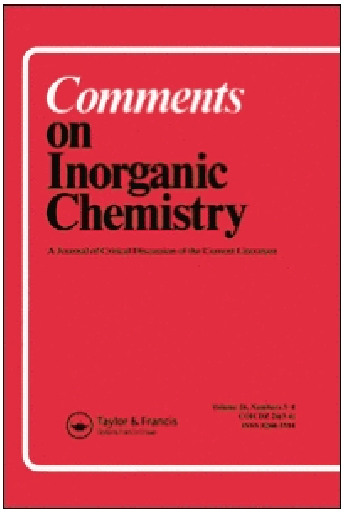

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Comments on the Chemistry of Low-Valent Alkylidyne Complexes of the Group 6 Transition Metals

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Comments on the Chemistry of Low-Valent Alkylidyne Complexes of the Group 6 Transition Metals

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Key Words: *Group 6 transition metal alkylidyne complexes, synthesis, alkylidyne hydride and alkylidene metal complexes, alkylidyne–carbonyl, alkylidyne–isocyanide, and alkylidyne–alkylidyne ligand coupling reactions, alkylidyne alkene metal complexes, vinylcarbene metal complexes, alkylidyne alkyne metal complexes*

1. INTRODUCTION

The chemistry of metal–carbon multiple bonds has grown into a major branch of organometallic chemistry since its beginning in 1963.[1] Metal alkylidene and alkylidyne[2] complexes, which originated from purely fundamental research efforts, are now used as building blocks for organometallic synthesis, and as catalytic and stoichiometric reagents for organic synthesis. The chemistry of metal alkylidenes has developed much further than the chemistry of metal alkylidynes. However, interest in alkylidyne complex chemistry has been rising in recent years as documented by several review articles.[3]

The chemistry of metal alkylidynes is still strongly influenced by

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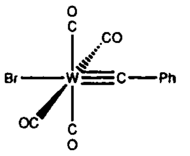
the pioneering work in three leading laboratories. Fischer[4] and co-workers reported the first complexes containing metal–carbon triple bonds in 1973: the now classical trans-alkylidyne(halo)-tetracarbonyl complexes of the group 6 transition metals, e.g., **1**. Soon a family of ligand-substituted derivatives and of related alkylidyne complexes of manganese and rhenium were established.[5] These compounds are now widely known as Fischer-type carbyne complexes. In 1975 Guggenberger and Schrock reported the first high-valent tantalum alkylidyne complex.[6] Schrock-type alkylidyne complexes of tungsten, molybdenum, and rhenium were synthesized in the following years, **2** being a representative example.[7] In 1980 Roper and co-workers reported the osmium carbyne complex **3**, the first example of an electron-rich carbyne complex of a late transition metal.[8] Several more Roper-type carbyne complexes of osmium and ruthenium have been characterized since.[9]



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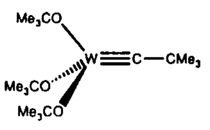

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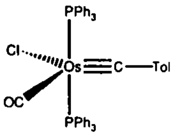

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Over the years chemical relationships between these types of alkylidyne complexes were discovered. Schrock demonstrated that high-valent tungsten alkylidyne complexes can be reduced to give derivatives of the Fischer-type,[10] and Roper successfully oxidized osmium carbynes such as **3** to obtain systems which are isoelectronic to Fischer-type complexes.[11] These reactions and the discovery of alkylidyne complexes of iron[12] and iridium[13] illustrate that metal–carbon triple bonds may exist for a range of transition metals in variable oxidation states.

The study of the reactivity of metal–carbon triple bonds, while still largely restricted to the three original types of metal alkylidyne complexes, has been progressing rapidly in recent years. The most significant achievement was certainly the demonstration of alkyne metathesis by high-valent alkylidyne complexes.[14] Other metathesis reactions with $C{=}O$ and $C{\equiv}N$,[15] as well as $M{\equiv}M$[16,17] multiple bonds were discovered, and more general chemical relationships with metal alkylidyne, imido, nitrido, and oxo complexes became apparent.[18] Based on the isolobal relationship of alkenes and alkynes with metal alkylidenes and alkylidynes as ligands for transition metal complexes, Stone's group realized the potential of low-valent alkylidyne complexes as building blocks for transition metal clusters.[19] Alkylidyne ligands were shown to undergo insertion reactions, in particular with carbon monoxide.[20] Metal–carbon triple bonds engage in a variety of typical multiple bond reactions such as addition[8] and cycloaddition.[21] These few selected highlights may serve to illustrate the complexity and richness of alkylidyne metal complex chemistry; they also provide a sense of the future potential of the chemistry of metal–carbon triple bonds.

This essay comments on various aspects of the chemistry of alkylidyne complexes of the group 6 transition metals, focussing on work from the author's laboratory. An attempt is made to present general aspects rather than to describe experimental details. Some of the comments are speculative, but if they stimulate research activities they will have fulfilled their purpose.

2. QUALITATIVE ASPECTS OF BONDING IN METAL ALKYLIDYNE COMPLEXES

From theoretical work a consistent molecular orbital description of metal–carbon triple bonds has emerged.[22] Figure 1 shows a qualitative energy level diagram for octahedral systems. The carbyne carbon has three orbitals available to interact with the metal center, a σ orbital, which may be taken as an sp hybrid, and two p orbitals. The sp hybrid interacts with an appropriate metal σ orbital to form a metal–carbon σ bond, and the two p orbitals interact with metal d_π orbitals, d_{xz} and d_{yz}, to form two π bonds. The remaining metal d_π orbital, d_{xy}, does not interact with the carbyne ligand. Above the d_{xy} orbital are the antibonding MC π^* orbitals. In all metal alkylidyne complexes the σ and π orbitals are filled, forming the metal–carbon triple bond. The d_{xy} orbital is filled in Fischer-type carbyne complexes, and empty in Schrock-type alkylidynes. Due to the presence of a filled metal d_π orbital the nature of Fischer-type carbyne complexes is characteristic of low valent transition metal complexes while the absence of easily available d electrons makes Schrock-type alkylidyne complexes behave like typical high-valent metal complexes.

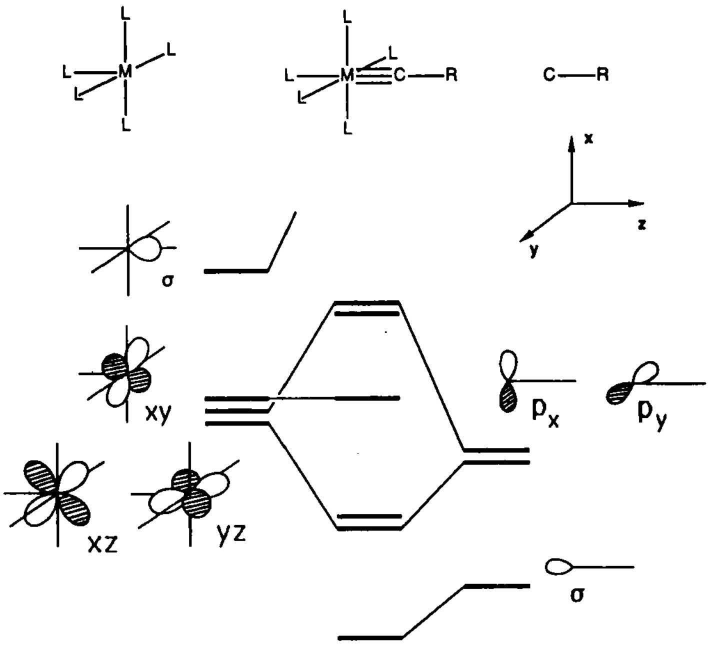


FIGURE 1 Qualitative molecular orbital scheme for a metal alkylidyne complex. ML_5 represents a metal complex fragment with five donor ligands.

This basic situation is modified slightly depending on the nature of the ancillary ligands. Figure 2 shows a simplified MO scheme for a representative Fischer-type carbyne complex. As in most Fischer-type carbyne complexes the filled d_{xy} orbital is stabilized by the presence of equatorial π acceptor ligands (Fig. 2). Its energy falls close to that of the lone pairs of the trans halide ligand X. If several very strong π acceptor ligands are present, e.g., in $[M(CR)X(CO)_4]$, the energy of the d_{xy} orbital falls below the energy of the halogen lone pairs.[23,24] (The interactions of the donor ligand p orbitals with the d_{xz} and d_{yz} orbitals are not as strong as other π effects in the molecule and are not shown in Fig. 2). Only one π* acceptor orbital (i.e., a symmetry adapted linear combination) can interact with the d_{xy} orbital. The remaining π* acceptor orbitals do not strongly interact with the metal center; they are close in energy to the MC π^* orbitals, and, as the case may be, are above or below the MC π^* orbitals. The metal–halogen σ^* orbital is found in the same region as the MC π^* orbitals (not shown in Fig. 2).[23]

In the following chapters we will use this molecular orbital picture as a basis for our discussions. The essential points concerning the bonding in low-valent alkylidyne complexes and some chemical consequences are summarized as follows:

(i) The HOMO is formed by a high-lying filled metal d orbital. π acceptor ligands interact with this orbital. In the presence of several strong π acceptor ligands the energy of the d orbital may come close or even fall below the energy of donor ligand lone pairs.

(ii) The LUMO is formed by MC π^* orbitals. If present, empty

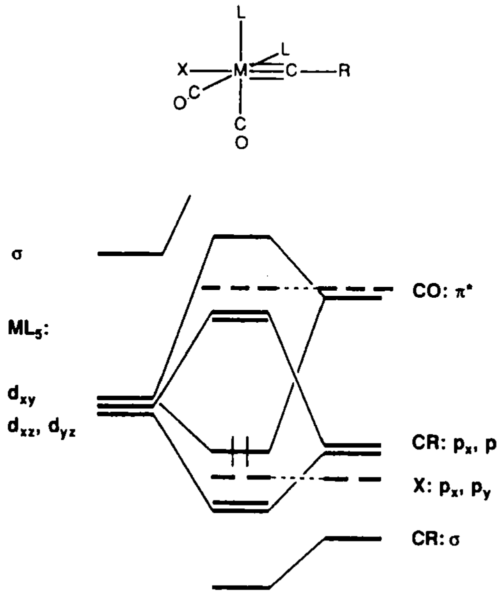


FIGURE 2 Qualitative molecular orbital scheme for a representative group 6 transition metal alkylidyne complex. This scheme is derived from Fig. 1 by adding additional ligand π orbitals to the *right* orbital column for interaction with the ML_5 fragment. Only the most important π interaction with carbon monoxide is shown.

orbitals of π acceptor ligands and ML σ^* orbitals may also be in the same energy region.

(iii) The MC π orbitals are lower[24] in energy than the metal d orbital, but chemically active. Experimental facts suggest that ordinary π acceptor ligands do not significantly interact with the MC π electrons, while stronger electrophiles, such as protons, may interact strongly.

(iv) The alkylidyne carbon carries a partial negative charge (due to polarization of the metal carbon bond), favoring charge-controlled attack of electrophiles at the alkylidyne carbon.[23,24]

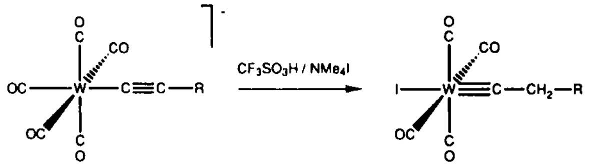
Due to the close spacing of orbitals in the HOMO and LUMO region the relative ordering of orbitals is easily affected by changes in the central metal atom or ancillary ligands (and concomitantly the overall charge of the molecule). Because of this situation and due to the highly covalent nature of metal–carbon triple bonds, the reactivity of metal alkylidynes is easily influenced. Depending on the nature of the system, electrophiles and nucleophiles are found to attack on either the metal center or the carbyne carbon, or on ancillary ligands. As a consequence, the chemistry of low-valent metal alkylidynes is complex and somewhat difficult to predict. On the other hand, however, for exactly the same reasons the reactivity of metal–carbon triple bonds is subject to subtle electronic and steric control.

3. SYNTHESIS OF METAL ALKYLIDYNE COMPLEXES

In recent years we have developed several new methods for the synthesis of metal alkylidyne complexes. This effort had three main objectives: (a) to widen the range of transition metal alkylidyne complexes, (b) to find effective ways to control the electronic properties of alkylidyne complexes, e.g., by introducing appropriate ligand sets, and (c) to design alkylidyne complexes containing coordinatively labile ligands for facile introduction of substrates under mild conditions. All three areas are still in need of further development, but some progress has been made, especially regarding points (b) and (c).

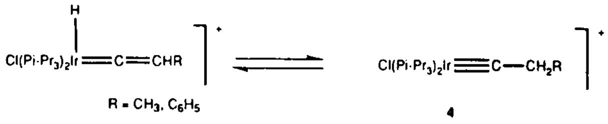
3.1. Double β-Addition of Electrophiles to Acetylide Ligands

Transformation of acetylide ligands into vinylidene ligands and transformation of vinylidene ligands into alkylidyne ligands by addition of electrophiles to the β carbon atom is well established.[25] The anionic acetylide complexes $[NEt_4][W(C{\equiv}CR)(CO)_5]$ ($R = CMe_3$, Ph) are sufficiently electron-rich to allow both steps to occur in the same system.[26] Double β protonation is especially attractive as a one-step synthesis of carbyne complexes from acetylide complexes (Eq. (1)). Related transformations were demonstrated involving the electron-rich acetylide complex $[W(C_2CO_2Me)H_2(dppe)_2]$ (dppe = bis-diphenylphosphino ethane).[27]



(1)

The observation of an equilibrium between iridium vinylidene and alkylidyne complexes by Werner[13] indicates both the potential and possible limitations of this method for the synthesis of alkylidyne complexes of late transition metals (Eq. (2)).



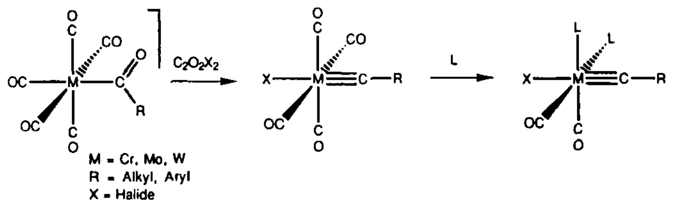
(2)

The limitation may be the preference of protonation at the metal center. Nevertheless, the spectroscopic characterization of iridium complex **4** is very significant, since it demonstrates the existence of a metal–carbon triple bond in an electron-rich late transition metal complex with a low coordination number. Such alkylidyne complexes can be expected to exhibit a distinctly different and unique chemistry. With Werner's discovery it is now almost certain that the exploration of this potentially rich area of chemistry only awaits the development of efficient synthetic methods.

3.2. Oxide Abstraction from Acyl Ligands

The Fischer-type carbyne complexes [$M(CR)X(CO)_4$] (M = Cr, Mo, W; R = alkyl, aryl; X = halide) still form the most versatile starting materials in the chemistry of metal–carbon triple bonds. These compounds are generally available by the original method of Fischer and Kreis, which involves treatment of the corresponding alkoxycarbene pentacarbonyl metal complexes with boron trihalides.[28] The alkoxycarbene complexes are in turn obtained by alkylation of the anionic acyl complexes Li[$M(COR)(CO)_5$].

A new method[29] combines several synthetic steps[30,31] previously described by Fischer. It circumvents the need for alkoxycarbene metal complexes as intermediates[30] and utilizes the stabilizing effect of donor ligands in Fischer-type carbyne complexes.[31] Reaction of the acyl pentacarbonylmetal complexes with phosgene or oxalyl halides at low temperatures affords the trans-alkylidyne halo tetracarbonyl metal complexes, which are directly transformed into donor ligand-stabilized derivatives (Eq. (3)).[26] Other Lewis-acids may be used for the formal abstraction of oxide from acyl ligands, e.g., trifluoroacetic anhydride, affording halide-free alkylidyne complexes.

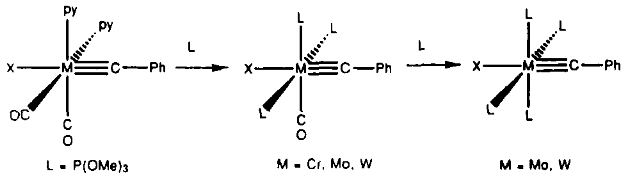


(3)

3.3. Modification by Ligand Substitution Reactions

Ligand substitution in carbyne complexes in the positions cis and trans to the carbyne ligand are well established.[31,32] Mechanistic studies on complexes of the type [$M(CR)X(CO)_4$] by H. Fischer showed that substitution of carbon monoxide occurs by a dissociative mechanism[33] while exchange of halide proceeds via an associative pathway.[34] When simple σ donor ligands are used, two carbonyl ligands are substituted in the tetracarbonyl systems.[31] When the donor ligand is bulky, such as triphenyl or triisopropylphosphine, monosubstituted derivatives may be isolated.[31]

Substitution of more than two carbonyl ligands occurs when the substituting ligand has π acceptor properties, such as trimethylphosphite (Eq. (4)).[35] The trimethylphosphite ligands may in turn be substituted by other ligands to afford further carbonyl-free derivatives (Eq. (5)). Filippou and Fischer recently demonstrated that tris and tetrakis-substituted derivatives may also be obtained using isocyanide ligands.[36]



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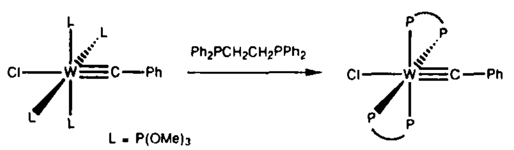
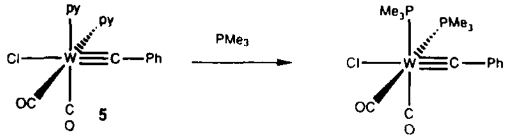


(5)

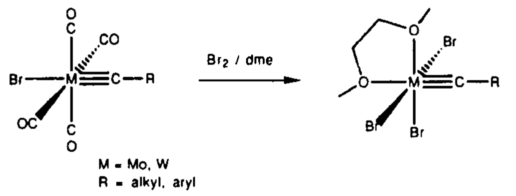
The bis-pyridine complexes $[M(CR)X(CO)_2(py)_2]$, e.g., **5**, are a convenient alternative to the tetracarbonyl systems as starting materials for ligand substitution reactions.[29] In many cases the products are the same. However, the presence of the two pyridine ligands suppresses the electrophilicity of the carbyne carbon, and this feature proved essential in the synthesis of the bis-trimethylphosphine-substituted complex $[W(CPh)Cl(CO)_2(PMe_3)_2]$ (Eq. (6)). In contrast, reaction of PMe_3 with $[W(CPh)Br(CO)_4]$ was shown to result in formation of the ylide complex $[W\{C(PMe_3)Ph\}Br(CO)_2(PMe_3)_2]$.[31]



(6)

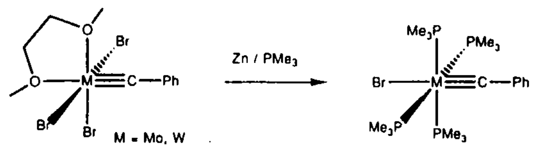
3.4. Oxidative and Reductive Interconversions of Alkylidyne Complexes

Bromine oxidation of the complexes $[M(CR)Br(CO)_4]$ in the presence of dimethoxyethane (dme) affords the tribromometal alkylidyne complexes $[M(CR)Br_3(dme)]$ (Eq. (7)).[37]



(7)

Thus Fischer-type and Schrock-type alkylidyne complexes are conveniently accessible from the same starting materials. The trihalometal alkylidyne complexes are among the most useful starting materials in the chemistry of high-valent metal alkylidynes.[38] The tribromometal alkylidyne complexes may in turn be used for the reductive synthesis of low-valent tetrakis-trimethylphosphine metal alkylidynes (Eq. (8)).[39]



(8)

Filippou and Fischer recently synthesized a series of oxidized tungsten aminocarbyne complexes, e.g., $[W(CNEt_2)I_2(\eta^5\text{-}C_5H_5)(CO)]$, which retain at least one carbonyl ligand.[40] The stability of the metal–carbonyl bond is a clear indication that an azavinylidene resonance form[41] makes a very important contribution to the bonding of the aminocarbyne ligand.

$$M{\equiv}C{-}NR_2 \longleftrightarrow M{=}C{=}\overset{+}{N}R_2$$

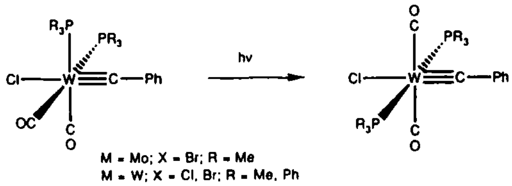
In oxidized systems containing alkyl- or aryl-substituted alkylidyne ligands such resonance effects would most likely be too insignificant to allow the existence of stable systems. We observed, however, the formation of carbonyl-containing products upon reaction of the $[W(CPh)Br(CO)_2(tmeda)]$ (tmeda = tetramethyl ethylenediamine) with bromine. Unfortunately, we were not able to fully characterize these complexes, but we postulate the addition of Br_2 across the metal–carbon triple bond to give a seven-coordinate complex containing a bromoalkylidene ligand. The addition of dihalogens across the metal–carbon triple bond in osmium alkylidyne complexes has been observed.[8]

The successful oxidation[11] of Roper-type carbyne complexes such as $[Os(CPh)Cl(CO)(PPh_3)_2]$ to afford derivatives which are isoelectronic with Fischer-type systems suggests that Fischer-type group 6 metal carbyne complexes may be reduced to a lower formal oxidation state. Attempts to reduce complexes such as $[W(CPh)Cl(CO)_2\{P(OPh)_3\}_2]$ by sodium amalgam or sodium naphtalenide do indeed afford reduced species in solution; however, full characterization of the expected reduced carbyne complexes has not yet been successful.[42]

Oxidative and reductive interconversions of rhenium alkylidyne complexes were recently demonstrated by Herrmann.[43] Pombeiro observed electrochemically induced reactivity of alkylidyne ligands.[44] Photo-induced redox reactions of tungsten alkylidyne complexes were demonstrated by Bocarsly[45] and by McElwee-White.[46] Clearly, alkylidyne ligands are capable of supporting an extensive redox chemistry.

3.5. Photochemical cis-trans Isomerization of bis-Phosphine-Substituted Complexes

Bis-donor ligand-substituted derivatives are generally obtained as the cis isomers as one might expect for electronic reasons. However, with increasing steric demand a preference for the trans arrangement of the donor ligands is observed. The cis bis-phosphine complexes $[M(CPh)X(CO)_2(PR_3)_2]$ were found to isomerize to the trans isomers upon irradiation with visible light (Eq. (9)).[47]



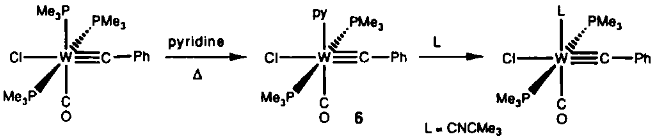
(9)

The isomerization process is believed to involve a pentacoordinate intermediate, generated by photo-induced carbyne–carbonyl coupling (Section 4.2). With the bulkier triisopropylphosphine the trans isomers form directly, i.e., thermally; the cis isomers were found to be too unstable to be isolated.[48]

Photochemical[47,49,60c] and photophysical[50] studies of transition metal alkylidyne complexes are still rare,[51] but the unique excited-state behavior of metal–carbon triple bonds is already evident.

3.6. Alkylidyne Complexes Containing Coordinatively Labile Ligands

Low-valent alkylidyne complexes of the group 6 transition metals are in almost all cases electronically saturated 18 electron species. Reactions with substrates will therefore be facilitated by prior dissociation of a ligand. Thus stable alkylidyne complexes containing coordinatively labile ligands should prove useful in the investigation of alkylidyne complex reactivity. The bis-pyridine-substituted complex **5** may serve as an example. One[83] or two[29b] pyridine ligands may be substituted, depending on the added ligand; the lability of the pyridine ligands was shown to be essential in the synthesis of new alkylidyne alkene complexes (see Section 4.4.1).[83] Treatment of [W(CPh)Cl(CO)(PMe$_3$)$_3$] with hot pyridine affords complex **6**. The pyridine ligand in **6** is easily substituted (Eq. (10)).[59]



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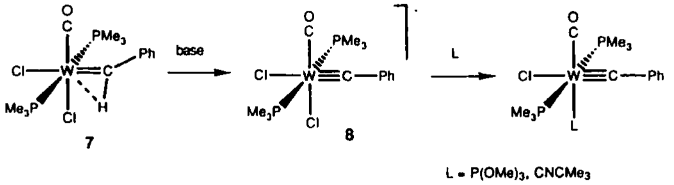
(10)

A related, even more reactive alkylidyne complex is generated by deprotonation of the activated alkylidene complex **7** (see Section 4.1). For example, reaction of **7** with butyl lithium at low temperatures results in quantitative formation of the anionic carbyne complex Li[W(CPh)Cl$_2$(CO)(PMe$_3$)$_2$], **8** (Eq. (11)). Complex **8** decomposes at room temperature, but undergoes clean substitution of one chloride ligand to give carbyne complexes of the type [W(CPh)Cl(CO)L(PMe$_3$)$_2$] (Eq. (11)).[39]



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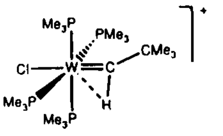
(11)

4. REACTIONS OF ALKYLIDYNE METAL COMPLEXES

4.1. Protonation Reactions

Reactions of alkylidyne complexes with protons are of special interest since this electrophile is one of the simplest reagents possible to test the reactivity of metal–carbon triple bonds. Studies by Schrock[52] and by Green[53] showed that the outcome of protonation of low-valent alkylidyne complexes depends strongly on the nature of the complex and that the location of the proton in the product may be different from the site of initial electrophilic attack. For example, protonation of $[W(CCMe_3)Cl(PMe_3)_4]$ with CF_3SO_3H gives $[W(CHCMe_3)Cl(PMe_3)_4]^+$, **9**, a complex containing an activated neopentylidene ligand, while protonation of sterically less congested $[W(CCMe_3)Cl(dmpe)_2]$ gives the neopentylidyne hydride complex $[W(CCMe3)Cl(H)(dmpe)_2]^+$, **10**.[52]



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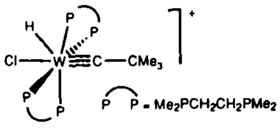

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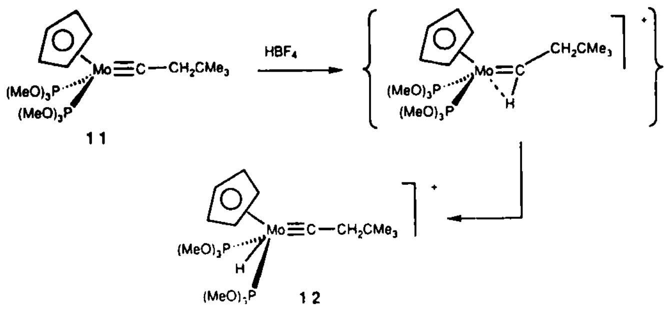
Indirect evidence was presented that protonation of $[Mo(CCH_2CMe_3)(\eta^5\text{-}C_5H_5)\{P(OMe)_3\}_2]$, **11**, with HBF_4 occurs initially at the alkylidyne carbon to give $[Mo\{CHCH_2CMe_3\}(\eta^5\text{-}C_5H_5)\{P(OMe)_3\}_2]^+$ containing an activated alkylidene ligand, which subsequently rearranges to the alkylidyne hydride complex $[Mo(CCH_2CMe_3)(\eta^5\text{-}C_5H_5)(H)\{P(OMe)_3\}_2]^+$, **12** (Eq. (12)).[53]

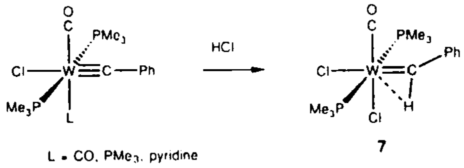
While additional studies are needed to arrive at general conclusions, it appears that the site of kinetic attack by protons is the alkylidyne carbon, or perhaps more appropriately, the π electrons of the metal–carbon triple bond.[54] This is in agreement with theoretical calculations which show that the alkylidyne carbon atom is carrying a net negative charge, even in the tetracarbonyl systems.[23,24]

We found that protonation of the complexes $[W(CPh)Cl(CO)L(PMe_3)_2]$ results in formation of the electronically unsatu-



(12)

rated benzylidene complex $[W(CHPh)Cl_2(CO)(PMe_3)_2]$, **7** (Eq. (13)).[27]



(13)

The molecular structure of **7** is shown in Fig. 3. The benzylidene ligand is highly activated as evidenced by the large W–C(8)–C(9) angle of 164.6°. However, complex **7** does not convert into an alkylidyne hydride complex. Since the complex is not sterically crowded, there must be a high electronic barrier for this transformation.[55] This barrier is proposed to be caused by the presence of the carbonyl ligand. Through full transfer of the proton to the metal center the d electrons would become localized in the metal–hydrogen bond and thus become unavailable for π backbonding to the carbonyl ligand. Formation of a localized metal–hydrogen bond would cause dissociation of carbon monoxide and therefore even greater electronic unsaturation of the metal center. Thus even though the metal d electrons are probably higher in energy than the electrons in the metal–carbon triple bond, the proton does not utilize these electrons for bond formation. The activated nature of the alkylidene ligand may thus be described as an arrested migration of the proton from the metal–carbon π electrons to the metal d electrons.

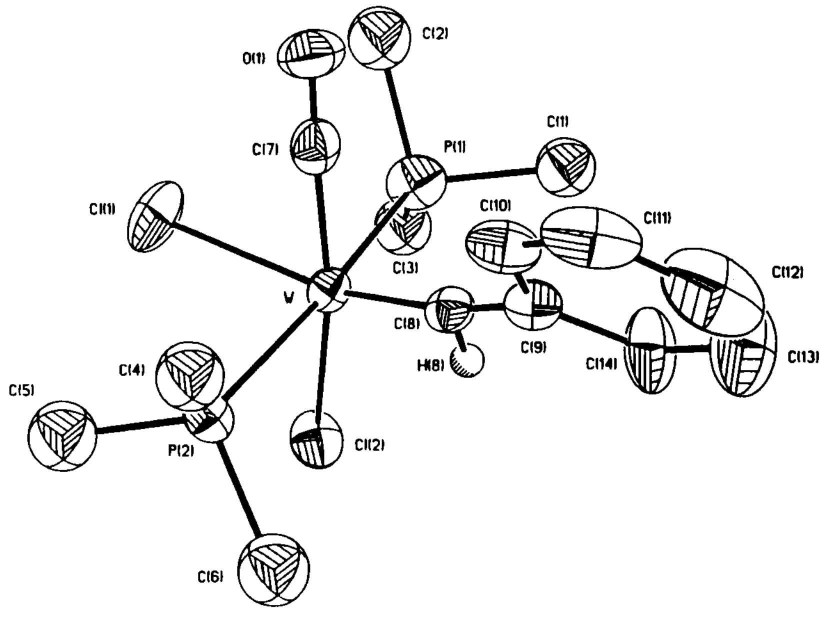
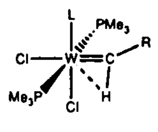
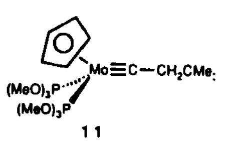


FIGURE 3 Molecular structure of $[W(CHPh)Cl_2(CO)(PMe_3)_2]$ (7). Important bond distances and angles: W–C(8), 186.0 (7)pm; W–C(8)–C(9), 164.6 (6)°. (From Ref. 39, with permission.)

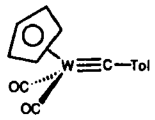
In light of this discussion it is interesting to ask how replacement of carbon monoxide in 7 by other ligands would affect the location of the proton along the metal–carbon triple bond. For example one might wish to determine the minimal π acceptor strength of L needed to prevent migration of the proton from the alkylidyne carbon to the metal center.



One additional member of this family of complexes is $[W(CHCMe_3)Cl_2(\eta^2\text{-}C_2H_4)(PMe_3)_2]$.[56] In this case the ligand L is ethylene. The molecular structure of this compound has not been determined, but the C–H coupling constant (J_{CH} = 70 Hz), which is similar to that found for **7** (J_{CH} = 82 Hz), indicates that the location of the hydrogen atom is very similar in these two systems. There are two additional complexes, which should be included in this discussion: $[W(CPh)Br_2(H)(PMe_3)_3]$, **13**,[57] and $[W(CHPh)Br_2(PhC_2Ph)(PMe_3)_2]$, **29**.[88] These compounds represent the two possible extremes for the positional range of the hydrogen atom. Complex **13** was obtained by protonation of $[W(CPh)Br(PMe_3)_4]$ with two equivalents of HBr. PMe_3 has essentially no π acceptor ability; therefore complex **13** exists as the hydride alkylidyne system. In complex **29** the hydrogen atom is located on the "alkylidyne" carbon, forming an almost undistorted alkylidene ligand. The bonding in this complex is described in detail in Section 4.4.3. In the present context, we focus on the π acceptor ability of the alkyne; it prevents formation of the metal hydride. The π donor ability of the alkyne "pushes" the hydrogen atom onto the "alkylidyne" carbon. A relevant pair of complexes is also formed by **11** and **14**. In Green's complex **11**, containing two phosphite ligands, full transfer of the proton to the metal center was found to occur, as mentioned above.[53] On the other hand, protonation reactions of the related dicarbonyl tungsten complex **14** afford only products derived from C-protonation.[58]

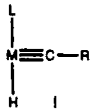


11

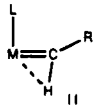


14

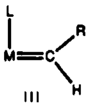
The nature of ancillary ligands thus has a decisive influence on the outcome of protonation of metal alkylidynes. In the complexes **7**, **13**, and **29** variation of the single ligand L is sufficient to control the position of the hydrogen atom "along the metal–carbon triple bond." If L has no or only weak π acceptor properties (phosphine), the hydrogen atom is located on the metal center (I). If L is a sufficiently strong π acceptor ligand (carbon monoxide), the hydrogen is located "over" the metal–carbon triple bond (II). If L is a π acceptor/π donor ligand, the hydrogen atom is located on the "alkylidyne" carbon (III).



I

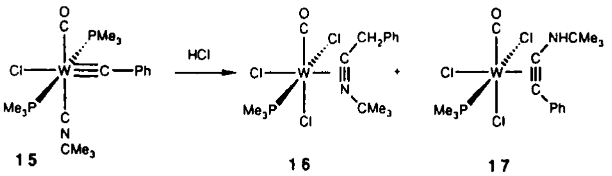


II



III

Exploring the possibility of preparing an isocyanide analogue of complex **7**, we studied the protonation of the alkylidyne isocyanide complex $[W(CPh)Cl(CO)(CNCMe_3)(PMe_3)_2]$, **15**.[59] With CF_3SO_3H protonation occurs, as expected, at the metal–carbon π system to afford an activated alkylidene ligand, but with HCl two products, **16** and **17**, resulting from carbon–carbon bond formation are obtained (Eq. (14)).



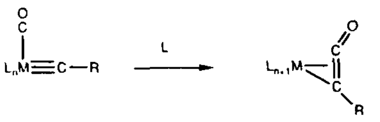
(14)

The relative ratio of **16** and **17** depends strongly on the reaction conditions. Formation of the nitrilium ligand in **16** is believed to involve double protonation at the benzylidyne ligand followed by migratory insertion of the generated benzyl ligand and the isocyanide ligand. An analogous reaction of $[W(CC_6H_4\text{-}4\text{-}CH_3)(\eta^5\text{-}C_5H_5)(CO)_2]$ with HCl resulted in formation of the η^2-acyl complex $[W(Cl_2)(OCCH_2C_6H_4\text{-}4\text{-}CH_3)(\eta^5\text{-}C_5H_5)(CO)]$.[58b] The aminoalkyne ligand in **17** is probably the result of protonation at the nitrogen of the isocyanide ligand and subsequent coupling with the alkylidyne ligand. The latter transformation belongs to the group of coupling reactions discussed in the following chapter.

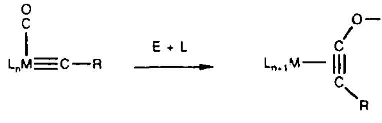
The behavior in protonation reactions clearly demonstrates the complex reactivity of low-valent alkylidyne complexes. Attack of the proton may occur at different sites, specifically, at the alkylidyne carbon, at the metal center, and at ancillary ligands. The nature of the products and the occurrence of secondary reactions may be controlled by altering the electronic properties of spectator ligands and sometimes only by changing the reaction conditions. While difficult to predict in detail, the essential features of this chemistry may be rationalized by simple qualitative molecular orbital arguments.

4.2. Coupling of Alkylidyne Ligands with Carbon Monoxide and Related Ligands

Carbonyl–alkylidyne coupling was discovered by Kreissl[20] and is now a well established reaction.[60,61] In recent years it became apparent that it is a member of a larger family of reactions involving the coupling of various two-faced π bonded ligands, such as carbonyl, isocyanide, thiocarbonyl, and alkylidyne ligands. These reactions range from the formal coupling of two carbonyl[62] or two isocyanide ligands,[63] and the coupling of carbonyl and thiocarbonyl ligands[64] to the coupling of alkylidyne ligands with carbonyl[60,61] or isocyanide ligands,[65] and to the extreme case of coupling of two alkylidyne ligands.[66] These reactions are mechanistically related, since at least one of the ligands being coupled is either a preexisting alkylidyne ligand[60,61,65,66] or a carbyne ligand generated by β electrophile addition to a carbonyl-like ligand.[64,67] Since carbonyl–alkylidyne coupling is the best documented of these reactions and the most easily amenable to systematic variation, may be chosen as the paradigmatic example. There are currently three prototypical reactions (Eqs. (15)–(17)). (i) Donor ligand-induced coupling, (ii) Lewis-acid induced coupling, and (iii) light-induced coupling.



(15)

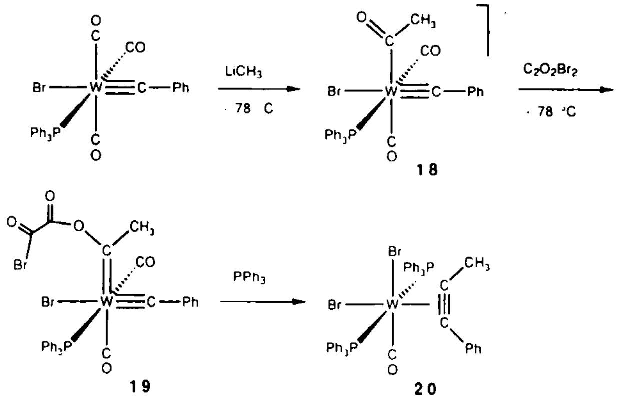


(16)

(17)

While no systematic studies have been done to elucidate the basic electronic factors controlling carbonyl–carbyne and related coupling reactions, it appears from available information in the literature that the reaction proceeds more easily in electron-rich systems. Electron-richness increases π backbonding from the metal to the carbonyl (or related) ligands. This effect is reinforced by addition of electrophiles to the carbonyl oxygen atom. In the case of very strong π backbonding the carbonyl ligand interacts with the metal center like a carbyne ligand. While recognizing the danger of oversimplification, this trend may be condensed into the statement that the coupling of carbyne ligands with carbonyl and related ligands proceeds more easily with increasing bis-carbyne character of the system.[61b]

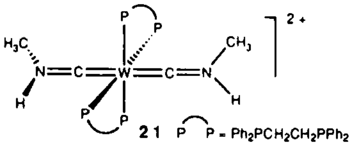
The extreme situation of coupling of two alkylidyne ligands[66] was recently achieved as shown in Eq. (18).



(18)

The reaction sequence resulting in the conversion of a carbonyl ligand into an alkylidyne ligand[29] could be performed a second time in the alkylidyne carbonyl complex $[W(CPh)Br(CO)_3(PPh_3)]$. The alkylidyne acyl intermediate **18** was spectroscopically characterized while the existence of the alkylidyne carbene intermediate **19** is only postulated. The acetylene ligand in product **20** is the result of formal alkylidyne–alkylidyne ligand coupling. However, it is unlikely that a bis-alkylidyne tungsten complex exists as a discrete intermediate. The octahedral metal center can neither provide sufficient dπ orbitals nor electrons for independent bonding of two alkylidyne ligands. (The π orbitals of the two alkylidyne ligands in the $M(CR)_2$ plane are equally competing for bonding to a single metal d orbital.) The coupling of the two alkylidyne units is probably induced simultaneously with the dissociation of the oxalate leaving group. The coupling of two alkylidyne ligands was previously predicted to be an electronically allowed process for metal centers with the same electron count as in the demonstrated case.[68]

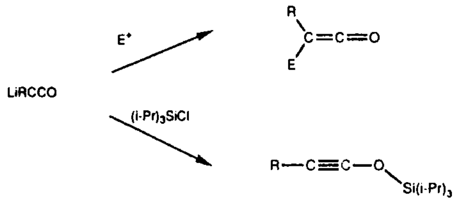
In this context it is worthwhile to mention the synthesis and spectroscopic characterization of the trans-bis(aminocarbyne) tungsten complex **21**.[69] The existence of this complex depends on two factors: steric support for the trans arrangement and electronic stabilization of the electron deficient carbyne carbon atoms by the nitrogen substituents.



21 P⌒P = $Ph_2PCH_2CH_2PPh_2$

4.3. Ketenyl, or Ynolate, Ligands as Synthetic Building Blocks

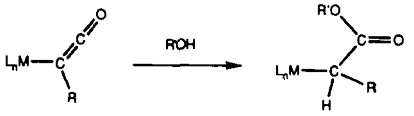
Free RCCO-ions (e.g., alkali metal salts) react with electrophiles in most cases at the terminal carbon atom to give ketenes (Eq. (19)).



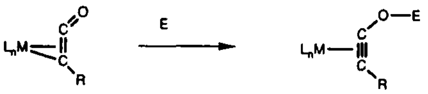
(19)

This selectivity has long prevented the development of an extensive chemistry of ynolate derivatives. Only recently it was shown that silylation with bulky silyl groups occurs at the oxygen atom to afford ynol silyl ethers (Eq. (19)).[70] In the last few years additional synthetic methods for ynolesters and related compounds were developed,[71] and it has become apparent that ynolates and their derivatives are useful synthetic reagents.[72]

The chemistry of ketenyl ligands is versatile; it was elucidated mainly by the research efforts of Kreissl and co-workers.[73] Ketenyl ligands are found to coordinate to transition metal centers in two ways, as η^1- and η^2-bonded ligands.[74] In the η^1-form the ketenyl ligands behave like transition metal-substituted ketenes, i.e., they add nucleophiles at the central carbon atom and electrophiles at the terminal carbon atom (Eq. (20)).[73a-c]



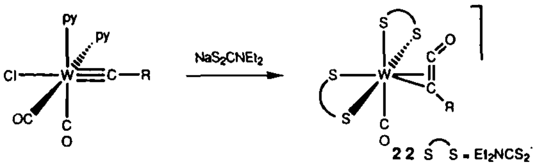
(20)



(21)

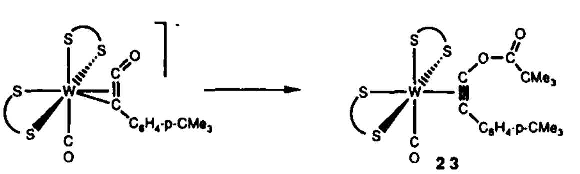
η^2-bonded ketenyl ligands behave like "ynolate" ions and react with electrophiles exclusively at oxygen to give oxyalkyne derivatives (Eq. (21)).[73d] The chemistry of transition metal coordinated ketenyl ligands is thus different and in some ways complementary to that of the free ligands. It therefore seems reasonable to expect that the further development of the chemistry of ketenyl, or ynolate, metal complexes will lead to the discovery of synthetically useful transformations.

We found that reaction of [$W(CPh)Cl(CO)_2(py)_2$] with sodium dithiocarbamate affords the anionic ketenyl complexes Na [$W(RCCO)(S_2CNEt_2)_2(CO)$] (R = alkyl, aryl), **22** (Eq. (22)).[61a]

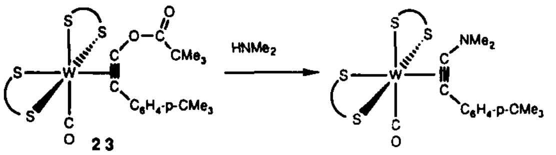


(22)

Analogous ketenyl complexes were also obtained by reaction with N-methyl pyrrole-2-carboxaldimine as the chelating ligand.[61b] Due to the electron richness of the anionic ketenyl complexes they readily react with electrophiles to give oxyalkyne derivatives, e.g., alkylating and silylating agents. The ketenyl complexes also react with acid chlorides to give ynolester complexes, e.g., **23** (Eq. (23)).[75]



(23)



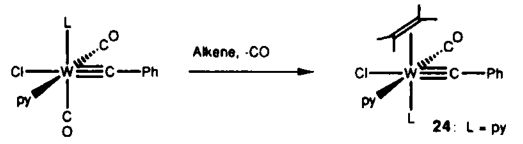
(24)

The reactivity of the coordinated ynol ester in **23** is unusual in the sense that the ester may be cleaved easily at the oxygen–alkynyl and at the oxygen–carbonyl linkage. When acyl group is bulky (R = CMe_3), a number of nucleophiles, e.g., dimethylamine, attack at the alkyne carbon atom with substitution of the carboxylate group (Eq. (24)). When the acyl group is sterically non-demanding (R = CH_3), normal cleavage of the ester group occurs.[76]

4.4. Reactions of Alkylidyne Complexes with Unsaturated Organic Substrates

Among the reactions of metal alkylidene and alkylidyne complexes, those with alkenes and alkynes are perhaps the most important. High-valent metal alkylidenes are established as the active species in olefin metathesis,[77] in ring-opening metathesis polymerization of olefins,[78] and in alkyne polymerization.[79] High-valent transition metal alkylidyne complexes were developed as alkyne metathesis catalysts.[14] Transition metal carbene complexes in lower formal oxidation states were found to participate in reactions with alkenes and alkynes to produce a variety of organic products.[80] In contrast, little is known about the reactivity of low-valent transition metal carbyne complexes towards alkenes and alkynes. Complexes of the type $[W(CR)Br(CO)_4]$ were shown to induce the polymerization of certain olefins and acetylenes.[81] With α,ω-diynes the formation of phenols was observed.[82] It seems unlikely that the relative paucity of known reactions of low-valent alkylidyne complexes with unsaturated organic substrates reflects some inherent lack of reactivity. It would therefore appear to be a rather promising endeavor to investigate this chemistry.

4.4.1. Reactions of tungsten alkylidyne complexes with alkenes. Several bis-donor ligand-substituted tungsten carbyne complexes of the type [W(CR)Cl(CO)2LL′] (L = pyridine, L′ = pyridine or Cl-, LL′ = tmeda; R = Me, Ph) were found to react with maleic anhydride and fumaronitrile to give the carbyne olefin tungsten complexes [W(CR)Cl(CO)(olefin)LL′] (Eq. (25)).[83]



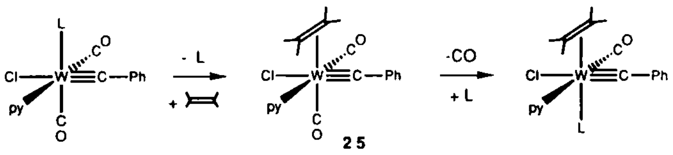
(25)

L = pyridine, chloride; alkene = maleic anhydride, fumaronitrile

In all products the ligand trans to the carbyne ligand is chloride while the remaining donor ligands are trans to the olefin and carbon monoxide. ^1H NMR NOE difference studies showed that in the anionic complexes $[W(CR)Cl_2(CO)(olefin)(py)]^-$ the pyridine ligand is trans to carbon monoxide while the second chloride ligand is trans to the olefin.

The solid state structure of [W(CPh)Cl(CO)(maleic anhydride) $(py)_2$], **24**, is shown in Fig. 4. The maleic anhydride ligand is oriented nearly perpendicular with respect to the metal–carbon triple bond axis. The alkene is thus interacting with the filled metal d orbital in the plane perpendicular to the metal–carbon triple bond, competing with the carbonyl ligand for π backbonding. Variable temperature ^1H NMR studies on the corresponding fumaronitrile complex indicate a high barrier for alkene rotation in these systems.

A two-step mechanism for the formation of the alkylidyne alkene tungsten complexes is consistent with available experimental information. In the first step the alkene is substituting the donor ligand L to afford intermediate **25** in which the alkene is occupying a coordination site trans to a carbonyl ligand.



The strongly π bonding alkene is postulated to labilize the trans CO which is substituted by the ligand L in the second step. In low-valent alkylidyne complexes π acceptor ligands have essentially

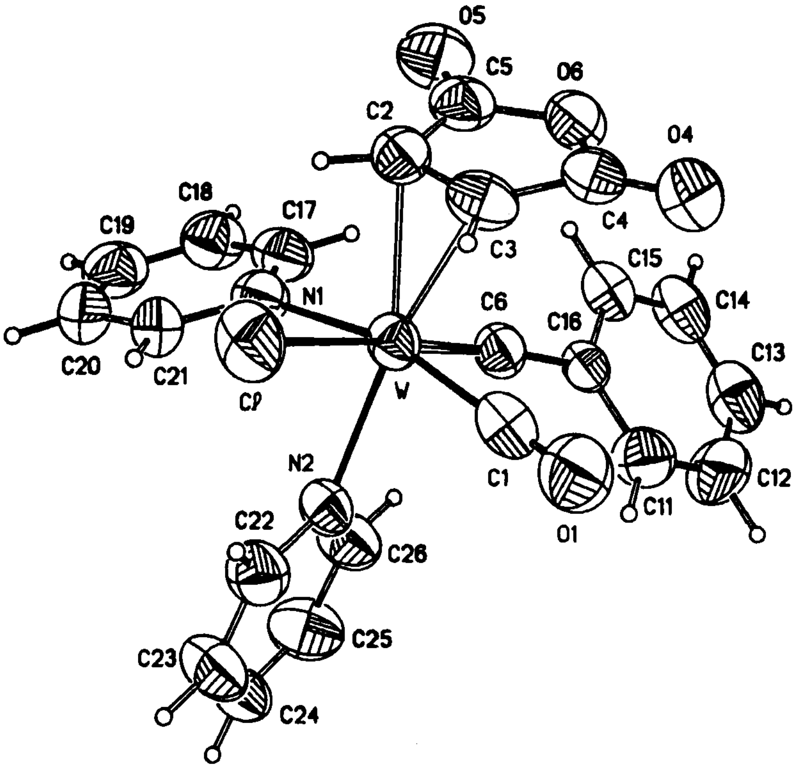


FIGURE 4 Molecular structure of [W(CPh)Cl(CO)(maleic anhydride)$(py)_2$] (24). Important bond distances and angles: W–C(6), 180.1 (6); W–C(2), 221.5 (6); W–C(3), 227.2 (6); C(2)–C(3), 140.8 (8) pm. M–W–C(6), 96.4 (2)°; C(2)–M–W–C6) 95.2° [M = midpoint of C(2)–C(3)]. (From Ref. 83a, with permission.)

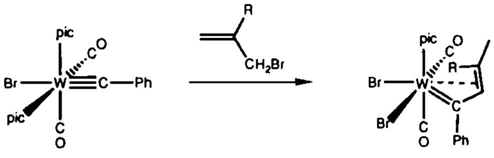
only one metal d orbital to interact with. In a situation like that maleic anhydride and fumaronitrile appear to be more powerful π acceptor ligands than carbon monoxide.[83b] The failure of non-activated alkenes to react according to Eq. (25) is believed to be a consequence of insufficient labilization of CO in the second step.

Only a few other reports regarding reactions of alkenes with transition metal alkylidyne complexes have appeared in the literature.[84] Schrock and co-workers observed formation of the methylidyne ethylene tungsten complex [W(CH)$(CF_3SO_3)(\eta^2\text{-}C_2H_4)(PMe_3)_3$].[80a] The dialuminated tungsten methylidyne complex

$[W(CAl_2Me_4Cl)(CH_3)(\eta^2\text{-}C_2H_4)(PMe_3)_2]$ was obtained by reaction of $[W(CHAlMe_2Cl)Cl(PMe_3)_3]$ with C_2H_4 and $AlMe_3$; Churchill *et al.* determined the crystal structure of this complex.[80b] Very recently, the molybdenum alkylidyne complex $[Mo(CCH_2CMe_3(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}C_2(CN)_4\}\{P(OMe)_3\}]$ was synthesized and structurally characterized by Green *et al.*[80c] In the existing alkylidyne alkene complexes the alkenes are either very strong π acceptors or there are no other π acceptor ligands present (or both). In all structurally characterized alkylidyne alkene metal complexes the alkene is oriented orthogonal to the metal–carbon triple bond.

As expected from qualitative molecular orbital considerations a parallel orientation of the carbon–carbon double bond and the metal–carbon triple bond is unfavorable. Thus carbon–carbon bond formation by direct interaction of alkylidyne and alkene ligands cannot be expected to occur easily. In looking for ways to develop new methods for carbon–carbon bond formation from metal alkylidynes, it therefore seemed more promising to turn to suitably functionalized olefins.

4.4.2. Reactions of tungsten alkylidyne complexes with allyl halides. The alkylidyne complex $[W(CPh)Br(CO)_2(4\text{-picoline})_2]$ reacts with allyl bromide and 2-methylallyl bromide to afford the allylidene, or vinylcarbene, complexes $[W(CPhCRCH_3)Br_2(CO)_2(4\text{-pic})]$, **26** (R = H)[85a] and **27** (R = CH_3), respectively (Eq. (26)).[85b]



(26)

26 R = H
27 R = CH_3

The structures of complexes **26** and **27** are shown in Figs. 5 and 6. The two complexes differ only in the presence of an additional methyl group on the γ carbon of the vinylcarbene ligand. However, this relatively minor change on the vinyl group has a significant effect on its interaction with the metal center. Table I contains a juxtaposition of key structural parameters of complexes **24** and **25**. The data clearly show that the two structures differ significantly only in the bonding parameters concerning the metal–vinyl inter-

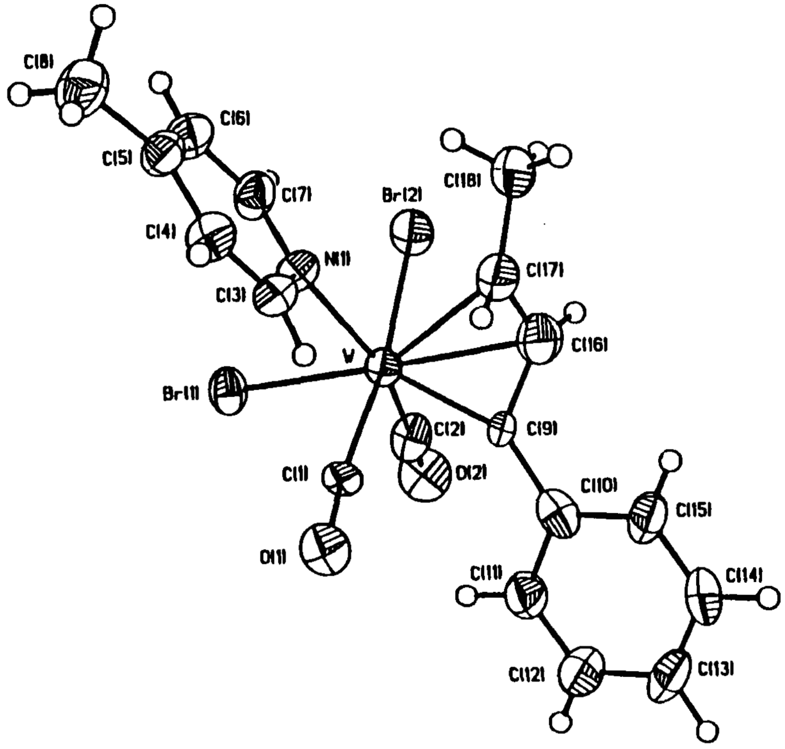


FIGURE 5 Molecular structure of complex **24**. (From Ref. 85a, with permission.)

action. The W–C(9) and W–C(1) distances in **26** and **27**, respectively, are typical for tungsten–carbon double bond lengths. The distances between tungsten and the vinyl carbon atoms in complex **26** of 238 and 260 pm are quite long for the interaction of a carbon–carbon double bond with tungsten and lengthen even further to 244.0 and 315.8 pm in **27**. The latter distance is longer than any established tungsten–carbon bond length. The dihedral angle W–C(9)–C(16)–C(17) of 54.4° in **26** widens to 91.8° for W–C(1)–C(2)–C(3) in **27**. Thus the difference in the arrangement of the vinylcarbene ligand in complexes **26** and **27** is caused by "rotation" about the single bond between the carbene carbon atom and the vinyl group. The cause for the rotation of the vinyl group may be

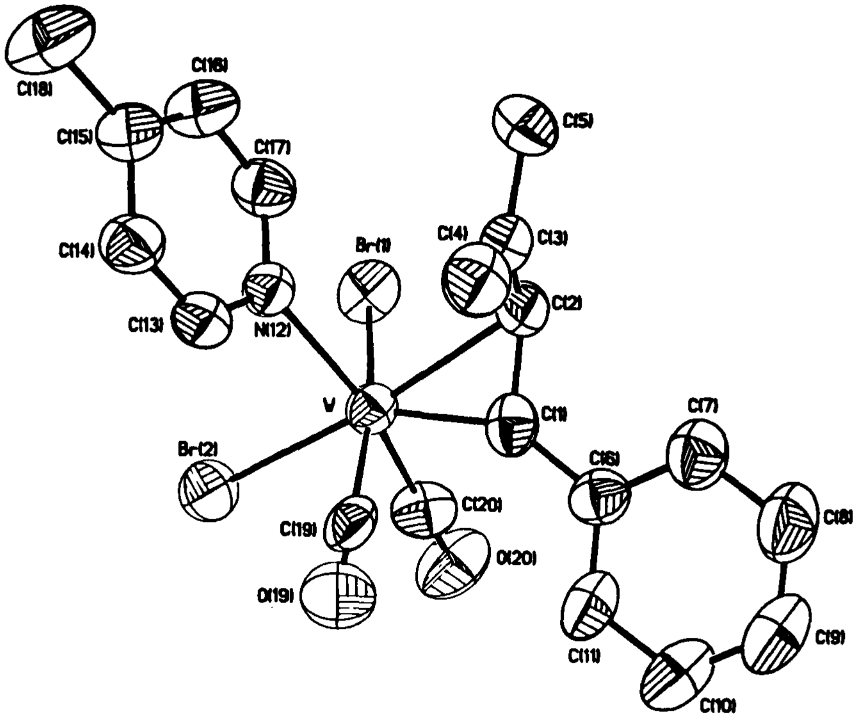


FIGURE 6 Molecular structure of complex 27. (From Ref. 85b, with permission.)

traced to steric repulsion between the additional methyl group in **27** and the picoline ligand.

In solution, a dynamic process is revealed for complexes **26** and **27** by variable temperature ^{1}H NMR. The vinyl group is postulated to undergo oscillation about the C–C single bond of the vinylcarbene ligands such that both sides of the vinyl group are brought into contact with the metal center. At the slow exchange limit two species are observed; they are proposed to be the two rotamers I and II.

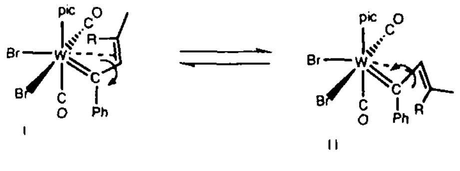


TABLE I

Selected bond distances (pm) and angles (°) for complexes **24** and **25**

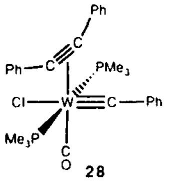
Complex **24**		Complex **25**	
W-C(9)	195.1(8)	W-C(1)	198(2)
W-C(16)	244.0(11)	W-C(2)	238(2)
W-C(17)	315.8(8)	W-C(3)	260(2)
C(9)-C(16)	149(2)	C(1)-C(2)	144(2)
C(16)-C(17)	134(2)	C(2)-C(3)	135(1)
W-C(1)	199.9(11)	W-C(19)	198(2)
W-C(2)	197.3(10)	W-C(20)	199(2)
W-Br(2)	262.6(1)	W-Br(1)	261.4(2)
W-Br(1)	258.7(1)	W-Br(2)	259.9(2)
W-N(1)	227.9(6)	W-N(12)	228(1)
W-C(9)-C(10)	148.0(9)	W-C(1)-C(6)	149(1)
W-C(9)-C(16)	89.3(5)	W-C(1)-C(2)	87.1(9)
C(9)-C(16)-C(17)	121.9(9)	C(1)-C(2)-C(3)	122(2)
W-C(9)-C(16)-C(17)	91.8(8)	W-C(1)-C(2)-C(3)	54.4(2)

The large dihedral angles between the planes of the metal–carbon and carbon–carbon double bonds preclude extensive conjugation between these π-systems. Therefore, the carbene and vinyl portions of the vinylcarbene ligands in **26** and **27** may be considered as electronically independent alkylidene and alkene ligands (which happen to be connected by a single bond). If the vinyl group is indeed acting as an independent alkene ligand, then the question of obvious interest is why its interaction with the metal center is so easily perturbed by the introduction of an additional methyl substituent. Simple qualitative electronic arguments suggest that the metal–vinyl interaction may be lacking a π back-bonding component, which normally is an essential part of metal–olefin interactions. Of the six tungsten valence electrons of tungsten two are used in the bonding of the bromine atoms, and two are involved in the metal–carbon double bond. The vinyl group lies close to the nodal plane of the metal–carbon π bond, so it cannot interact with these π electrons. The remaining two tungsten electrons are involved in π back-bonding to the two carbonyl ligands. To satisfy the π back-bonding requirements of both carbonyl ligands these electrons need to occupy a d orbital oriented in the $W(CO)_2$ plane. Since the vinyl–metal axis lies off this plane, the metal can provide no electrons for π back-bonding to the vinyl group, which consequently can only act as a σ donor ligand.

There is an interesting electronic relationship between the vinylcarbene complexes **26** and **27** and the alkylidene complex **7**. Both systems are formally electron deficient alkylidene complexes of the general formula $[W(CRPh)X_2(CO)_nL_{3-n}]$ (R = vinyl or H). In both cases the metal center interacts with the most easily available electron density on the alkylidene ligand, in **26** and **27** with the π electrons of the vinyl group, in **7** with the σ electrons of the C–H bond. In both cases the presence of carbonyl ligands is preventing "full" interaction between the metal and the "activated" groups. We have seen that replacement of CO in **7** by donor ligands allows for "full C–H bond activation." In the vinylcarbene complexes the absence of CO ligands should permit π backbonding to the vinyl group and strong coordination of all three carbon atoms of the vinylcarbene, as observed in many other allylidene ligand complexes.[86]

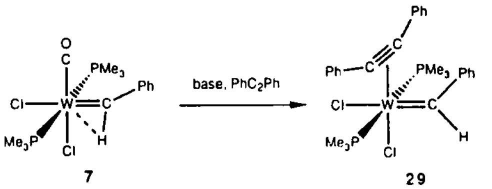
Recently, Geoffroy reported the structure of the tungsten vinylcarbene complex $[W(CPhCPhCHTol)I(\eta^5\text{-}C_5H_5)(CO)]$.[58c] The electronic situation in this complex should be very similar to **24** and **25**. However, the vinylcarbene ligand in this compound appears to be bonded firmly to the metal center via all three carbon atoms of the vinylcarbene group. Based on the above qualitative bonding description, a weaker interaction of the metal with the vinyl group could have been expected. Clearly, a better understanding of the bonding of vinylcarbene ligands requires and deserves detailed theoretical analysis.[87]

4.4.3. Reactions with alkynes. One of the initial goals in the investigation of the reactivity of alkylidyne complexes towards alkynes was to synthesize stable alkylidyne complexes containing alkyne ligands. While this goal has not yet been achieved, some interesting reactions were discovered and novel products were isolated which allow us to draw conclusions about the existence and reactivity of such species. Reaction of $[W(CHPh)Cl_2(CO)(PMe_3)_2]$, **7**, with 1,8-bis(dimethylamino)naphthalene and diphenylacetylene was expected to give the alkylidyne alkyne complex $[W(CPh)Cl(CO)(PhC_2Ph)(PMe_3)_2]$, **28**.



28

However, the product was characterized to be the benzylidene alkyne complex $[W(CHPh)Cl_2(PhC_2Ph)(PMe_3)_2]$, **29** (Eq. (27)).[88]



(27)

An analogous compound was obtained using phenylacetylene. Formally, the outcome of the reaction is substitution of carbon monoxide in **7** by the alkyne, but the actual ligand substitution process must involve several steps. Complex **28** is believed to be a key intermediate, even though we were unable to confirm its existence. The trans arrangement of carbon monoxide and the alkyne in **28** could assist in labilization of the CO ligand in a fashion similar to that proposed for the formation of the alkylidyne alkene complexes.

The solid state structure of **29** is shown in Fig. 7. The alkyne ligand is strongly interacting with the metal center as indicated by the short bonding distances [W–C(14), 206.1 pm and W–C(21), 204 pm]. The benzylidene ligand is "fairly normal" with a W–C(7)–C(8) bonding angle of 137°. Complex **29** may be considered electronically saturated with the alkyne acting as a four electron donor ligand. The smaller bonding angle of the benzylidene ligand in **29** compared to the corresponding angle in the carbonyl complex **7** is thus a structural consequence of four electron donation by the alkyne ligand. Four electron donation of the alkyne ligand in **29** is also indicated by low chemical shifts of the alkyne carbon atoms. A variable temperature ^{31}P NMR study on the analogous phenylacetylene complex showed that rotation of the alkyne ligand occurs easily with an activation barrier of only 51 kJ mol^{-1}.

The bonding situation in the alkylidene alkyne complex **29** is easily understood in qualitative terms, focussing on the metal–ligand π interactions (Fig. 8). The metal–benzylidene π orbital (in the d_{xy} plane using the coordinate system of Fig. 8) is strongly stabilized due to strong contribution of the carbon p orbital. The alkyne ligand can interact with the metal d_{xz} and d_{yz} orbitals. If

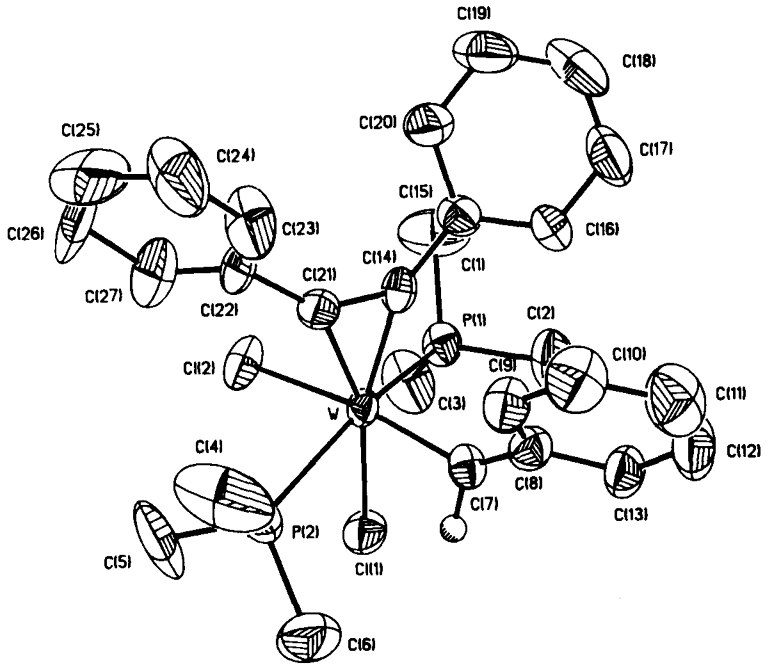


FIGURE 7 Molecular structure of $[W(CHPh)(Cl)_2(PhC_2Ph)(PMe_3)_2]$ (29). W–C(7), 197 (2); W–C(14), 206.1 (7); W–C(21), 204 (2); C(14)–C(21), 133 (3) pm. W–C(7)–C(8), 137 (1)°. Dihedral angle, plane [C(14)–W–C(21)]-plane [Cl(1)–W–C(7)], 59.4°. (From Ref. 88, with permission.)

the alkyne is oriented in the xz plane the d_{xz} orbital will be stabilized by interaction with the alkyne $\pi_{\parallel}{}^*$ orbital and consequently will be filled with the two available metal d electrons. The d_{yz} orbital remains empty and is of the proper symmetry to interact with the filled alkyne $\pi_{\perp}$ orbital. If the alkyne is rotated by 90° to be oriented in the yz plane, the role of the d_{xz} and d_{yz} orbitals interchanges. Therefore, the electronic barrier to alkyne rotation is expected to be low.

This bonding picture may also be used to comment on the nature of the (so far) elusive alkylidyne alkyne metal complexes. For this discussion the alkylidyne alkyne complex is generated from the alkylidene alkyne complex by deprotonation of the alkylidene ligand, whereby the alkyne ligand is thought to be perpendicular to

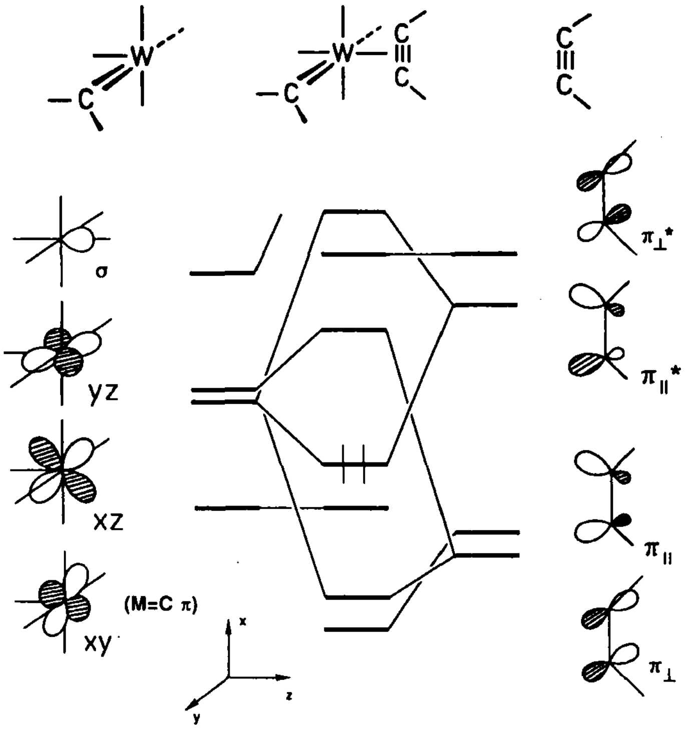
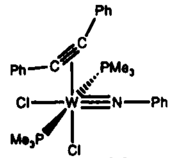


FIGURE 8 Qualitative molecular orbital scheme for an alkylidene(alkyne)metal complex: $[W(CR_2)X_2L_2(alkyne)]$.

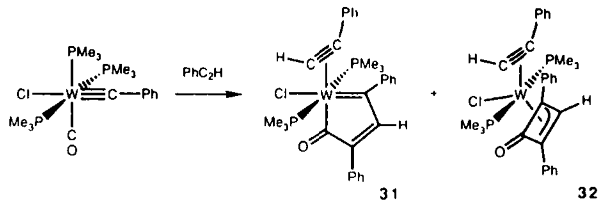
the MC double bond. Deprotonation "frees" the electrons of the C–H bond to form a second M–C π bond by interaction with the empty metal d orbital. The new metal–carbon π bond counteracts alkyne π donation, resulting in a three-center four electron interaction.[89] This repulsive electronic situation may be seen as the primary reason for the apparent instability and enhanced reactivity of low-valent alkylidyne alkyne complexes. The interaction of the filled alkyne $\pi_\perp$ orbital with the metal–carbon π bond should increase the basicity of the alkylidyne carbon, possibly explaining formation of the alkylidene alkyne complex **29** under the reaction conditions of Eq. (27). It is interesting to note here the existence of the phenylimido alkyne complex **30**.[90]



30

It has exactly the same ligand set as the benzylidene complex **29**. Attempts to obtain the isoelectronic alkylidyne alkyne complex by deprotonation of **29** were unsuccessful. The stability of the imido alkyne complex versus the instability (or at least high reactivity) of the alkylidyne alkyne complex may be explained by the much lower energy of the nitrogen p orbitals compared to those of carbon and consequently strong polarization of the metal–nitrogen π bonds. Similar arguments, incidentally, would suggest a higher intrinsic reactivity of late transition metal alkylidyne complexes compared to imido or oxo complexes,[91] e.g., the recently characterized complex $[\mathrm{Ir(NCMe_3)(\eta^5\text{-}C_5Me_5)}]$.[92]

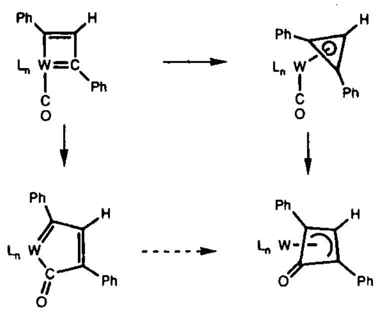
When the alkylidyne complex $[\mathrm{W(CPh)Cl(CO)(PMe_3)_3}]$, which contains a labile trimethylphosphine ligand, was allowed to react with phenylacetylene in the absence of proton sources, a very different outcome was observed. Under these conditions complexes **31** and **32** formed (Eq. (28)).[93]



(28)

Complex **31** contains a metallacyclopentadienone ring system, and **32** an η^3-oxocylobutenyl ligand. Complex **31** transforms irreversibly to complex **32** at elevated temperatures, however, the rate of conversion is too slow to account for the formation of **32** under the conditions of Eq. (28).

While the mechanism of formation of **31** and **32** is not fully established, the observation of complete scrambling of labeled ^{13}C over all CPh positions in the products when Ph^{13}CCH is used prompted the postulation of a mechanism involving the formation



of a metallacyclobutadiene from an initial alkylidyne alkyne intermediate. Direct CO insertion into the metallacyclobutadiene ring could generate the metallacyclopentadienone ring. The oxocyclobutenyl ligand could form via CO insertion in a metal cyclopropenyl intermediate.

Thus, in the absence of alternative reaction pathways, e.g., protonation, low-valent alkylidyne alkyne complexes seem to be able to transform into metallacyclobutadienes. Whether this step is reversible in the sense of a metathesis reaction is currently unknown. While it is extremely unlikely that low-valent alkylidyne complexes will emerge as catalysts for alkyne metathesis, they may prove useful for metathesis reactions of special molecules. For example, Stone recently demonstrated the metathesis of a phosphorus–carbon triple bond by a low-valent molybdenum alkylidyne complex.[94]

5. CONCLUDING REMARKS

The chemistry of alkylidyne metal complexes is an active area of research. The three original types of alkylidyne complex discovered by Fischer, Schrock, and Roper still form the focus of the major research efforts. The existence of isolated examples of iron and iridium carbyne complexes indicates that the range of metal–carbon triple bond chemistry may be extended to transition metals for which currently no alkylidyne complexes are known. The most efficient and versatile methods of synthesis are available for the group 6 transition metals. These complexes are also the most intensively studied. Important chemical relationships between metal–

carbon triple bonds and other molecules with multiple bonds are now firmly established. Nevertheless, the exploration of the reactivity of metal alkylidyne complexes is still at an early stage and our ability to predict the outcome of reactions is still quite limited. As illustrated for low-valent alkylidyne complexes of the group 6 transition metals, new discoveries still raise more questions than they answer.

Even for reactions as simple as protonation a variety of reaction channels are available. Proton attack can occur at either end of the metal–carbon triple bond or at ancillary ligands. Protonation reactions are easily influenced by electronic as well as steric effects, and the nature of the products may differ depending on kinetic or thermodynamic controlling factors. Initial protonation may be followed by other bond forming steps.

Alkylidyne ligands are now well established to undergo coupling reactions with other two-faced π bonding ligands, such as carbon monoxide, isocyanide, or alkylidyne ligands. These reactions encompass the coupling of two carbonyl or isocyanide ligands, since at least one of the ligands being coupled is first transformed into an alkylidyne ligand by interaction with an electrophile. In this group of reactions alkylidyne–carbonyl coupling is best established and most easily amenable to systematic variation. A detailed mechanistic investigation of this reaction could provide deeper insight into the basic factors controlling all of these reactions. Ketenyl ligands possess substantial potential as reagents for organic synthetic reactions. Very little is known about other fundamental coupling reactions of alkylidyne ligands, e.g., coupling with alkylidene or alkyl ligands.

The reactivity of low-valent alkylidyne complexes towards alkenes and alkynes is still little investigated. It is now established that alkene ligands may coordinate to give stable complexes provided the alkenes are strong π acids or no other π acceptor ligands compete with the olefin for π backbonding. The alkene ligands are oriented perpendicular to the metal–carbon triple bond to maximize π bonding. A parallel orientation of the alkene ligand and the metal–carbon triple bond is strongly disfavored for electronic reasons. Therefore, one cannot expect carbon–carbon bonds to form easily by reaction of low-valent alkylidyne complexes with alkenes. However, this situation may be exploited in reactions with suitable functional alkenes. For example, reactions with allyl halides were found to result in formation of vinylcarbene ligands. In contrast to the preparation of stable alkylidyne alkene metal complexes, no alkylidyne alkyne metal complexes have yet been isolated. A major reason for the lower stability and increased reactivity of alkylidyne alkyne complexes appears to be a repulsive interaction between the MC and CC triple bond systems. Depending on the system and the reaction conditions alkylidyne alkyne complexes easily undergo further reactions, including carbon–carbon bond forming steps. Among the reactions of low-valent alkylidyne complexes with unsaturated organic molecules those with alkynes can be expected to be especially interesting.

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