2001
DALTON
MILLENNIUM
PERSPECTIVE

Transition metal–carbon multiple bonds

Richard R. Schrock

Massachusetts Institute of Technology, Department of Chemistry, Cambridge, MA, 02139-4307, USA. E-mail: rrs@mit.edu

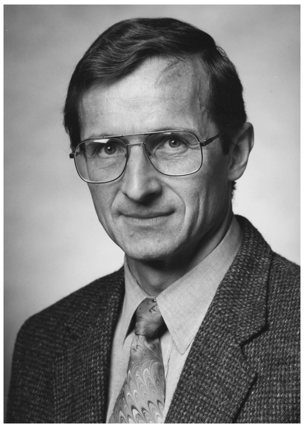
Received 1st March 2001, Accepted 22nd June 2001
First published as an Advance Article on the web 4th September 2001

Since the discovery of the first example of a transition metal carbene complex 37 years ago, and a transition metal carbyne complex a few years later, investigations into the chemistry of compounds that contain multiple metal–carbon bonds have continued steadily. Many compounds that contain multiple metal–carbon bonds are now established as catalysts or stoichiometric reagents in organic chemistry. In this perspective, important steps in the development of transition metal–carbon multiple bond chemistry, in particular chemistry in which the metal is in it's highest possible oxidation state, are highlighted, and possible avenues for further advances are suggested.

Introduction

Transition metal complexes that contain a metal–carbon single bond (metal–alkyl, metal–aryl, *etc.*) comprise an important fraction of organotransition metal chemistry.[1] Their importance stems (in part) from the fact that they are intermediates in a wide variety of transition metal catalyzed processes.[2] In the last thirty years, complexes that contain formally a metal–carbon double bond (so-called carbene or alkylidene complexes) or a metal–carbon triple bond (so-called carbyne or alkylidyne complexes), especially metal–carbon double bonds, have also become established as catalysts and as stoichiometric reagents in organic chemistry. Many of these advances have been made in the last decade and many areas are still under active investigation today. In this perspective, I will cover the highlights of the development of transition metal–carbon multiple bond chemistry, in particular, chemistry in which the metal is in its highest possible oxidation state.

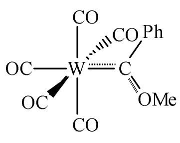
Richard R. Schrock received his Ph.D. degree in inorganic chemistry from Harvard in 1971 under the tutelage of John Osborn. After spending one year as an NSF postdoctoral fellow at Cambridge University working for Lord Jack Lewis, and three years at the Central Research and Development Department of E.I. duPont de Nemours and Company, he moved to M.I.T. in 1975. He became full professor in 1980 and the Frederick G. Keyes Professor of Chemistry in 1989. His interests include the inorganic and organometallic chemistry of high oxidation state, early metal complexes (especially those that contain an alkylidene ligand), catalysis and mechanisms, the chemistry of high oxidation state dinitrogen and related complexes, and the controlled polymerization of olefins and acetylenes.



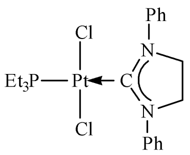
Heteroatom-stabilized "carbene" complexes *versus* tantalum alkylidene complexes

In 1964, Fischer and Maasböl reported the reaction of phenyllithium with W(CO)$_6$ to give an anionic complex containing an acyl ligand.[3] After protonation and treatment with diazomethane, the first deliberately synthesized "metal–carbene" complex (**1**) was isolated and its structure proposed. Hundreds of compounds containing heteroatom-stabilized (usually O or N) carbene ligands soon followed.[4] In these 18 electron species, the carbene ligand is best viewed as a singlet carbene which binds to the metal as a σ donor/π acceptor ligand analogous to CO, olefins, alkynes, and a variety of other ligands that make the field of transition metal chemistry what it is today. However, as a consequence of multiple bonding between the carbene carbon atom and the heteroatom, the metal–carbon bond in compounds of this type is longer than a metal–carbon double bond might be expected to be and the carbon–heteroatom bond is shorter than expected. Therefore, the metal–carbon bond is not a full double bond. In such species, the carbene carbon is attacked by nucleophiles and the heteroatom by electrophiles, a fact that has led to the characterization of these species as "electrophilic carbene" complexes in which the M–C bond is polarized δ− on the metal and δ+ on the carbene carbon. The most highly stabilized carbene in the family of heteroatom-stabilized carbenes is one that contains two nitrogen atoms (*e.g.*, in **2**). Hundreds of compounds that contain diaminocarbenes have been prepared, largely of late transition metals.[5–7] Such strongly stabilized carbenes are believed to bind to a metal as almost pure σ donors. In fact, many carbenes of this type are known to be stable in the metal-free state.[8] In most circumstances, it is appropriate to view a carbene ligand that contains one or two heteroatoms bound to the carbene carbon as being neutral, with a varying degree of metal–carbon double bond character. The metal in a complex such as **1**, therefore, is in the M(O) oxidation state. In the early 70's a large volume of work on heteroatom-stabilized carbene complexes was carried out and several comprehensive reviews were published.[4,5] Since that time heteroatom-stabilized carbene complexes have become increasingly important as stoichiometric reagents for the synthesis of small organic molecules.[9–11]

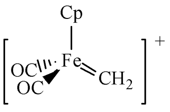
Missing from the collection of carbene complexes were



1



2

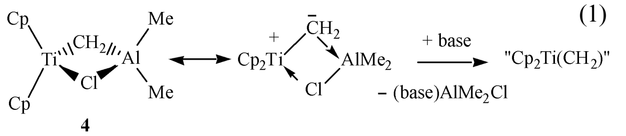


3

DOI: 10.1039/b104609h

"simple" carbenes, *i.e.*, those that did not contain a stabilizing heteroatom, the simplest being a methylene complex. Evidence suggested that unstable and highly reactive methylene complexes, *e.g.*, **3** ($Cp = \eta^5\text{-}C_5H_5$), could be generated by protonation of the methoxide in $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2OMe)$.[12] Since such a compound could be regarded as a metal-substituted carbonium ion, the α carbon atom would be expected to behave as an electrophile. There are now several examples of well-characterized and relatively stable cationic methylene complexes.[13] In one case it has been demonstrated that a "weakly coordinating" anion is required in order for the cation to be stable.[13g]

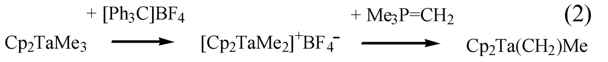
In approximately 1973, the reaction between Cp_2TiCl_2 and excess $AlMe_3$ to give methane and **4** (eqn. 1) was discovered by F. N. Tebbe at E. I. duPont de Nemours and Company.[14] Although the methylene is bridging between Ti and Al, later work suggested that **4** could serve as a source of "$Cp_2Ti(CH_2)$" in the presence of a base that would form an adduct with $AlMe_2Cl$.[15] Therefore, one could argue that the Ti–CH_2 bond is polarized δ+ on Ti and δ− on carbon, exactly the opposite of a heteroatom-stabilized carbene complex, and that the methylene ligand is generated by "deprotonation" of a Ti–CH_3 species with an $AlCH_3$ species.



(1)

4

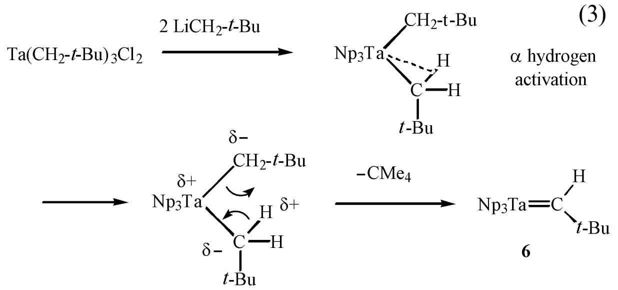
In the same laboratory at that time, I was exploring the organometallic chemistry of tantalum. Extensive work by Schmidbaur[16] on pentaalkyls and alkylidene trialkyls of phosphorus and arsenic provided the inspiration to view tantalum as "metallic phosphorus," *i.e.*, to attempt to prepare cationic alkyl species and deprotonate them to yield a "tantalum ylide." The reaction between $TaMe_3Cl_2$[17] and two equivalents of TlCp yielded Cp_2TaMe_3,[18] from which a suitable "tantalonium" salt was prepared as shown in eqn. 2. The cation subsequently could be deprotonated by a phosphorus ylide to yield the hoped-for "tantalum ylide," $Cp_2Ta(CH_2)Me$ (**5**, eqn. 2).[18] This methylene complex was stable enough at room temperature to isolate and completely characterize. It could be demonstrated convincingly that it also behaved as if the Ta=CH_2 bond were polarized δ+ on Ta and δ− on the methylene carbon. For example, $Cp_2Ta(CH_2)Me$ would react with $AlMe_3$ to yield $Cp_2TaMe(CH_2AlMe_3)$, a cousin of **4**; $Cp_2TaMe(CH_2AlMe_3)$ also could be prepared by treating Cp_2TaMe_3 with $AlMe_3$ in toluene, a reaction that is proposed to yield $[Cp_2TaMe_2][AlMe_4]$ in the first step, followed by deprotonation of a Ta–Me group by an Al–Me group. It was clear from X-ray studies that the tantalum–carbon bond was a full double bond, judging from the difference between the Ta–Me bond length (2.25 Å) and the Ta=CH_2 bond length (2.02 Å). These data suggested that the methylene ligand in this circumstance should be viewed in its "closed shell" configuration, *i.e.*, CH_2^{2-}. The metal, therefore is in its highest possible oxidation state, Ta(5+), and has the d^0 configuration. Therefore, one can argue that an alkylidene ligand bound to a metal such as Ta(5+) is isoelectronic with an imido (M=NR) or an oxo (M=O) ligand. However, donation of a lone pair on N or O to the metal leads to formation of a triple bond to the metal in most circumstances, a fact that contributes to a sharp decrease in the reactivity of an imido or oxo ligand relative to an alkylidene in general in early transition metal chemistry. Therefore with 20/20 hindsight at least, one might have suspected that oxo and imido ligands would be compatible with alkylidene ligands.



$$Cp_2TaMe_3 \xrightarrow[-\,Ph_3CMe]{+\,[Ph_3C]BF_4} [Cp_2TaMe_2]^+BF_4^- \xrightarrow[-\,PMe_4^+BF_4^-]{+\,Me_3P{=}CH_2} Cp_2Ta(CH_2)Me \quad (2)$$

5

The first attempt to prepare a pentaalkyl complex of tantalum consisted of the reaction between $TaMe_3Cl_2$ and two equivalents of LiMe. The product was highly unstable $TaMe_5$,[19] a relative of the just published, and highly unusual, WMe_6.[20] Pentamethyltantalum was shown to decompose in a complex intermolecular fashion.[21] Therefore, larger alkyls were employed in an attempt to prevent intermolecular decomposition. The reaction between TaR_3Cl_2 and two equivalents of LiR when $R = CH_2Ph$ yielded red crystalline $Ta(CH_2Ph)_5$, a species that is much more stable than $TaMe_5$.[21] When R = CH_2CMe_3 the product was not $Ta(CH_2CMe_3)_5$, but $(Me_3CCH_2)_3Ta{=}CHCMe_3$ (**6**), another "tantalum ylide" that bears a more obvious structural relationship to a phosphorus ylide, along with neopentane (eqn. 3).[22] Compound **6** is quite stable thermally, melting at ~70 °C and *distilling* readily in a good vacuum. It is sensitive to oxygen, water, and a variety of functionalities, among them the organic carbonyl functionality, with which it reacts in a Wittig-like fashion to yield polymeric $(Me_3CCH_2)_3Ta{=}O$ and the expected olefin,[23] a type of reactivity that is also exhibited by **4**.[24,25] All of these properties are reminiscent of phosphorus ylides.[16] It cannot be overstated how important to the development of high oxidation state alkylidene chemistry is the principle of employing bulky covalently bound ligands in order to stabilize pseudotetrahedral species against bimolecular decomposition.

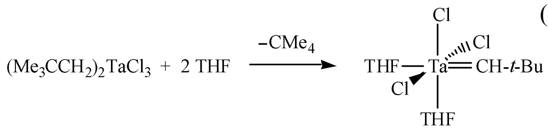


(3)

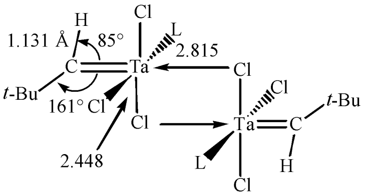
6

It soon became apparent that the neopentyl ligand in a d^0 complex of Ta promotes steric crowding and consequently is subject to a distortion that opens up the Ta–C_α–C_β angle and pushes the α hydrogens toward the metal. In a highly electrophilic metal complex (*e.g.*, hypothetical $Ta(CH_2CMe_3)_5$ has a total of only 10 electrons in bonding and nonbonding metal-based orbitals) the electrons in a CH_α bond are attracted toward the metal and H_α thereby becomes acidic (eqn. 3). Interaction of a C–H electron pair with the metal came to be called an α "agostic" interaction.[26] The acidity of H_α is also enhanced as a consequence of a lower s character in a C–H_α bond of a distorted neopentyl ligand. Migration of an α proton to a nearby nucleophilic neopentyl α carbon atom generates alkane and the Ta=C bond. This proposed "α hydrogen abstraction," here essentially an intramolecular deprotonation reaction, is attractive in view of the deprotonation of $[Cp_2TaMe_2]^+$ noted above. However, metal–carbon bond homolysis is a viable alternative in a crowded circumstance, and tends to be the preferred result when the metal–carbon bond and the presumed agostic interaction are weaker, *e.g.*, for niobium. Therefore, α hydrogen abstraction tends to be observed in an intramolecular fashion most often for Ta, Mo, W, and Re.[27] The neopentyl ligand was chosen instead of the more popular and less expensive trimethylsilylmethyl ligand on the basis of the fact that reactions involving trimethylsilylmethyl reagents in Nb and Ta were known to yield dimeric species with the formulation $[(Me_3SiCH_2)_2M(CSiMe_3)]_2$.[28,29] As a consequence of the longer C–Si bonds, the trimethylsilyl ligand does not produce as crowded an environment at a metal center, and consequently is also more susceptible to *inter*molecular α hydrogen abstraction reactions. For example, $(Me_3SiCH_2)_3Ta{=}CHSiMe_3$, a relative of

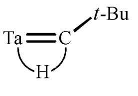
$(Me_3CCH_2)_3Ta{=}CHCMe_3$, can be prepared below −30 °C, but it readily decomposes to yield $[(Me_3SiCH_2)_2Ta(CSiMe_3)]_2$ above ~0 °C (depending on concentration).[30,31] The methyl ligand is the least sterically protected and the least prone to be activated intramolecularly *via* an α agostic interaction. Therefore a methyl complex only rarely decomposes to give an *observable* methylene species. (The instability of electron deficient methylene species toward bimolecular decomposition also militates against observation of many methylene complexes prepared by α abstraction under forcing conditions.) Finally, steric crowding and subsequent α hydrogen abstraction can be induced by addition of a base. For example, $Ta(CH_2CMe_3)_2Cl_3$ is stable in pentane, but instantly turns purple in THF as a consequence of the quantitative formation of 14 electron $Ta(CHCMe_3)(THF)_2Cl_3$ (eqn. 4).[32]


(4)

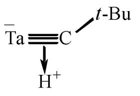
An important feature of "high oxidation state" alkylidene complexes that do not attain an 18 electron count about the metal was documented in a neutron diffraction study of $[Ta(CH\text{-}t\text{-}Bu)Cl_3(PMe_3)]_2$ (**7**).[33] In this compound, the Ta=C bond (1.90 Å) was found to be ~0.10 Å shorter than expected, the Ta=C–C angle to be 161°, and the Ta=C–H angle to be only 85°, *i.e.*, the alkylidene is distorted through an α agostic interaction, one that is driven sterically to some extent by the bulk of the *t*-butyl group. Therefore H_α could be said to be bonded to an orbital that has high p character on carbon, as if C_α were essentially sp hybridized. This is the reason why both J_{CH} (~90 Hz) and ν_{CH} (~2600 cm^{-1}) are unusually low. The Ta–alkylidene bonding in this situation can be viewed either in terms of a three-center, six electron bond (**A**) or, in the extreme, even as a protonated triple bond (**B**). The short Ta–C bond can be rationalized on the basis of either description **A** or **B**.



7



A

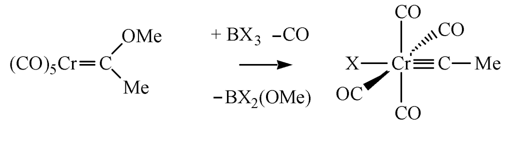


B

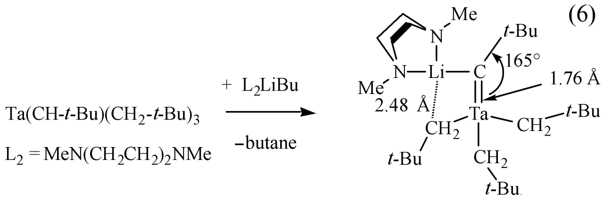
A variety of theoretical studies have confirmed the essential electronic differences between "low oxidation state" heteroatom-stabilized carbene complexes and "high oxidation state" alkylidene complexes.[34] As one moves to the right in the transition metal series metal–carbon bonds are less polar in general (at least in neutral complexes), and even carbenes that do not contain heteroatoms are best viewed as neutral ligands.

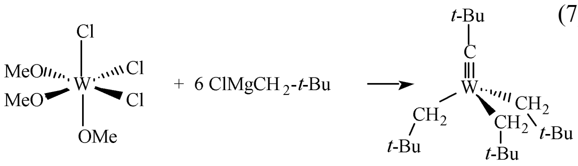
Metal–carbon triple bonds

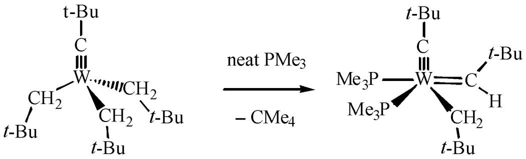
"Carbyne" complexes were first prepared in 1973[35] as a consequence of an attempt to prepare α halo-substituted carbene complexes (*e.g.*, eqn. 5). They are now known for a wide variety of metals, although they are generally restricted to the heavier metals in group 6, Re and Os.[36,37] Although carbynes substituted with a heteroatom are known, a heteroatom is not required in order to stabilize such species. In fact, a heteroatom more often creates synthetic challenges.[38–40] Structural studies have shown that, in the absence of a heteroatom, the metal–carbon bond is 1.75 to 1.90 Å in length in the case of a second or third row metal, or ~0.20 Å shorter than a double bond. The oxidation state of the metal is even less certain in carbyne complexes than in carbene complexes, as is the "polarity" of the metal–carbon bond.


(5)

The reaction between $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ and butyllithium to give "$[(Me_3CCH_2)_3Ta{\equiv}CCMe_3]^-$" (eqn. 6) a short time later was the first evidence that it was possible to deprotonate an alkylidene ligand in a high oxidation state complex.[41] Neutral tantalum alkylidyne complexes formed by α hydrogen abstraction reactions were soon discovered.[42,43] However, high oxidation state alkylidyne chemistry found its natural home in W and Mo.[44,45] The reaction between $WCl_3(OMe)_3$ and six equivalents of neopentylmagnesium chloride probably proceeds *via* α hydrogen abstraction at some stage to give a neopentylidene complex. α Abstraction from the neopentylidene ligand then ultimately leads (after total alkylation at the metal) to $(Me_3CCH_2)_3W{\equiv}CCMe_3$ (eqn. 7), a volatile, yellow, crystalline compound that melts at approximately 70 °C and that can be distilled *in vacuo*, properties that are reminiscent of $(Me_3CCH_2)_3Ta{=}CHCMe_3$. The principles of α abstraction for tungsten appear to be similar to those for tantalum. For example, α abstraction can be induced in $W(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ in neat PMe_3 to yield a compound in which a neopentyl, a neopentylidene, and a neopentylidyne ligand are found in the same complex (eqn. 8). The tungsten–carbon bond lengths, W–C–C bond angles, and magnitude of coupling of C_α to ^{183}W are all consistent with the multiplicity of the metal–carbon bond in question.

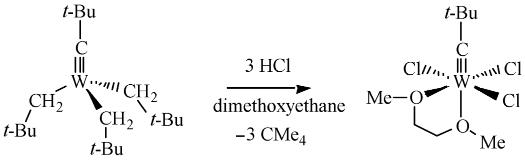

(6)


(7)

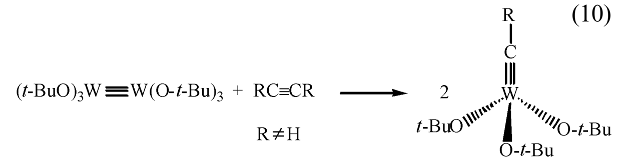

(8)

W–C = 2.26 Å W–C–C = 125° J_{CW} = 80 Hz
W=C = 1.98 Å W=C–C = 150° J_{CW} = 120 Hz
W≡C = 1.81 Å W≡C–C = 175° J_{CW} = 210 Hz

The reaction shown in eqn. 9 suggests that an alkylidyne

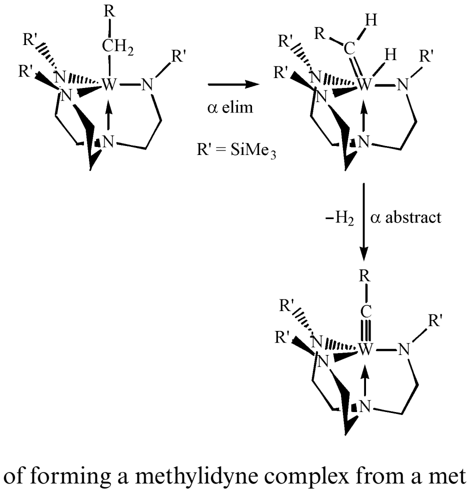

(9)

ligand bound to tungsten is robust toward complete protonolysis. The reaction is likely to involve (three times) protonation of a neopentylidyne ligand to give a neopentylidene ligand, which subsequently loses the α proton to a neopentyl ligand to regenerate the neopentylidyne ligand. The trichloride complex, $W(C\text{-}t\text{-}Bu)Cl_3(dme)$, served as an entry to a wide variety of $W(C\text{-}t\text{-}Bu)X_3$ species, where X is a bulky alkoxide such as $OCMe_3$, $OCMe(CF_3)_2$, or $O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$. These species fall in the category of pseudotetrahedral complexes containing covalently bound bulky ligands, and figured prominently in the development of alkyne metathesis catalysts (see later). It must be noted that a variety of *tert*-butoxide alkylidyne complexes (primarily) also can be prepared readily *via* the extraordinary reaction shown in eqn. 10.[45,46] This reaction served to illustrate the similar energies of W≡W and W≡C bonds, and the surprising facility with which compounds that contain strong triple bonds can be interconverted, possibly *via* a species having a W_2C_2 "dimetallatetrahedrane" core in which there are only single bonds between any pair of atoms.[47]



(10)

It has been shown recently that high oxidation state tungsten–carbon triple bonds are so favorable that they can be formed from tungsten alkyl complexes by loss of molecular hydrogen (eqn. 11),[48] a type of reaction that was proposed as one way of forming a methylidyne complex from a methyl complex in 1981.[49] Not only can R be a proton, but it can be an alkyl that contains one or more β protons, *i.e.*, β hydride elimination processes do not compete with what is overall "α,α dehydrogenation," a process that consists of α elimination to give first an alkylidene hydride, followed by abstraction of the alkylidene's α hydrogen by the hydride ligand (eqn. 11). In related compounds it has been shown that the rate of α hydride elimination in certain cases can be as much as a *million times faster* than the rate of β hydride elimination. This is a surprising result that almost certainly is attributable to the ability of tungsten to activate α hydrogen atoms and to form strong multiple metal–carbon bonds. One could argue that loss of molecular hydrogen from an alkyl (*via* an alkylidene hydride) constitutes an oxidation of the metal from W(IV) to W(VI). High oxidation state alkylidyne complexes also can be formed *via* simple oxidation of low oxidation state alkylidyne complexes. For example, $M(CPh)Br_3(dme)$ (M = Mo or W) can be prepared by addition of bromine to $M(CPh)(CO)_4Br$ in dimethoxyethane.[50]

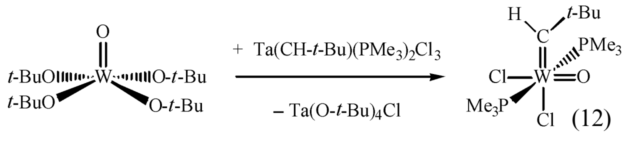


(11)

The fact that α hydrogen abstraction reactions lead to high oxidation state alkylidyne complexes suggests that the alkylidyne ligand can be viewed as a trianionic ligand analogous to the nitride ligand, at least in $X_3M{\equiv}CR$ species (M = Mo or W). This point of view would be consistent with the reaction of W alkylidynes with nitriles to give W nitrides and alkynes.[51]

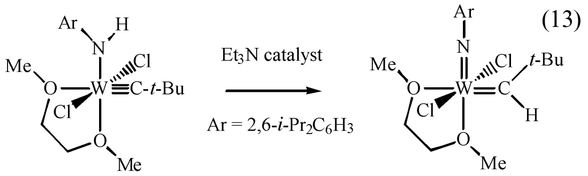
Tungsten and molybdenum alkylidene and rhenium alkylidene/alkylidyne complexes

Although tungsten and molybdenum alkylidyne complexes had been prepared, there was considerable doubt at the time as to what *alkylidene* complexes might be prepared, *i.e.*, what other ligands would successfully maintain the 6+ oxidation state, prevent formation of an alkylidyne complex by loss of a proton, and contribute to and maintain the desirable crowded pseudotetrahedral environment that discourages bimolecular decomposition. It also was questionable as to whether alkylidenes that contain one or more protons on the β carbon atom would be stable with respect to rearrangement of that alkylidene to an olefin. One compound that was thought to be a plausible target (before pseudotetrahedral possibilities were formulated) was $(Me_3CO)_4W{=}CHCMe_3$. The reaction shown in eqn. 12 was an attempt to prepare that compound *via* exchange of an oxo ligand on tungsten with an alkylidene ligand on tantalum.[52,53] Formation of the oxo alkylidene complex **8** instead suggested that the oxo/alkylidene combination was a favorable one. The 18 electron count in **8** is a consequence of π donation of one electron pair on the oxo ligand to the metal. In the belief that an oxo ligand is not sterically protected enough to prevent bimolecular decomposition of a compound in which the electron count was less than 18, an analogous imido alkylidene complex **9** was prepared *by moving an α proton from nitrogen to carbon* with the aid of a base, as shown in eqn. 13.[54] Upon replacement of the chlorides in **9** with bulky alkoxide ligands (OR = $OCMe_3$, $OCMe(CF_3)_2$, $O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$, *etc.*; eqn. 14) four-coordinate 14 electron species **10** were formed (assuming donation of an electron pair from the imido ligand); for steric reasons neither dimethoxyethane nor chloride is retained in the coordination sphere of **10**. The sterically bulky nature of all four ligands in four-coordinate $W(NAr)(CHCMe_3)(OR)_2$ prevented bimolecular decomposition of an electronically unsaturated and potentially reactive four-coordinate species, a theme that harkens back to $(Me_3CO)_3W{\equiv}CCMe_3$ and $(Me_3CCH_2)_3Ta{=}CHCMe_3$.



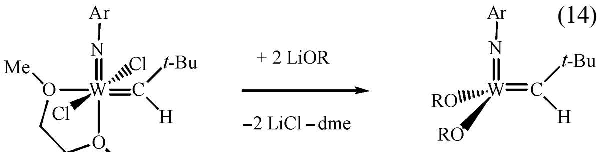
(12)

8



(13)

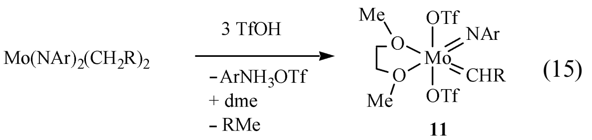
9



(14)

10

The remarkable reaction shown in eqn. 15 (R = *t*-Bu or CMe_2Ph) was developed as part of a relatively efficient



(15)

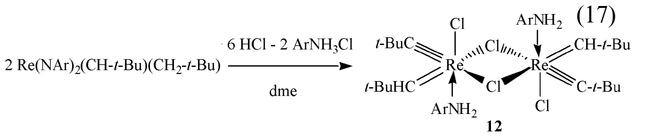
11

synthesis of an important class of molybdenum imido alkylidene complexes of the type Mo(CH-*t*-Bu)(NAr)(alkoxide)$_2$.[55] It is believed that Mo(NAr)(triflate)$_2$(CH$_2$R)$_2$ is the precursor to **11**, and that it is especially susceptible to α hydrogen abstraction as a consequence of it being a crowded five-coordinate species that contains electron-withdrawing triflate ligands. Strong coordination of dimethoxyethane then creates an 18 electron species that is relatively unreactive toward even triflic acid, but relatively reactive toward even alkoxides that are poor nucleophiles (*e.g.*, LiOCMe(CF$_3$)$_2$). The decision to employ alkoxide ligands in imido alkylidene complexes was based on findings in tantalum chemistry that suggested that olefin metathesis reactions (see below) were more favorable in the presence of alkoxide ligands.[56,57] Osborn also had shown that complexes that contained cations of the type [W(CHR)(OR′)$_2$X]$^+$ (*e.g.*, as GaX$_4^-$ salts) were observable intermediates in an olefin metathesis reaction.[58]

By this time it became clear that electron deficient, reactive, four-coordinate species containing multiple metal–carbon bonds and bulky ligands could be synthesized and isolated. If so, then how could this chemistry be extended to "Re(VII)," *i.e.*, what would the Y^{3-} ligand be in (for example) a hypothetical Re(Y)(CHCMe$_3$)(OR)$_2$ complex, and how would that species be prepared? The only sterically protected Y^{3-} ligand that seemed feasible was an alkylidyne ligand. Indeed, Re(CHCMe$_3$)(CCMe$_3$)(CH$_2$CMe$_3$)$_2$ was found to be a stable species,[59] one that completes the list of neutral pseudotetrahedral high oxidation state complexes derived only from neopentyl ligands, a list that includes Ta(CHCMe$_3$)(CH$_2$CMe$_3$)$_3$, Mo(CCMe$_3$)(CH$_2$CMe$_3$)$_3$, and W(CCMe$_3$)(CH$_2$CMe$_3$)$_3$. The reactions shown in eqn. 16 and 17 ultimately led to complexes that contained the desired Re(CHCMe$_3$)(CCMe$_3$) core, and to complexes of the type Re(CHCMe$_3$)(CCMe$_3$)(OR)$_2$.[60] The reaction in eqn. 17 is remarkable in the degree to which α protons on carbon and nitrogen are mobile, and because in this circumstance the lowest energy form contains a rhenium–carbon triple bond, not a rhenium–nitrogen pseudo triple bond.

$$\mathrm{Re(NAr)_2(py)Cl_3} \xrightarrow[-1.5\ \mathrm{ZnCl_2}\ -\ \mathrm{py}\ -\ \mathrm{CMe_4}]{1.5\ \mathrm{Zn(CH_2}\text{-}t\text{-}\mathrm{Bu)_2}} \mathrm{Re(NAr)_2(CH}\text{-}t\text{-}\mathrm{Bu)(CH_2}\text{-}t\text{-}\mathrm{Bu)} \quad (16)$$

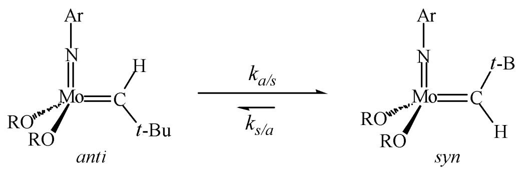
(Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$)



(17)

12

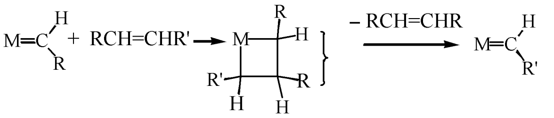
An important feature of all four-coordinate Mo, W, and Re alkylidene complexes is the formation of *syn* isomers, in which the alkylidene substituent points toward the imido (Mo or W) or alkylidyne (Re) ligand, or *anti* isomers, in which the alkylidene substituent points away from the imido or alkylidyne ligand (*e.g.*, eqn. 18). The *syn* isomer is normally the one observed in the solid state and in solution in Mo or W complexes. However, the rate at which these two isomers interconvert by rotation about the metal–carbon bond can vary dramatically as a function of the OR ligand in Mo and W species (from $k_{s/a}$ ~1 s^{-1} in the case of OR = OCMe$_3$ to $k_{s/a}$ ~10^{-5} s^{-1} for OR = OCMe(CF$_3$)$_2$ in Mo imido complexes[61]). Therefore both *syn* and *anti* species must be considered in any reaction scenario. Important questions include whether a reaction involving the alkylidene ligand is faster than the rate of interconversion of *syn* and *anti* isomers, or not, and whether one isomer is much more reactive than the other.



(18)

Alkylidene complexes and alkene metathesis

The main driving force of research concerning metal–carbon double bonds was the fact that tungsten, molybdenum, and rhenium were known to yield homogeneous catalysts of unknown composition that were active for the "metathesis" of olefins,[62] *i.e.*, a redistribution of the alkylidene components of olefins *via* formation of metallacyclobutane intermediates,[63] as shown in eqn. 19a and 19b for simple internal olefins.



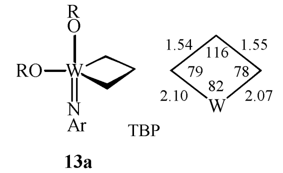
(19a)

$$\text{Therefore } 2\ \mathrm{RCH{=}CHR'} \rightleftharpoons \mathrm{RCH{=}CHR} + \mathrm{R'CH{=}CHR'}$$

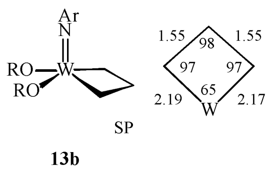
(*cis* and *trans* equilibrated also) (19b)

Research involving tantalum alkylidene complexes revealed that high oxidation state alkylidene species did react with olefins to form metallacycles, but the metallacycles rearranged to olefins faster than they metathesized, *unless alkoxide ligands were present*.[56,57] When alkoxide ligands were present, productive metathesis was observed, but alkylidenes that contained β protons still rearranged to olefins, thereby removing catalyst from the system. Therefore no significant *sustained* metathesis activity with tantalum alkylidene complexes was ever found. Tantalum is also not known to be a metathesis catalyst in classical "black box" metathesis systems.[62]

In contrast, the activity of "well-characterized" W complexes of the type W(NAr)(CHCMe$_3$)(OR)$_2$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) for metathesis of (especially internal) olefins is high. In many circumstances, trigonal bipyramidal or square pyramidal tungstacyclobutane intermediates can be observed.[64] In any system in which ethylene can be formed, unsubstituted metallacycles form, *e.g.*, trigonal bipyramidal **13a** and square pyramidal **13b**. They are especially stable toward loss of ethylene for a variety of alkoxides, and themselves do not react with olefins. Methylene complexes of the type W(NAr)(CH$_2$)(OR)$_2$ generally cannot be observed because of their high reactivity and tendency to decompose readily in a bimolecular fashion. However, alkylidenes that contain β protons do not appear to rearrange readily to olefins. High oxidation state tungsten complexes that will metathesize olefins, but that do not contain imido ligands, have been prepared and studied by both Osborn[58,65] and Basset.[66,67]



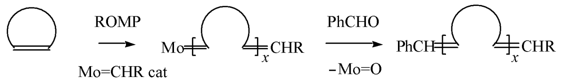
13a



13b

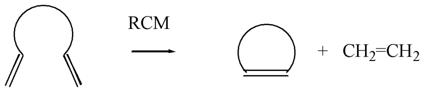
Molybdenum complexes of the type Mo(NAr)(CHCMe$_3$)(OR)$_2$ also are highly active for the metathesis of olefins, especially when the alkoxide ligand is the highly electron-withdrawing OCMe(CF$_3$)$_2$ ligand. A distinct advantage of Mo *versus* W is that metallacyclobutane intermediates generally break up readily for Mo; therefore they cannot serve as sinks or traps in a metathesis reaction. Rhenium complexes of the type Re(CHCMe$_3$)(CCMe$_3$)(OR)$_2$ also are active for olefin metathesis, although they have not been investigated extensively.[68]

Several variations of the basic metathesis reaction have been explored with Mo(NAr)(CHCMe$_3$)(OR)$_2$ catalysts.[69,70] In ring-opening metathesis polymerization (or ROMP) reactions, a cyclic olefin such as a norbornene is attacked by the alkylidene to give a metallacyclobutane that opens to give a new alkylidene into which the cyclic species has been incorporated.[71–74] If this step is irreversible, the new alkylidene can react with more cyclic olefin in a similar manner to form a polymer having repeating units that consist of the "opened" cyclic olefin (eqn. 20). If no intermediate of this type decomposes during the process then such ROMP reactions are "living." Consequently, another monomer can be added after consumption of the first monomer and block copolymers prepared. The polymer also can be cleaved from the metal in a Wittig-like reaction with a benzaldehyde. One of the more enlightening fundamental findings in this area was elucidation of the origin of *cis* or *trans* double bonds in the ROMP polymer, and control of tacticity, *i.e.*, the stereochemical relationship between neighboring repeat units in the ROMP polymer. It was found that the *syn* isomer gave rise to *cis* double bonds in the polymer, while the *anti* isomer gave rise to *trans* double bonds in the polymer.[61] It was also shown that catalysts of the type Mo(NAr)(CHCMe$_3$)(*rac*-diolate), where *rac*-diolate is a racemic chiral diolate such as a binaphtholate, can control the tacticity of the polymer to a remarkable degree by enantiomorphic site control.[75] In the process it also was proven that an all *cis* polymer was isotactic, while an all *trans* polymer was syndiotactic.[76] Perhaps most interesting from a fundamental point of view was the fact that the *anti* isomer in one circumstance was estimated to be ~10^5 times more reactive than the *syn* isomer, even though the *anti* isomer could not be observed at any point before or during the ROMP reaction.[61]

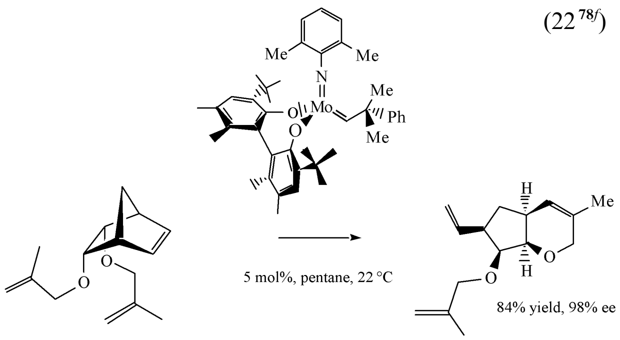


(20)

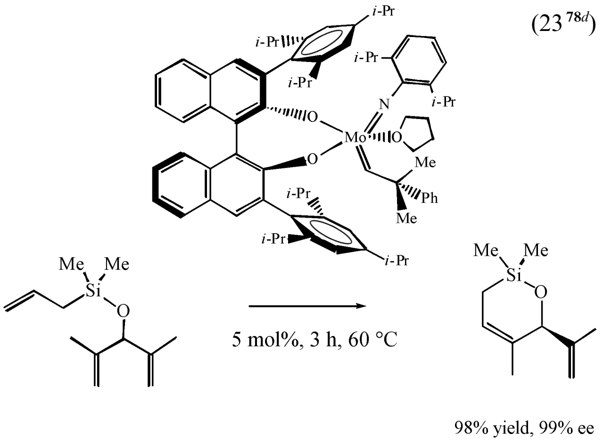
Another important variation of the metathesis reaction is ring-closing metathesis or RCM, a simplified generic example of which is shown in eqn. 21. RCM reactions catalyzed by Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$were shown to be a remarkably facile and "clean" means of forming a variety of cyclic olefins.[77] Many papers have appeared in the last several years in which Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ is the catalyst for RCM,[70] although the catalyst of choice for many RCM reactions has been one of a variety of ruthenium carbene complexes (see below). Molybdenum catalyst systems that contain enantiomerically pure biphenolate or binaphtholate ligands have now been synthesized and shown to catalyze a variety of enantioselective ring-closing, ring-opening, and cross metathesis reactions efficiently, *e.g.*, those shown in eqn. 22–24.[78] (In contrast, analogous enantiomerically pure catalysts that contain the $\{(R,R)\text{-}1,2\text{-}[OC(CF_3)_2CH_2]_2C_5H_8\}^{2-}$ ligand were found to be inefficient catalysts in several kinetic resolutions of comparable substrates.[79,80]) The modular nature of molybdenum catalysts (*i.e.*, the ability to vary the imido and diolate ligands) is an important asset that leads to maximum efficiency. Rapid interconversion of *syn* and *anti* isomers[78e] allows both isomers to be available for enantioselective reactions. Asymmetric metathesis reactions hold considerable promise as a means of relatively quickly preparing enantiomerically pure organic compounds from simple starting materials that, in many cases, cannot be prepared readily by any other combination of methods.[78h]



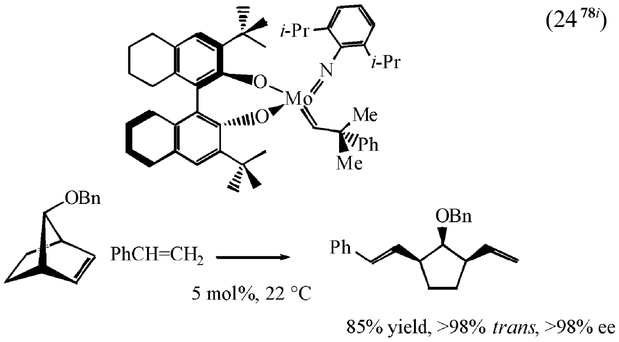
(21)



(22[78f])



(23[78d])



(24[78i])

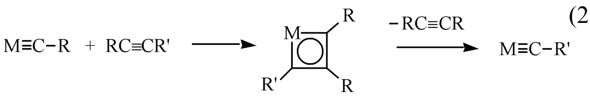
Molybdenum imido alkylidene complexes also have been employed for a variety of other catalytic reactions of interest to the organic or polymer chemist, among them selective cross-couplings of olefins,[81] polymerization of terminal alkynes,[82] step-growth polymerization of dienes,[83,84] or cyclopolymerization of 1,6-heptadiynes.[85]

It should be noted that the original Fischer-type carbene complexes (of Cr, Mo, or W) do not show any sustained olefin metathesis activity, although they appear to react with olefins (and acetylenes) to yield metallacyclic intermediates which decompose in a variety of useful ways of interest to organic chemists. It is also clear that electron-withdrawing alkoxides in M(NAr)(CHR)(OR′)$_2$ complexes dramatically increase the rate of reaction of an olefin with the M=CHR bond. Finally, no other anionic ligands X in M(NAr)(CHR)X$_2$ complexes are as successful as alkoxides for sustained metathesis activity,[57] either because they are not bulky enough to stabilize an electron deficient metal center and prevent decomposition (*e.g.*, halides) or because they donate too much electron density to the metal in a σ and/or π fashion (*e.g.*, amides). A recent example of the latter is Mo(NAr)(CHR)(diamide) where the diamide is a

N,*N*′-disubstituted-2,2′-bisamido-1,1′-binaphthyl ligand; no ready reaction was observed between this complex and ethylene or even benzaldehyde.[86]

Alkylidyne complexes and alkyne metathesis

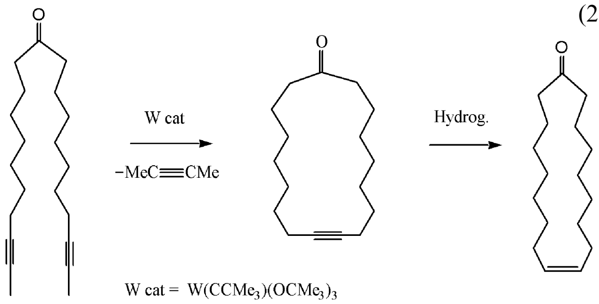
Alkyne metathesis is a reaction in which alkylidyne components of disubstituted alkynes are scrambled statistically to give all possible alkynes (eqn. 25a and 25b). It was known to be catalyzed slowly by a homogeneous catalyst ($Mo(CO)_6$ in a phenol solvent[87]) or heterogeneous catalysts (tungsten oxides on silica at 400 °C[88]). Katz first proposed[89] that it might proceed by a reaction between the appropriate carbyne species and an alkyne *via* metallacyclobutadiene intermediates. No Fischer-type carbyne complexes had been shown to be active for alkyne metathesis to any sustained degree. However, alkylidyne complexes such as $(Me_3CO)_3W{\equiv}CCMe_3$ were found to be remarkably active for the metathesis of alkynes such as 3-heptyne.[90] Hundreds of turnovers per minute at room temperature were found and the expected alkylidyne intermediates could be observed. Moreover, in many cases tungstacyclobutadiene complexes could be isolated and shown to be metathetically active, especially when a relatively electron-withdrawing alkoxide is present.[91,92] Interestingly, alkylidyne complexes do not react with olefins readily,[46] so it is possible to metathesize alkynes in the presence of alkenes.[93]



(25a)

$$\text{Therefore } 2\,RC{\equiv}CR' \rightleftharpoons RC{\equiv}CR + R'C{\equiv}CR' \qquad (25b)$$

For more than ten years the high reactivity and tolerance of high oxidation state alkylidyne complexes toward various functional groups were not recognized by organic chemists interested in new methods. However, the enormous interest in alkene metathesis sparked an interest in alkyne metathesis. Two types of alkyne metathesis reactions that have attracted attention are the formation of rings ("ring-closing alkyne metathesis", *e.g.*, the synthesis of civetone in eqn. 26)[94] and the formation of poly(aryleneethynylene)s in a step-growth polymerization.[94e,95,96] Alkyne metathesis is the method of choice for forming large rings that contain a *cis* double bond, since the *cis* conformation is guaranteed through a selective *cis* hydrogenation with a Lindlar catalyst. In contrast, a *trans* double bond is usually formed preferentially in an olefin metathesis reaction. Although alkyne metathesis would not appear to have the scope of alkene metathesis at this point, alkyne metathesis is a unique and attractive option that remains to be explored and exploited fully.



(26)

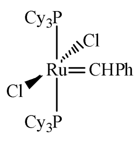
At this stage, high oxidation state alkylidyne complexes appear to be the only types of species that will catalyze extended alkyne metathesis, and bulky alkoxides are the most desirable ligands for long term activity. It seems likely that recently reported recipes for alkyne metathesis involving improved $Mo(CO)_6$/phenol catalysts[96] or $Mo[N(aryl)(t\text{-}Bu)]_3Cl$[97,98] involve formation of small amounts of a high oxidation state species *in situ*.

Other carbene complexes and reactions involving them

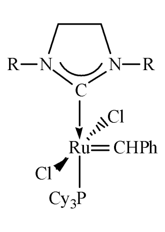
Fischer carbene and carbyne complexes have enjoyed a significant degree of success as stoichiometric reagents in organic synthesis. The advantage is that small quantities of relatively highly elaborated products can be prepared relatively simply. The disadvantage is that these reactions are not catalytic. This extensive chemistry will not be discussed in detail here.[9–11] In contrast, high oxidation state alkylidene and alkylidyne complexes have not been employed to any significant degree for stoichiometric reactions. A notable exception is the use of alkylidene complexes in Wittig-like olefination reactions.[24,99,100]

One of the most significant recent developments in the area of carbene chemistry has been the synthesis of ruthenium carbene complexes and their use as olefin metathesis catalysts.[101] The most successful early version is **14a**.[101d–f] This 16 electron species is unusual in that the carbene bears no stabilizing heteroatom, because it is highly reactive toward a variety of olefins, and because it is relatively unreactive toward water, oxygen, and a variety of functional groups, including carboxylic acids, alcohols, and aldehydes. It has been extensively used in the last several years in a variety of increasingly sophisticated ROMPs and organic syntheses, including natural product syntheses.[100,101] The most active species in solution is believed to be 14 electron $Ru(CHR)(PCy_3)Cl_2$, although that species cannot be observed. No metallacycle intermediates have been observed, although in one case an intermediate carbene/olefin complex has been isolated and crystallographically characterized.[102] Almost certainly it is best to view these species as Ru(II) complexes. Some of the most successful and reactive ruthenium carbene complexes contain a heavily stabilized carbene ligand in place of one of the phosphines (*e.g.*, **14b**).[103–106] The stabilized carbene is believed to be strongly bound to the metal and to not take part in any metathesis reactions directly. As a consequence of its steric bulk and strong donor ability, the diaminocarbene more efficiently protects intermediate carbene species from decomposing bimolecularly, and also increases the amount of available four-coordinate carbene as a consequence of slowing reassociation of PCy_3 (*versus* an olefin) with Ru.[107] Catalysts that contain one diaminocarbene ligand therefore tend to be more long-lasting and capable of accomplishing more difficult metathesis transformations. Compound **14c** is a variation that contains no phosphine ligand(s); it is highly active and can be recovered by chromatography.[108,109] Other types of ruthenium carbene complexes have now been prepared, and many of them have been shown to be active for metathesis.[110] Metathesis activity can be quenched if the ruthenium center does not contain halides or is not cationic. For example, **15** and related species that contain electron-withdrawing fluorinated alkoxides can be prepared, but they have been found to be inactive for metathesis at room temperature and somewhat active, but unstable, at high temperatures.[111]

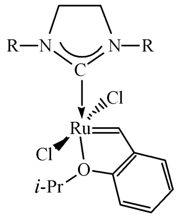
Reactions between diazoorganic compounds and olefins to give cyclopropanes have long been known to be catalyzed by late transition metals such as rhodium, palladium, or copper.[2] Such reactions have proven to be most useful for preparing cyclopropanes in an enantioselective manner the presence of asymmetric ligands or complexes thereof. On this basis, it would appear that the metal is directly involved in some manner. However, although cyclopropanes have been prepared from isolated (electrophilic) carbene complexes,[112] carbene complexes have not been shown to be intermediates in cyclopropanations that involve diazo compounds and Rh, Pd, or Cu catalysts. Indeed, unstabilized carbene complexes are quite rare in group 8 and beyond.[113,114]



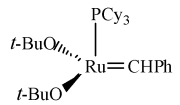
14a



14b



14c



15

Conclusions, comments, and predictions

Although stoichiometric reactions that involve (usually heteroatom-substituted) carbene complexes will continue to be useful for preparing relatively elaborate organic molecules stoichiometrically, the most exciting applications of complexes that contain multiple metal–carbon bonds currently appear to be alkene and (to a lesser extent at this stage) alkyne metathesis reactions. The emphasis so far has been largely on applications of alkene metathesis in organic synthesis,[100,101] where metathesis reactions have been shown to shorten traditional synthetic approaches to organic molecules dramatically. Other applications of metathesis are also emerging; the synthesis of specific oligosaccharides on a solid support,[115] applications in combinatorial chemistry,[100,101] and studies of cell surface recognition involving carbohydrates attached to a ROMP polymer backbone,[116] serve as representative examples. Much of the interest in metathesis in the last decade can be ascribed to the isolation of well-characterized Mo or Ru catalysts. As metathesis catalysts become more available and easier to prepare and use, the number of applications is destined to increase even further. It seems likely that molybdenum and ruthenium metathesis catalysts will complement each other in many circumstances. There is some possibility that metathesis catalysts that contain other metals (*e.g.*, iron) eventually will be prepared. The next decade promises to be at least as exciting as the last for the development of reactions involving a metal–carbon multiple bond.

Acknowledgements

I thank the chemistry division of the National Science Foundation for supporting research on multiple metal–carbon bonds for many years and the many graduate and postdoctoral students who have dedicated their time and talent to this area of research.

References

1 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.

2 L. S. Hegedus, *Transition Metals in the Synthesis of Complex Organic Molecules*, University Science Books, Mill Valley, CA, 1999.

3 E. O. Fischer and A. Maasböl, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 580.

4 (*a*) E. O. Fischer, *Pure Appl. Chem.*, 1970, **24**, 407; (*b*) E. O. Fischer, *Pure Appl. Chem.*, 1972, **30**, 353; (*c*) E. O. Fischer, *Adv. Organomet. Chem.*, 1976, **14**, 1.

5 (*a*) D. J. Cardin, B. Cetinkaya, M. J. Doyle and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99; (*b*) D. J. Cardin, B. Cetinkaya and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545; (*c*) F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, 1972, **16**, 487.

6 F. Fache, E. Schulz, M. L. Tommasino and M. Lemaire, *Chem. Rev.*, 2000, **100**, 2159.

7 D. Bourissou, O. Guerret, F. P. Gaggaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39.

8 A. J. Arduengo, *Acc. Chem. Res.*, 1999, **32**, 913.

9 (*a*) R. Aumann and H. Nienaber, *Adv. Organomet. Chem.*, 1997, **41**, 163; (*b*) K. H. Dötz, in *Reactions of Coordinated Ligands*, ed. P. R. Braterman, Plenum, New York, 1986, ch. 4, p. 285; (*c*) D. F. Harvey and D. M. Sigano, *Chem. Rev.*, 1996, **96**, 271; (*d*) L. S. Hegedus, *Acc. Chem. Res.*, 1995, **28**, 299; (*e*) W. D. Wulff, *Comp. Organometal. Chem.*, 1995, **12**, 470.

10 F. Zaragoza-Dörwald, *Metal Carbenes in Organic Synthesis*, Wiley-VCH, Weinheim, 1999.

11 M. A. Sierra, *Chem. Rev.*, 2000, **100**, 3591.

12 M. L. H. Green, M. Ishaq and R. N. Whiteley, *J. Chem. Soc. A*, 1967, 1508.

13 (*a*) M. Brookhart, J. R. Tucker and G. R. Husk, *J. Am. Chem. Soc.*, 1983, **105**, 258; (*b*) M. Brookhart and W. B. Studabaker, *Chem. Rev.*, 1987, **87**, 411; (*c*) M. Brookhart, J. R. Tucker, T. C. Flood and J. Jensen, *J. Am. Chem. Soc.*, 1980, **102**, 1203; (*d*) V. Guerchais and C. Lapinte, *J. Chem. Soc., Chem. Commun.*, 1986, 663; (*e*) V. Guerchais, D. Astruc, C. M. Nunn and A. H. Cowley, *Organometallics*, 1990, **9**, 1036; (*f*) C. Roger and C. Lapinte, *J. Chem. Soc., Chem. Commun.*, 1989, 1598; (*g*) D. M. Heinekey and C. E. Radzewich, *Organometallics*, 1998, **17**, 51; (*h*) A. T. Patton, C. E. Strouse, C. B. Knobler and J. A. Gladysz, *J. Am. Chem. Soc.*, 1983, **105**, 5804.

14 F. N. Tebbe, G. W. Parshall and G. S. Reddy, *J. Am. Chem. Soc.*, 1978, **100**, 3611.

15 K. C. Ott and R. H. Grubbs, *J. Am. Chem. Soc.*, 1981, **103**, 5922.

16 H. Schmidbaur, *Adv. Organomet. Chem.*, 1976, **14**, 205.

17 G. L. Juvinall, *J. Am. Chem. Soc.*, 1964, **86**, 4202.

18 R. R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 6577.

19 R. R. Schrock and P. Meakin, *J. Am. Chem. Soc.*, 1974, **96**, 5288.

20 A. J. Shortland and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 872.

21 R. R. Schrock, *J. Organomet. Chem.*, 1976, **122**, 209.

22 R. R. Schrock, *J. Am. Chem. Soc.*, 1974, **96**, 6796.

23 R. R. Schrock, *J. Am. Chem. Soc.*, 1976, **98**, 5399.

24 S. H. Pine, *Org. React. (NY)*, 1993, **43**, 1.

25 L. F. Cannizzo and R. H. Grubbs, *J. Org. Chem.*, 1985, **50**, 2316.

26 M. Brookhart, M. L. H. Green and L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1.

27 R. R. Schrock, in *Reactions of Coordinated Ligands*, ed. P. R. Braterman, Plenum, New York, 1986, ch. 3, p. 221.

28 F. Huq, W. Mowat, A. C. Skapski and G. Wilkinson, *Chem. Commun.*, 1971, 1477.

29 W. Mowat and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, **10**, 1120.

30 G. A. Rupprecht, Ph.D. Thesis, Massachusetts Institute of Technology, 1979.

31 L. Li, M. Hung and Z. Xue, *J. Am. Chem. Soc.*, 1995, **117**, 12746.

32 G. A. Rupprecht, L. W. Messerle, J. D. Fellmann and R. R. Schrock, *J. Am. Chem. Soc.*, 1980, **102**, 6236.

33 A. J. Schultz, J. M. Williams, R. R. Schrock, G. A. Rupprecht and J. D. Fellmann, *J. Am. Chem. Soc.*, 1979, **101**, 1593.

34 (*a*) D. S. Marynick and C. M. Kirkpatrick, *J. Am. Chem. Soc.*, 1985, **107**, 1993; (*b*) M. Sodupe, J. M. Lluch, A. Oliva and J. Bertran, *Organometallics*, 1989, **8**, 1837; (*c*) T. Upton and A. K. Rappe, *J. Am. Chem. Soc.*, 1985, **107**, 1206; (*d*) J. Ushio, H. Nakatsuji and T. Yonezawa, *J. Am. Chem. Soc.*, 1984, **106**, 5892; (*e*) M. Sodupe, J. M. Lluch, A. Oliva and J. Bertran, *Nouv. J. Chim.*, 1991, **15**, 321; (*f*) Y.-D. Wu and Z.-H. Peng, *J. Am. Chem. Soc.*, 1997, **119**, 8043; (*g*) K. Monteyne and T. Ziegler, *Organometallics*, 1998, **17**, 5901; (*h*) S.-H. Choi, Z. Lin and Z. Xue, *Organometallics*, 1999, **18**, 5488; (*i*) E. Folga and T. Ziegler, *Organometallics*, 1993, **12**, 325; (*j*) K. Monteyne and T. Ziegler, *Organometallics*, 1998, **17**, 5901; (*k*) T. R. Cundari and M. S. Gordon, *J. Am. Chem. Soc.*, 1991, **113**, 5231; (*l*) T. R. Cundari and M. S. Gordon, *J. Am. Chem. Soc.*, 1992, **114**, 539; (*m*) T. R. Cundari and M. S. Gordon, *Organometallics*, 1992, **11**, 55.

35 E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner and H. Lorenz, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 564.

36 H. Fischer, P. Hofmann, F. R. Kreissl, R. R. Schrock, U. Schubert and K. Weiss, *Carbyne Complexes*, VCH, New York/Weinheim, 1988.

37 *Transition Metal Carbyne Complexes*, ed. F. R. Kreissl, Dordrecht/Boston/London, 1993.

38 A. C. Filippou, W. Grünleitner and E. O. Fischer, *J. Organomet. Chem.*, 1991, **401**, C37.

39 A. C. Filippou, P. Hofmann, P. Kiprof, H. R. Schmidt and C. Wagner, *J. Organomet. Chem.*, 1993, **459**, 233.

40 A. C. Filippou, B. Lungwitz, K. M. A. Wanninger and E. Herdtweck, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 924.

41 L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 2935.

42 M. R. Churchill, H. J. Wasserman, H. W. Turner and R. R. Schrock, *J. Am. Chem. Soc.*, 1982, **104**, 1710.

43 S. J. McLain, C. D. Wood, L. W. Messerle, R. R. Schrock, F. J. Hollander, W. J. Youngs and M. R. Churchill, *J. Am. Chem. Soc.*, 1978, **100**, 5962.

44 R. R. Schrock, *Acc. Chem. Res.*, 1986, **19**, 342.

45 J. S. Murdzek and R. R. Schrock, in *Carbyne Complexes*, VCH, New York/Weinheim, 1988, p. 147.

46 M. L. Listemann and R. R. Schrock, *Organometallics*, 1985, **4**, 74.

47 (*a*) M. H. Chisholm, J. C. Huffman and D. M. Hoffman, *Chem. Soc. Rev.*, 1985, **14**, 69; (*b*) M. H. Chisholm, *Acc. Chem. Res.*, 1990, **23**, 419.

48 R. R. Schrock, S. W. Seidel, N. C. Mösch-Zanetti, D. A. Dobbs, K.-Y. Shih and W. M. Davis, *Organometallics*, 1997, **16**, 5195.

49 P. R. Sharp, S. J. Holmes, R. R. Schrock, M. R. Churchill and H. J. Wasserman, *J. Am. Chem. Soc.*, 1981, **103**, 965.

50 A. Mayr and G. A. McDermott, *J. Am. Chem. Soc.*, 1986, **108**, 548.

51 R. R. Schrock, M. L. Listemann and L. G. Sturgeoff, *J. Am. Chem. Soc.*, 1982, **104**, 4291.

52 J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert and W. J. Youngs, *J. Am. Chem. Soc.*, 1980, **102**, 4515.

53 M. R. Churchill, A. L. Rheingold, W. J. Youngs and R. R. Schrock, *J. Organomet. Chem.*, 1981, **204**, C17.

54 R. R. Schrock, R. DePue, J. Feldman, C. J. Schaverien, J. C. Dewan and A. H. Liu, *J. Am. Chem. Soc.*, 1988, **110**, 1423.

55 R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare and M. O'Regan, *J. Am. Chem. Soc.*, 1990, **112**, 3875.

56 S. M. Rocklage, J. D. Fellmann, G. A. Rupprecht, L. W. Messerle and R. R. Schrock, *J. Am. Chem. Soc.*, 1981, **103**, 1440.

57 R. R. Schrock, *Polyhedron*, 1995, **14**, 3177.

58 J. Kress, M. Wesolek and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1982, 514.

59 D. S. Edwards, L. V. Biondi, J. W. Ziller, M. R. Churchill and R. R. Schrock, *Organometallics*, 1983, **2**, 1505.

60 R. Toreki and R. R. Schrock, *J. Am. Chem. Soc.*, 1992, **114**, 3367.

61 J. H. Oskam and R. R. Schrock, *J. Am. Chem. Soc.*, 1993, **115**, 11831.

62 K. J. Ivin and J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997.

63 J. L. Herrison and Y. Chauvin, *Makromol. Chem.*, 1970, **141**, 161.

64 J. Feldman and R. R. Schrock, *Prog. Inorg. Chem.*, 1991, **39**, 1.

65 J. Kress, A. Aguero and J. A. Osborn, *J. Mol. Catal.*, 1986, **36**, 1.

66 J. L. Couturier, C. Paillet, M. Leconte, J. M. Basset and K. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 628.

67 F. Lefebvre, M. Leconte, S. Pagano, A. Mutch and J.-M. Basset, *Polyhedron*, 1995, **14**, 3209.

68 R. Toreki, G. A. Vaughan, R. R. Schrock and W. M. Davis, *J. Am. Chem. Soc.*, 1993, **115**, 127.

69 R. R. Schrock, in *Topics in Organometallic Chemistry. Alkene Metathesis in Organic Synthesis*, ed. A. Fürstner, Springer, Berlin, 1998, p. 1.

70 R. R. Schrock, *Tetrahedron*, 1999, **55**, 8141.

71 R. H. Grubbs and W. Tumas, *Science*, 1989, **243**, 907.

72 R. R. Schrock in *Ring-Opening Polymerization*, ed. D. J. Brunelle, Hanser, Munich, 1993, ch. 4, p. 129.

73 R. R. Schrock, in *Metathesis Polymerization of Olefins and Polymerization of Alkynes*, ed. Y. Imamoglu, Kluwer, Dordrecht, 1998, p. 1.

74 M. R. Buchmeiser, *Chem. Rev.*, 2000, **100**, 1565.

75 K. M. Totland, T. J. Boyd, G. G. Lavoie, W. M. Davis and R. R. Schrock, *Macromolecules*, 1996, **29**, 6114.

76 D. H. McConville, J. R. Wolf and R. R. Schrock, *J. Am. Chem. Soc.*, 1993, **115**, 4413.

77 (*a*) G. C. Fu and R. H. Grubbs, *J. Am. Chem. Soc.*, 1992, **114**, 7324; (*b*) G. C. Fu and R. H. Grubbs, *J. Am. Chem. Soc.*, 1992, **114**, 5426; (*c*) G. C. Fu and R. H. Grubbs, *J. Am. Chem. Soc.*, 1993, **115**, 3800.

78 (*a*) J. B. Alexander, D. S. La, D. R. Cefalo, A. Hoveyda and R. R. Schrock, *J. Am. Chem. Soc.*, 1998, **120**, 4041; (*b*) D. S. La, J. B. Alexander, D. R. Cefalo, D. D. Graf, A. H. Hoveyda and R. R. Schrock, *J. Am. Chem. Soc.*, 1998, **120**, 9720; (*c*) D. S. La, J. G. Ford, E. S. Sattely, P. J. Bonitatebus, R. R. Schrock and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1999, **121**, 11603; (*d*) S. S. Zhu, D. R. Cefalo, D. S. La, J. Y. Jamieson, W. M. Davis, A. H. Hoveyda and R. R. Schrock, *J. Am. Chem. Soc.*, 1999, **121**, 8251; (*e*) J. B. Alexander, R. R. Schrock, W. M. Davis, K. C. Hultzsch, A. H. Hoveyda and J. H. Houser, *Organometallics*, 2000, **19**, 3700; (*f*) G. S. Weatherhead, J. G. Ford, E. J. Alexanian, R. R. Schrock and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 1828; (*g*) G. S. Weatherhead, J. H. Houser, J. G. Ford, J. Y. Jamieson, R. R. Schrock and A. H. Hoveyda, *Tetrahedron Lett.*, 2000, **49**, 9553; (*h*) A. Hoveyda and R. R. Schrock, *Chem. Eur. J.*, 2001, **7**, 945; (*i*) S. L. Aeilts, D. R. Cefalo, P. J. Bonitatebus, Jr., J. H. Houser, A. H. Hoveyda and R. R. Schrock, *Angew. Chem.*, 2001, **40**, 1452; (*j*) D. R. Cefalo, A. F. Kiely, M. Wuchrer, J. Y. Jamieson, R. R. Schrock and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2001, **123**, 3139.

79 O. Fujimura, F. J. De la mata and R. H. Grubbs, *Organometallics*, 1996, **15**, 1865.

80 O. Fujimura and R. H. Grubbs, *J. Org. Chem.*, 1998, **63**, 824.

81 (*a*) W. E. Crowe and Z. J. Zhang, *J. Am. Chem. Soc.*, 1993, **115**, 10998; (*b*) W. E. Crowe and D. R. Goldberg, *J. Am. Chem. Soc.*, 1995, **117**, 5162; (*c*) W. E. Crowe, D. R. Goldberg and Z. J. Zhang, *Tetrahedron Lett.*, 1996, **37**, 2117.

82 T. Masuda and H. Tachimori, *J. Macromol. Sci., Pure Appl. Chem.*, 1994, **A31**, 1675.

83 (*a*) E. Thorn-Csanyi and K. P. Pflug, *Makromol. Chem., Rapid Commun.*, 1993, **14**, 619; (*b*) E. Thorn-Csanyi and P. Kraxner, *Macromol. Rapid Commun.*, 1995, **16**, 147.

84 (*a*) J. Konzelman and K. B. Wagener, *Macromolecules*, 1995, **28**, 4686; (*b*) J. Konzelman and K. B. Wagener, *Macromolecules*, 1996, **29**, 7657; (*c*) K. B. Wagener, K. Brzezinska, J. D. Anderson, T. R. Younkin, K. Steppe and W. DeBoer, *Macromolecules*, 1997, **30**, 7363.

85 S.-K. Choi, Y.-S. Gal, S.-H. Jin and H. K. Kim, *Chem. Rev.*, 2000, **100**, 1645.

86 J. Y. Jamieson, R. R. Schrock, W. M. Davis, P. J. Bonitatebus, S. S. Zhu and A. H. Hoveyda, *Organometallics*, 2000, **19**, 925.

87 A. Mortreux, J. C. Delgrange, M. Blanchard and B. Labochinsky, *J. Mol. Catal.*, 1977, **2**, 73.

88 F. Pannella, R. L. Banks and G. C. Bailey, *Chem. Commun.*, 1968, 1548.

89 T. J. Katz, *J. Am. Chem. Soc.*, 1975, **97**, 1592.

90 J. H. Wengrovius, J. Sancho and R. R. Schrock, *J. Am. Chem. Soc.*, 1981, **103**, 3932.

91 M. R. Churchill, J. W. Ziller, J. H. Freudenberger and R. R. Schrock, *Organometallics*, 1984, **3**, 1554.

92 J. H. Freudenberger, R. R. Schrock, M. R. Churchill, A. L. Rheingold and J. W. Ziller, *Organometallics*, 1984, **3**, 1563.

93 G. Brizius, N. G. Pschirer, W. Steffen, K. Stitzer, H.-C. zur Loye and U. H. F. Bunz, *J. Am. Chem. Soc.*, 2000, **122**, 12435.

94 (*a*) A. Fürstner and G. Seidel, *Angew. Chem., Int. Ed.*, 1998, **37**, 1734; (*b*) A. Fürstner, O. Guth, A. Rumbo and G. Seidel, *J. Am. Chem. Soc.*, 1999, **121**, 11108; (*c*) A. Fürstner and G. Seidel, *J. Organomet. Chem.*, 2000, **606**, 75; (*d*) N. G. Pschirer, W. Fu, R. D. Adams and U. H. F. Bunz, *Chem. Commun.*, 2000, 87; (*e*) U. H. F. Bunz and L. Kloppenburg, *Angew. Chem., Int. Ed.*, 1999, **38**, 478; (*f*) A. Fürstner and K. Grela, *Angew. Chem., Int. Ed.*, 2000, **39**, 1234.

95 U. H. F. Bunz, *Chem. Rev.*, 2000, **100**, 1605.

96 L. Kloppenburg, D. Song and U. H. F. Bunz, *J. Am. Chem. Soc.*, 1998, **120**, 7973.

97 Y. C. Tsai, P. L. Diaconescu and C. C. Cummins, *Organometallics*, 2000, **19**, 5260.

98 A. Fürstner, C. Mathes and C. W. Lehmann, *J. Am. Chem. Soc.*, 1999, **121**, 9453.

99 (*a*) E. Alvarez, M.-L. Candenas, R. Pérez, J. L. Ravelo and D. D. Martín, *Chem. Rev.*, 1995, **95**, 1953; (*b*) N. A. Petasis and E. I. Bzowej, *J. Am. Chem. Soc.*, 1990, **112**, 6392.

100 A. Fürstner, *Angew. Chem., Int. Ed.*, 2000, **39**, 3012.

101 (*a*) A. Fürstner, *Top. Catal.*, 1997, **4**, 285; (*b*) R. H. Grubbs, S. J. Miller and G. Fu, *Acc. Chem. Res.*, 1995, **28**, 446; (*c*) M. Schuster and S. Blechert, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2036; (*d*) P. Schwab, M. B. France, J. W. Ziller and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2039; (*e*) P. Schwab, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1996, **118**, 100; (*f*) R. H. Grubbs, S. J. Miller and G. C. Fu, *Acc. Chem. Res.*, 1995, **28**, 446.

102 J. A. Tallarico, P. J. Bonitatebus and M. L. Snapper, *J. Am. Chem. Soc.*, 1997, **119**, 7157.

103 J. Huang, E. D. Stevens, S. P. Nolan and J. L. Peterson, *J. Am. Chem. Soc.*, 1999, **121**, 2674.

104 M. Scholl, T. M. Trnka, J. P. Morgan and R. H. Grubbs, *Tetrahedron Lett.*, 1999, **40**, 2247.

105 L. Ackermann, A. Fürstner, T. Weskamp and F. J. Kohl, *Tetrahedron Lett.*, 1999, **40**, 4787.

106 T. Weskamp, F. J. Kohl, W. Hieringer, D. Gliech and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 1999, **38**, 2416.

107 M. S. Sanford, M. Ulman and R. H. Grubbs, *J. Am. Chem. Soc.*, 2001, **123**, 749.

108 J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1999, **121**, 791.

109 S. B. Garber, J. S. Kingsbury, B. L. Gray and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 8168.

110 (*a*) T. Weskamp, W. S. C. Schattenmann, M. Spiegler and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 1998, **37**, 2490; (*b*) A. Fürstner, M. Picquet, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1998, 1315; (*c*) S. M. Hansen, F. Rominger, M. Metz and P. Hofmann, *Chem. Eur. J.*, 1999, **5**, 557; (*d*) S. M. Hansen, M. A. O. Volland, R. Rominger, F. Eisenträger and P. Hofmann, *Angew. Chem., Int. Ed.*, 1999, **38**, 1273; (*e*) W. A. Herrmann, W. C. Schattenmann, O. Nuyken and S. C. Glander, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1087; (*f*) W. Buchowicz, J. C. Mol, M. Lutz and A. L. Spek, *J. Organomet. Chem.*, 1999, **588**, 205; (*g*) H. Katayama and F. Ozawa, *Organometallics*, 1998, **17**, 5190; (*h*) I. del Rio and G. van Koten, *Tetrahedron Lett.*, 1999, **40**, 1401; (*i*) E. Lindner, S. Pautz, R. Fawzi and M. Steimann, *Organometallics*, 1998, **17**, 3006; (*j*) P. O. Nubel and C. L. Hunt, *J. Mol. Catal. A*, 1999, **40**, 323.

111 M. S. Sanford, L. M. Henling, M. W. Day and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2000, **39**, 3451.

112 M. Brookhart and W. B. Studabaker, *Chem. Rev.*, 1987, **87**, 411.

113 M. D. Fryzuk, X. L. Gao, K. Joshi, P. A. MacNeil and R. L. Massey, *J. Am. Chem. Soc.*, 1993, **115**, 10581.

114 M. D. Fryzuk, X. L. Gao and S. J. Rettig, *J. Am. Chem. Soc.*, 1995, **117**, 3106.

115 R. B. Andrade, O. J. Plante, L. G. Melean and P. H. Seeberger, *Org. Lett.*, 1999, **1**, 1811.

116 L. L. Kiessling and L. E. Strong, in *Topics in Organometallic Chemistry. Alkene Metathesis in Organic Synthesis*, ed. A. Fürstner, Springer, Berlin, 1998, p. 199.