

REACTIVE INTERMEDIATES IN ORGANOTRANSITION METAL CHEMISTRY

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Abstract - Cationic alkylidene complexes form an important class of reactive intermediates containing transition metal to carbon double bonds. Examples can be prepared by hydrogen atom abstraction from tungstenocene dialkyl radical cations, and the resulting electrophilic alkylidene/alkyl complexes can be trapped by nucleophiles such as phosphanes. In the absence of trapping agents the tungstenocene alkylidene complexes undergo facile migratory insertion reactions to form homologated alkyl complexes which isomerise to alkylenehydride cations. Abstraction from the diethylradical cation is α -selective, giving an intermediate ethylidene, and it is suggested that spin delocalization from the metal center onto α -C-H bonds is responsible for this selectivity. In the case of the mixed ethylmethyl cation the abstraction is methyl selective. The same intermediate cationic alkylidene complexes can be generated by hydride abstraction from neutral tungstenocenedialkyls, and it has been shown that abstraction from these readily oxidised alkyl complexes occurs by an electron transfer mechanism.

INTRODUCTION

The synthesis and reactivity of molecules containing multiple bonds between carbon and transition metals has been one of the most rapidly developing areas of organotransition metal chemistry since Fischer and Maasböl reported the first carbene complexes in 1964 (1). This is partly because of the role of such species as intermediates in a variety of important catalytic reactions, including alkene metathesis (2), transition metal catalyzed cyclopropanation (3), and Fischer-Tropsch reduction of carbon monoxide (4). More fundamentally, however, the excitement in this area has reflected the rapid changes which it has brought in our understanding of the nature of the bonding between transition metals and carbon and of the range of reactivity exhibited by complexes containing such bonds.

The transition metal to carbon double bond is one of the most important new functional groups to emerge from the study of complexes containing multiple bonds between transition metals and carbon. The bonding in this functional group can be described in many ways, but the simplest approach is to consider the bond as derived from a formally sp^2 -hybridized carbon atom (Fig. 1). Two of the three sp^2 -orbitals are used to form σ -bonds to the substituents X and Y, and the third doubly occupied orbital is used to form a σ -donor bond to the

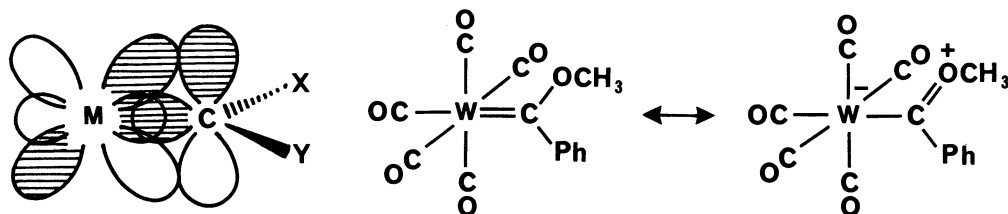


Fig. 1. Bonding in typical carbene complexes.

transition metal center. This leaves an empty p-orbital on carbon, perpendicular to the sp^2 -plane, which forms the π -component of the double bond by interaction with a filled d-orbital on the metal atom. The net result is a synergistic bonding interaction reminiscent of that between low valent transition metal complexes and carbonyl ligands.

It is now clear that there are two major general classes of complexes containing transition metal to carbon double bonds which differ markedly in their structures and reactivities.

The first major class consists of the Fischer-type carbene complexes, which are generally complexes in which the metal is in a low formal oxidation state, and which are distinguished by the presence of α -heteroatomic substituents such as the methoxy group in $[\text{W}(\text{CO})_5\text{C}(\text{OMe})\text{Ph}]$ (Fig. 1). Such heteroatomic substituents commonly have O, N, or S heteroatoms, and the sometimes remarkable stabilities of the complexes are attributed to the stabilizing effect of π -donation of non-bonding electrons on the heteroatom into the empty p-orbital on carbon.

Although the short heteroatom-carbon bonds in structurally characterized carbene complexes show that this π -donation is an important component of the bonding in the complexes, reactivity studies indicate that π -donation alone does not control the chemistry of the complexes. Another important factor is apparently the electronegativity of the heteroatomic substituents, which renders the unsaturated carbon electrophilic and results in the existence of extensive parallels between the chemistry of such complexes and that of organic esters (5,6).

The second major class of complexes containing transition metal to carbon double bonds are the alkylidene complexes extensively studied by Schrock and his coworkers (7). These do not contain the stabilizing heteroatomic substituents characteristic of Fischer carbene complexes and are most typically complexes of Nb, Ta, or, more recently, W. The bonding within the complexes can be discussed in terms similar to those used above, in which case the π -component of the bond is now formed entirely by interaction of the empty p-orbital on carbon with a filled metal orbital. Since none of the groups attached to carbon are now electronegative the net effect of the π -interaction should be to increase electron density on the carbon atom, and it has in practice been observed that the unsaturated carbons are nucleophilic in character (7). An alternative approach to the bonding in these alkylidene complexes is to regard the ligands as CR_2^{2-} dianions: this is equivalent to regarding the alkylidene ligand as a triplet carbene with one electron in an sp^2 -hybrid orbital and one in a p-orbital perpendicular to the sp^2 -plane, and the metal carbon double bond is then precisely analogous to the C=C double bond in ethylene. An important consequence of this description is that it leads to the classification of the alkylidene complexes as high valent complexes of the early transition metals and hence provides informative parallels between their chemistry and that of high valent alkyl-, oxo-, halo- and nitrido- complexes of the same metals.

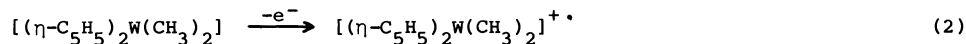
It has recently become clear that there is a third category of complexes containing transition metal to carbon double bonds which can usefully be distinguished from Fischer and Schrock carbene and alkylidene complexes. These are the cationic alkylidene complexes (most commonly methylidene complexes) (3,8-22), and although they formally resemble the Schrock complexes in lacking heteroatomic substituents, they differ significantly in their reactivity. This is primarily because the positive charge on the metal renders the carbenoid center markedly electrophilic rather than nucleophilic. The chemical distinction is such that it may be more appropriate in some circumstances to regard the complexes as metallocarbocations, although in one case there is structural evidence to support a bonding description involving a metal-carbon double bond (18). Cationic alkylidene complexes are in general so reactive that they are rarely isolable, but their high reactivity makes their chemistry particularly diverse. This has recently led us to explore the synthesis and reactivity of such cationic alkylidene complexes in a number of metal-ligand environments, and the present manuscript summarizes some of our observations on cationic alkylidene complexes of tungstenocene (24,46).

SYNTHESIS OF CATIONIC ALKYLIDENE COMPLEXES BY HYDROGEN ATOM ABSTRACTION

Most of the preparations of cationic alkylidene complexes reported to date have involved the electrophilic cleavage of alkoxymethyl complexes (8-16), although a few have employed alternative routes such as hydride abstraction using the triphenylcarbenium (trityl) cation (11, 17-20), thermal loss of SMe_2 from a dimethylsulfonium alkyl complex (3), or protonation of a vinyl complex (16,21,22). An alternative approach which has been pursued recently in our laboratories is the reaction of cationic and paramagnetic alkyl complexes with hydrogen atom abstractors such as the triphenylmethyl (trityl) radical. Loss of hydrogen atoms from such complexes should give cationic alkylidenes as shown:



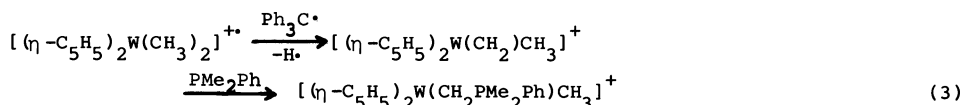
This approach was made possible by the discovery that a suitable substrate for such a reaction could be prepared by oxidizing $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]$ with I_2 or Ag^+ to give a 17e, paramagnetic cation as shown (23):



This dimethylcation is remarkably stable; it is indefinitely thermally stable in the solid state, and can be exposed to air for hours without noticeable decomposition. It is even

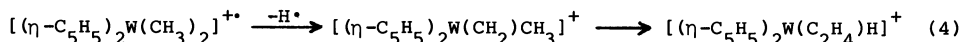
possible to handle the complex in water, and exchange of PF_6^- for I^- counterion is normally carried out in this solvent. The oxidation can be readily reversed chemically using sodium amalgam, or, in an unusual reduction of considerable utility in this system, reaction with a biphasic mixture of saturated aq. KOH and acetone. The oxidation is also electrochemically reversible; cyclic voltammograms recorded in CH_3CN exhibit symmetrical oxidation and reduction waves with $i_a = i_c$ and a peak to peak separation of 62 mV with $(E_a + E_c)/2 = -450$ mV (vs. SCE).

Hydrogen atom abstraction from $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]^+$ should generate $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_2)\text{CH}_3]^+$ but, as discussed below, this species is unstable with respect to intramolecular rearrangement. Convincing evidence for its formation can be obtained, however, by carrying out the reaction in the presence of a phosphane (eq. 3). The powerfully electrophilic methylenide cation reacts with the phosphane to give a tungsten substituted phosphonium salt. This can also be regarded as an ylide complex, but the spectral characteristics of the product suggest that the phosphonium salt formulation provides a closer description of the molecule.

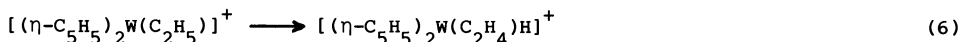
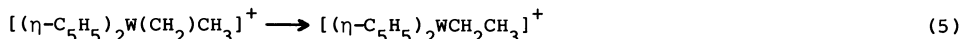


INSERTION WITHIN CATIONIC TUNGSTENOCENE ALKYLIDENE ALKYL COMPLEXES

In the absence of a phosphane the product of hydrogen abstraction from the dimethyl cation is the known ethylene hydride cation (eq. 4). Formation of the ethylene ligand in this



molecule must involve a carbon-carbon bond forming step, and we have proposed (24) that this step is insertion within the electrophilic alkylidene alkyl complex (eq. 5). Subsequent β -elimination within the unsaturated ethyl cation could then give rise to the observed product (eq. 6).



Although insertion within the methylenide methyl complex provides a straightforward interpretation of our results, the novelty of the suggestion (there was only one other example of such a reaction in the literature at the time of this work (25)), and the observation that the isoelectronic species $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{CH}_2)\text{CH}_3]$ (the first methylenide complex to be isolated (26,27)) undergoes instead an intermolecular decomposition to form $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{C}_2\text{H}_4)\text{-CH}_3]$ (27) made it vital to establish that the reaction was indeed intramolecular. We accordingly carried out a crossover experiment in which a 1:1 mixture of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CD}_3)_2]^+$ and $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]^+$ were converted into a mixture of isotopically isomeric ethylene hydride cations. Deprotonation of this mixture gave an analogous mixture of neutral $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_4)]$ complexes whose isotopic composition could be determined by mass spectroscopy. The results indicated that the mixture contained none of the d_2 -complex which would be the statistically dominant species in an intermolecular reaction, but instead consisted primarily of the d_0 and d_4 complexes, the expected products of an intramolecular reaction, contaminated with a little d_1 and d_3 complex (4 and 8%, respectively). Although the precise origin of these has not been determined, control experiments have shown that they are not produced in the deprotonation step, but that similar quantities of the d_1 and d_3 ethylene complexes are produced if a 1:1 mixture of d_0 and d_5 ethylene hydride complexes is stirred under the reaction conditions and deprotonated in the same way. We conclude that the d_1 and d_3 ethylenes are primarily the result of scrambling processes subsequent to ethylene hydride formation, and that the insertion is intramolecular in nature.

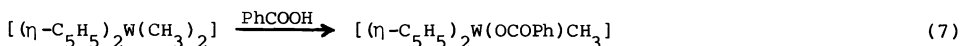
INSERTION VERSUS INTERMOLECULAR ALKENE FORMATION IN ALKYLIDENE-ALKYL COMPLEXES

The contrast between the facile insertion observed in $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_2)\text{CH}_3]^+$ and the relatively slow intermolecular decomposition observed in the isoelectronic molecule $[(\eta\text{-C}_5\text{H}_5)_2\text{-Ta}(\text{CH}_2)\text{CH}_3]$ (27) raises questions as to the factors controlling the course of reaction in the two molecules. The most obvious difference between the two is the positive charge on the tungsten complex, and this could influence the course of reaction in two ways.

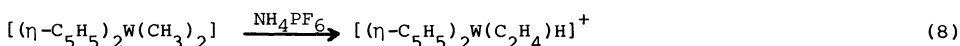
The first possibility is that the positive charge simply inhibits electrostatically the close approach of two molecules of the tungsten complex and hence prevents the dimerization reaction. We do not, however, feel that this is a major factor for two reasons. First, there is literature precedent which shows that intermolecular alkene formation by methyli-

dene complexes can be facile even if the complexes are positively charged. Both Pettit (14) and Green (13) reported some years ago that treatment of a methoxymethyl complex of iron with an acid with a non-coordinating counterion led to formation (*inter alia*) of the corresponding ethylene complex, and suggested that this was formed from an intermediate methyldene cation in an intermolecular reaction. More recently, Brookhart and Nelson have not only confirmed this but have also shown that the reaction is too rapid in $\text{HSO}_3\text{F}/\text{SO}_2\text{ClF}$ at -100°C to permit n.m.r. observation of the intermediate methyldene cation (9).

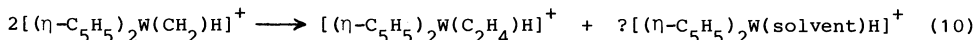
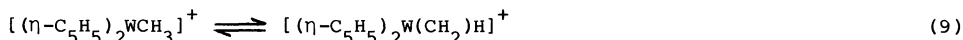
The facility of this reaction would argue that a positive charge is in general unlikely to inhibit significantly intermolecular dimerisation of methyldene complexes, and we have recently obtained evidence that this is also true in the specific case of cationic tungstenocene methyldenes. It has previously been shown that reaction of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]$ with a protonic acid results in electrophilic removal of a methyl group, and in the case of an acid like benzoic acid subsequent coordination of the counterion leads to formation of an $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)\text{X}]$ complex (23):



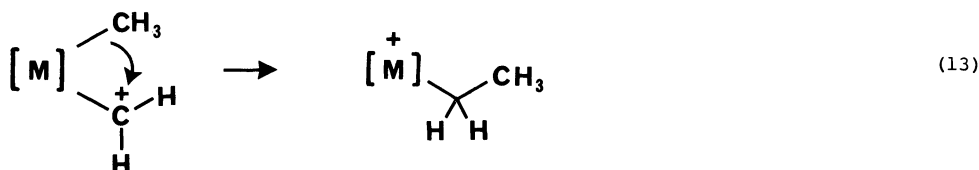
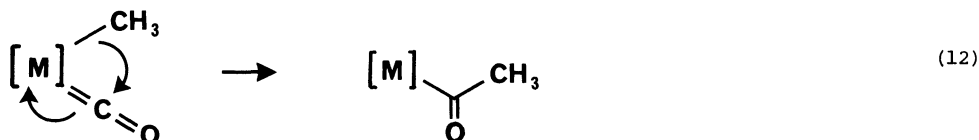
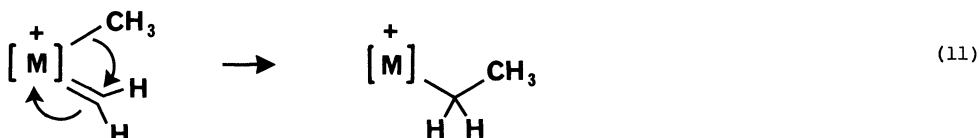
We have recently examined the use of acids with non-coordinating counterions in this reaction, and have discovered that NH_4PF_6 , for example, will react with the dimethyl complex in acetone to give a complex mixture of cyclopentadienyl complexes including a 25% spectroscopic yield of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_4)\text{H}]^+$:

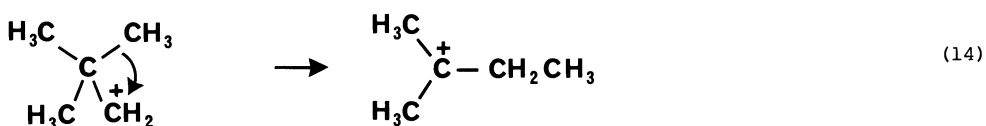


The obvious interpretation of this result is that electrophilic removal of a methyl group leads to formation of a coordinatively unsaturated methyl cation which, as previously established (28), is in equilibrium (eq. 9) with a methyldene hydride complex which can give the ethylene hydride by an intermolecular reaction (eq. 10).



If the charged nature of the methyldene hydride cation does not inhibit intermolecular alkene formation in this case, there is no obvious reason why it should inhibit intermolecular reactions of the methyldenemethyl cation. We would prefer to suggest that the preference for intramolecular insertion in this complex arises because the electrophilicity of the unsaturated carbon center facilitates an insertion which is better regarded as a migratory insertion in which the alkyl group migrates with its bonding electron pair on to the unsaturated center (eq. 11). A similar explanation has been advanced by Bercaw to account for the facility of insertion reactions in neutral niobium carbene complexes in which the unsaturated carbon is rendered electrophilic by the presence of electron withdrawing zirconoxy substituents (29), and both results support the analogy drawn (25) between alkylidene/alkyl insertion and migratory carbonyl/alkyl insertion (eqs. 11 and 12). The facility of the insertion in cationic alkylidene/alkyl complexes also suggests an analogy with Wagner-Meerwein rearrangements of carbonium ions (eq. 13 and, e.g., eq. 14).





The validity of the assumption that migratory insertion is a characteristic reaction of electrophilic alkylidene/alkyl complexes is strongly supported by recent results from three other groups. Thorn and Tulip (30) have observed that electrophilic cleavage of a methoxy group from an Ir methoxymethyl complex containing a *cis*-methyl group results in formation of an ethyl complex, and have obtained evidence that this occurs via insertion in a cationic methylidenemethyl complex, and Werner and coworkers (31) have discovered that hydride abstraction from a dimethylruthenium complex leads to formation of a cationic ethylenehydride ruthenium complex. Both this reaction and recent results from Green's group (32) closely parallel our results.

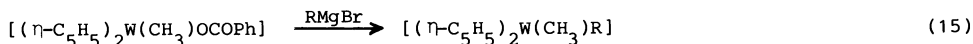
Although it is clear that migratory insertion is particularly facile in cationic alkylidene alkyl complexes, it should be emphasized that insertion can also be observed in neutral alkylidene alkyl complexes under appropriate conditions. Thus, reaction of $[\text{W}(\text{CCMe}_3)(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)(\text{dmpe})]$ with neat *dmpe* at 140°C results in formation of $[\text{W}(\text{CCMe}_3)(\text{dmpe})_2\text{H}]$ together with 2,2,5,5-tetramethyl-*trans*-3-hexene in a reaction which probably involves insertion as the C-C bond forming step (33), and $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{CHCH}_3)\text{CH}_3]$ forms the isomeric propene hydride in toluene at 75°C in the first reported example of alkylidene alkyl insertion (25). This latter reaction is particularly interesting when compared with the room temperature intermolecular decomposition observed for $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{CH}_2)\text{CH}_3]$ (27): the most probable explanation is that there is a fine balance between insertion and dimerization in this system, and that unfavorable 1,3-diaxial steric interactions in the dimetallacyclobutane which would be the putative intermediate in intermolecular decomposition of the ethylidene complex allow insertion to become the dominant reaction mode under forcing conditions.

REGIOSPECIFICITY OF THE HYDROGEN ATOM ABSTRACTION REACTION

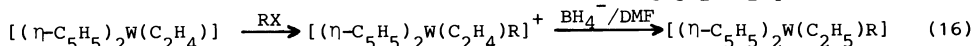
Preparation of substrates for regiochemical studies

The presence of a single type of removable hydrogen in $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]^+$ leaves the reaction with trityl radical regiochemically unambiguous, but the use of alternative tungstenocene dialkyl radical cations as substrates could in principle give rise to a number of alternatives to α -hydrogen abstraction. This is particularly true in the case of alkyls carrying hydrogens β to the metal atom, since α -hydrogen removal from such a substrate would lead to cationic alkene complexes of the general formula $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\eta^2\text{-CHR})\text{R}']^+$, and several examples of stable complexes of this type have been reported previously in this system (34,35).

The preparation of suitable substrates for regioselectivity studies required the development of new routes to tungstenocene dialkyls, since direct alkylation of $[(\eta\text{-C}_5\text{H}_5)_2\text{WCl}_2]$ only leads to dialkyls in the case of alkyls lacking β -hydrogens (34). In the case of other alkyls (e.g. C_2H_5 and C_3H_7) the corresponding $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{alkene})\text{H}]^+$ complexes are formed (34), presumably by β -elimination within an intermediate coordinatively unsaturated tungstenocene alkyl. The first new route developed allows access to $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)\text{R}]$ complexes, and involves reaction of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)\text{OCOPh}]$ or $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)\text{I}]_2$ with the corresponding Grignard (eq. 15). We have used this route to prepare $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)(\text{C}_2\text{H}_5)]$ and $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)\text{Ph}]$, and it can probably be extended to give a wide range of other substrates.



A slightly less direct route, which allows access to some substrates not available by the first route, involves BH_4^- reduction of tungstenocenealkenealkyl cations which are themselves prepared by oxidative addition of alkyl halides to $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_4)]$ (35):

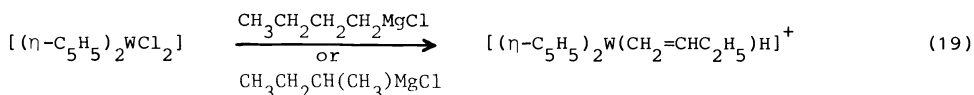
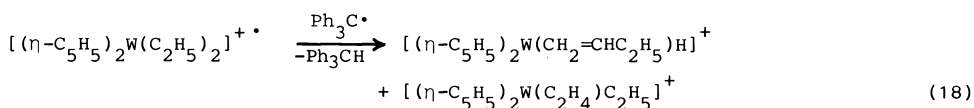
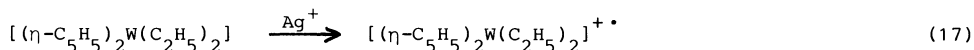


We have used this as an alternative route to $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)(\text{C}_2\text{H}_5)]$ and to prepare $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_5)_2]$ and $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}]$, but have yet to extend it beyond cases in which the alkene is ethylene. The most obvious limitation on this route to date is that only relatively reactive addends such as CH_3I and PhCH_2Br react readily with the neutral ethylene complex: to prepare the substrate for the preparation of the diethyl complex it was necessary to react the neutral ethylene complex with neat EtI .

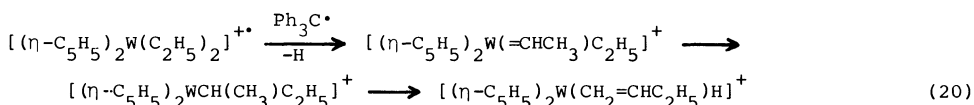
Regiospecificity in abstraction from the diethyl complex

The diethyl complex, although one of the more difficult substrates to prepare, is in many ways the most straightforward for regiochemical studies. The complex is readily oxidized to

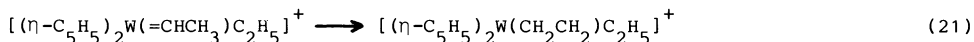
the diethyl radical cation (eq. 17), and reaction of this with $\text{Ph}_3\text{C}\cdot$ leads to formation of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_2=\text{CHCH}_2\text{CH}_3)\text{H}]^+$ in 78% yield, together with a 7% yield of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_4)\text{-C}_2\text{H}_5]^+$ (eq. 18). The butene hydride has been shown to be a mixture of the *exo* and *endo* isomers of the 1-butenehydride by analysis of the 300 MHz ^1H n.m.r. spectrum of the cation. Decoupling experiments have shown that no 2-butenehydrides are formed, and the identity of the complex has been confirmed by independent synthesis (eq. 19).



Formation of the 1-butenehydride from the diethyl radical cation strongly suggests that $\text{Ph}_3\text{C}\cdot$ selectively abstracts an α -hydrogen to give an ethylidene cation (eq. 20). Migratory insertion within this would lead to an isobutyl cation which could form the butenehydride by β -elimination. The 2-butyl cation could in principle give rise to the 2-butenehydride as well as the terminal isomer, but the latter is apparently preferred. This is probably due to steric factors: steric control is usually assumed to be responsible, for example, for the preferential formation of terminal alkyls in hydrozirconation reactions (36).



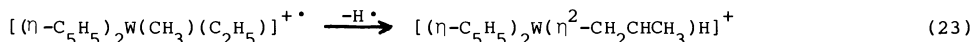
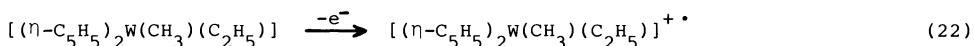
The origin of the $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)]^+$ formed remains ambiguous. Although this is formally the product of β -hydrogen atom abstraction for the diethyl radical, this would be an unprecedented regioselectivity for hydrogen atom removal (as distinct from hydride ion abstraction: *vide infra*). It would seem more probable that the ethyleneethyl cation is formed from the ethylidene intermediate by a 1,2-hydride shift which competes efficiently with migratory insertion (eq. 21). Such reactions have been reported previously to be facile in cationic alkylidene complexes (16).



Whatever the mechanism of formation of the ethyleneethyl cation, it is clear that hydrogen atom abstraction from the diethyl radical cation is predominantly α -selective. This suggests that the π -component of the metal-carbon double bond is sufficiently well developed in the transition state to produce significant stabilization, and we speculate that this may reflect significant ground state spin delocalization *via* metal-carbon π -interactions. Arguments for precisely such a delocalization have been presented recently on the basis of ^1H n.m.r. (37) and photoelectron spectrometry (38) studies of paramagnetic vanadium alkyls.

Regiospecificity of abstraction from the ethyl methyl complex

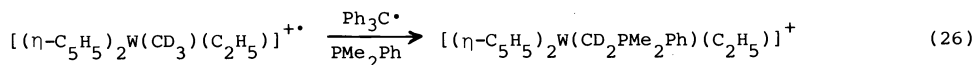
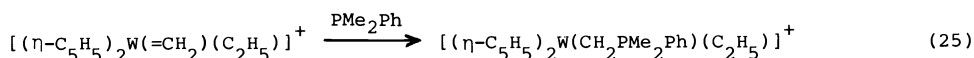
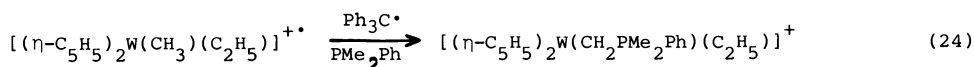
Selective α -hydrogen atom abstraction is also observed from the ethyl methyl cation prepared by oxidation of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)(\text{C}_2\text{H}_5)]$ (eq. 22). Reaction of this with $\text{Ph}_3\text{C}\cdot$ leads to formation of the propene hydride cation (eq. 23), and there is no evidence for the formation of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_4)\text{CH}_3]^+$. This would be the product of β -hydrogen abstraction, and it is a known molecule (35) which we have shown to be stable under the reaction conditions.



It is not *a priori* obvious whether the propene hydride is formed *via* an ethylidene or a methylidene cation. Either of these could in principle give rise to the observed product by an insertion/elimination sequence and, to determine the regiospecificity of $\text{H}\cdot$ loss from the radical cation, we have had to carry out two trapping experiments.

The first trapping experiment involved the reaction of the ethylmethyl radical cation with $\text{Ph}_3\text{C}\cdot$ in the presence of a phosphane (eq. 24) and led to formation of a phosphonium cation analogous to that formed in the reaction of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]^+$ with $\text{Ph}_3\text{C}\cdot$ in the presence of PMe_2Ph . The particular phosphonium salt obtained is that which would be formed by reaction with the methylidene intermediate (eq. 25) rather than the alternative ethylidene intermediate, but the possibility remained that initial formation of the ethylidene cation $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{=CHCH}_3)(\text{CH}_3)]^+$ was followed by rapid conversion to the methylidene cation by intramolecular hydride transfer. It is even conceivable that there could be an equilibrium

between the methyldiene and ethyldiene cations, and the phosphane trapping experiment was accordingly repeated using labelled radical cation (eq. 26).



This reaction resulted in formation of the phosphonium salt with essentially quantitative deuterium labelling at the methylene group and no deuterium incorporation into the ethyl group, indicating that hydrogen atom abstraction from the ethylmethyl radical cation occurred exclusively from the methyl group.

The origin of the methyl selectivity in this reaction is not at this point clear. It may simply reflect steric control and arise because the hydrogens of the methyl group are more accessible than the methylene hydrogens of the ethyl group. It is also possible, however, that the selectivity reflects an underlying electronic control mechanism, and one such possibility is shown in Fig. 2.

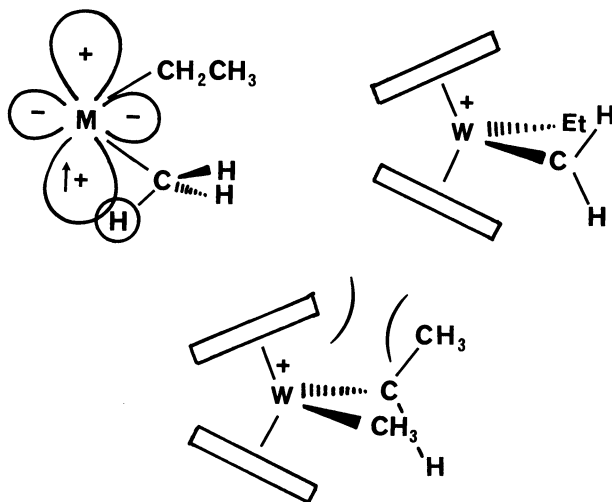
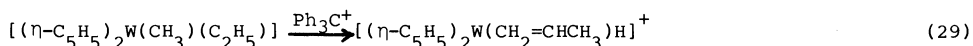
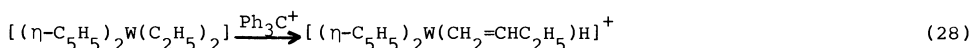
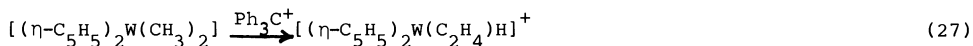


Fig. 2. Possible electronic origin of methyl selectivity.

If we are correct in assuming that there is significant ground state interaction between the metal center and the α -carbons, this could involve overlap of an α -C-H bond with the half-filled frontier orbital (39). Such a 3-center 3-electron interaction is reminiscent of the 3-center 2-electron interactions for which the term "agostic" was recently coined (40), and would force the remaining substituents on the α -carbon to adopt a conformation perpendicular to the mirror plane between the cyclopentadienyl rings. Such an orientation would involve no steric problems if both of the substituents were hydrogens, but, in the case of the ethyl group, studies of the closely related complex $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{CHCH}_3)(\text{CH}_3)]$ suggest that there should be significant steric interactions with the cyclopentadienyl rings (25). This could render α -C-H overlap with the frontier orbital less favorable for the ethyl ligand and result in greater spin delocalization on to the methyl ligand and hence produce the observed methyl selectivity.

CATIONIC ALKYLIDENE COMPLEXES BY HYDRIDE ABSTRACTION FROM NEUTRAL TUNGSTENOCENE DIALKYLS

The intermediate alkylidene complexes prepared by hydrogen atom abstraction from tungstenocenedialkyl radical cations are formally the products of hydride abstraction from the corresponding neutral tungstenocene dialkyls. Since the trityl cation, the oxidation product of the trityl radical, is a commonly used hydride abstraction reagent, this led us to investigate the reactions of the neutral dialkyls with the trityl cation as shown in eqs. 27-29.



In the case of all of the simple dialkyls whose conjugate cations had been previously examined, the results precisely paralleled those of the radical reactions, and the products were alkenehydride complexes which presumably had been formed by insertion/elimination sequences following the production of transient alkylidene/alkyl complexes (eq. 5,6, and 20).

The formation of the initial alkylidene complexes by both hydrogen atom and hydride ion abstraction routes raised the interesting possibility that the hydride abstraction reactions had in fact occurred by a multi-step electron transfer/hydrogen atom transfer mechanism. It has been established in recent years that many organometallic reactions which result in overall two electron changes in fact occur by sequential one electron steps. Ashby in particular has recently provided evidence that hydride transfers (41-43) and alkyl anion transfers (44,45) from main group organometallics and from both simple and complex hydrides can occur by mechanisms involving initial electron transfer. Similar mechanisms had not, however, been reported for hydride transfers from transition metal alkyls, and we accordingly decided to examine the mechanisms of these hydride transfers (46).

Preliminary experiments involved mixing $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]$ with Ph_3CPF_6 in an EPR tube and rapidly freezing the CH_2Cl_2 solution to -140°C . The EPR spectrum of this glass showed that both $\text{Ph}_3\text{C}^\bullet$ and $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]^{+\bullet}$ had indeed been formed, and it was further observed that if the glass was melted, maintained at 20°C for 1 hr, and refrozen the signal due to $\text{Ph}_3\text{C}^\bullet$ disappeared as a result of further reaction to give, presumably, $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_4)\text{H}]^+$ and Ph_3CH . The expected decrease in the signal due to the tungsten centered radical was also observed, but the final mixture still contained a tungsten centered radical (possibly because some $\text{Ph}_3\text{C}^\bullet$ was consumed in reactions with the solvent).

Although this EPR experiment suggested that a radical pathway was operative, it remained unclear whether this provided the principal pathway for the reaction and we accordingly attempted to trap the intermediate radical cation. This required that we quantify the amounts of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_4)\text{H}]^+$ and $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]^{+\bullet}$ present in mixtures of the two cations. The similar solubilities of the cations precluded high yield separation and only the ethylene complex was directly observable by ^1H n.m.r. We therefore developed an indirect ^1H n.m.r. determination in which mixtures of the cation, which had been washed with toluene to ensure that no excess $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]$ was present, were treated with saturated aqueous potassium hydroxide in acetone for 5 h. Under these conditions the ethylenehydride was deprotonated to give $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_4)]$ in 90% yield, while the radical cation was reduced to $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]$ in 80-90% yield. The approximate composition of the cation mixture was then inferred from ^1H n.m.r. measurements of the ratio of the two neutral species.

This technique has enabled us to determine that the reaction of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]$ with Ph_3C^+ at -78°C results in essentially exclusive oxidation to the dimethyl radical cation, which can be isolated in 73% yield using a low temperature work-up. The only variable which has been changed in this experiment is the reaction temperature, and we conclude that hydride abstraction from $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]$ occurs exclusively by an electron transfer mechanism. Since similar reactions of $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{C}_2\text{H}_5)_2]$ and $[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)(\text{C}_2\text{H}_5)]$ with Ph_3C^+ at -78° also resulted in high yield oxidations of the neutral dialkyls, we further conclude that hydride abstractions from these readily oxidised tungstenocene dialkyls generally occur by electron transfer mechanisms.

The relationship between the electron transfer mechanism by which hydride abstraction occurs in this system and the observed α -selectivity in the abstractions is not, as yet, completely clear. It is tempting to speculate, however, as discussed above, that the selectivity is associated with spin delocalization from the metal center on to α -C-H bonds in the intermediate radical cations. If this is the case, it seems probable that α -selectivity will generally be observed for hydride abstraction if the redox potential of a transition metal alkyl is sufficiently negative to allow electron transfer to provide a kinetically competent route for hydride abstraction, and if the orientation and extent of the frontier orbital in the intermediate radical allows for interaction with the α -C-H bonds.

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