conditions [39]. Intermediate olefinallylanthanum compounds are not observed. The lanthanum centres in the methyl compounds do not have accessible valency electron suitable for stabilising formal oxidative addition products such as the carbene hydride  $M(\eta\text{-C}_5\text{Me}_5)_2\text{H}(\text{=CH}_2)$ . This observation also supports an insertion mechanism which does not involve oxidative addition of an  $\alpha\text{-C-H}$  bond to the metal centre. However, other possible mechanisms such as those involving reversible migration of H or alkyl groups between the metal centre and the  $\eta$ -cyclopentadienyl ring cannot be excluded on the available data.

Studies on the stereochemistry of polypropylene formation by  $\delta\text{-TiCl}_3/\text{Al}(\text{}^{13}\text{CH}_3)_2\text{I}$  show that steric control must arise from the chirality of the catalytic centre [40] but does not distinguish between the possible mechanisms described above [41].

It has been shown that the alkylidene hydride  $\text{Ta}(\text{CHCMe}_3)\text{H}(\text{PMe}_3)_3\text{I}_2$  reacts with ethylene to give new compounds  $\text{Ta}[\text{CHCH}_2(\text{CH}_2\text{CH}_2)_n\text{CH}_2\text{CMe}_3]\text{H}(\text{PMe}_3)_3\text{I}_2$ , where  $n$  varies from 2 to 80 [42]. Although this observation does not show that the carbon-carbon bond forming step proceeds by the formation of a metallacyclic intermediate this possibility certainly seems plausible.

It seems worthwhile to consider here implications of the observation of the

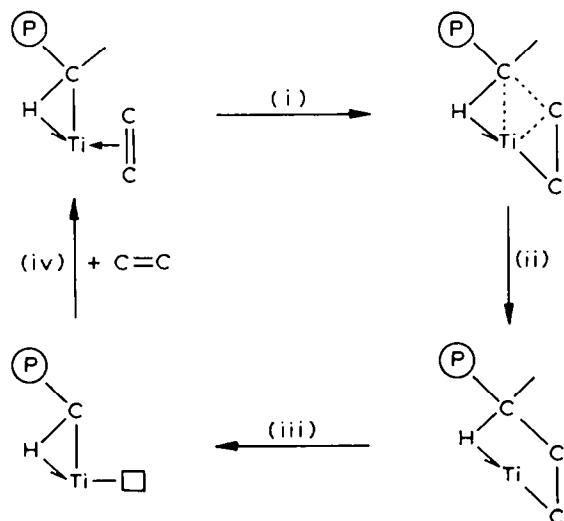


Fig. 6. (i) Carbon-carbon bond forming step assisted by the partial migration of an  $\alpha$ -hydrogen to the metal giving a C-H-Ti bond. (ii) The metallacycle intermediate with a  $\gamma$ -C-H-Ti bond. (iii) Rearrangement of the agostic hydrogen from the  $\gamma$ - to the  $\alpha$ -position. (iv) Addition of the next olefin. Encircled P represents the growing polymer chain.

agostic alkyl groups in the compounds  $\text{TiRCl}_3(\text{dmpe})$  regarding the mechanism of Ziegler–Natta polymerisation. There seems no reason a priori why an  $\alpha$ -hydrogen of the growing alkyl side-chain should not form a  $\text{C-H-Ti}$  bridge. This could assist in the formation of the carbon–carbon bond since it would allow the other atoms on the  $\alpha$ -carbon to more readily move away from an approaching carbon of the olefin. The formation of an alpha bridging hydrogen by the alkyl group would reduce the steric inhibition to the carbon–carbon bond forming step. This implies that electronic unsaturation favours olefin insertion. Moreover, the bidentate nature of the  $\text{Ti-H-C}$  interaction could provide a means for controlling the stereochemistry (orientation) of the alkyl chain with respect to the incoming olefin.

The resting state of the alkyl chain could have an  $\alpha\text{-C-H-Ti}$  bridge. One can conceive that the bridging hydrogen of a  $\text{Ti-H-C}$  group could move along a relatively smooth reaction profile from a position where it was primarily bonded to the  $\alpha$ -carbon to being more strongly bonding with the titanium. Large isotope effects would not be expected for such movements of an  $\alpha$ -hydrogen.

Figure 6 shows a possible reaction pathway involving agostic hydrogens.

If, as shown, there is a  $\gamma\text{-C-H-Ti}$  interaction after the carbon–carbon bond forming step then one can envisage a return to  $\alpha$ -hydrogen interaction via a step-wise conversion to a  $\beta$ -hydrogen interaction, such as is found in the compound  $(\text{TiCH}_2\text{CH}_2\text{-}\mu\text{-H})\text{Cl}_3(\text{dmpe})$ .

The Cossee mechanism on one hand and the hydrogen migration/metallacarbene mechanism on the other hand can be seen as extreme representations of an olefin insertion reaction involving agostic  $\alpha$ -hydrogen interactions.

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