Carbon–Carbon and Carbon–Heteroatom Coupling Reactions of Metallacarbynes
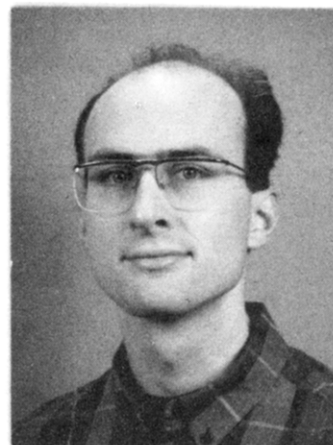
Philippus F. Engel and Michel Pfeffer*

Laboratoire de Synthèses Métallo-induites, Université Louis Pasteur, URA 416 du CNRS, 4, rue Blaise Pascal, F-67008 Strasbourg Cedex, France

Contents

I. Introduction

Since the discovery of the first complex containing a metal–carbon multiple bond in 1964, the chemistry

Philippus F. Engel was born in Utrecht, The Netherlands, in 1965. He was educated in the State University of Utrecht and specialized in Organometallic Chemistry with Professor G. van Koten in 1989. He then moved to Strasbourg where he obtained his Thèse de l'Université Louis Pasteur in 1993. The subject of his Ph.D. thesis was on the organometallic chemistry of "Fischer-type" metallacarbynes. He recently joined Shell Research in Amsterdam, The Netherlands, as an associate research chemist.

Michel Pfeffer was born in Alsace in 1948 and he received his Doctorat d'Etat from the Université Louis Pasteur in 1975. In 1976 he spent one year wth Professor F. G. A. Stone at the University of Bristol. Since 1973 he has held a position in the CNRS at ULP Strasbourg where he became Directeur de Recherche in 1985. His main research interests are in the field of organometallic chemistry with an emphasis on metal-mediated syntheses of carbon–carbon and carbon–heteroatom bonds.

of these compounds has been developing rapidly. By far the most exploited species are the metallacarbenes (or alkylidene complexes), which contain a metal to carbon double bond. Originally, they drew attention as exotic new complexes and as possible models for intermediates in heterogeneous catalysis. Nowadays, metallacarbenes have proven their value as precursors in a number of organic syntheses, as

has been amply demonstrated in the reviews by K. H. Dötz.[1,2] One example, which will serve later in the text, is given below.

Fischer-type metallacarbenes react with alkynes to form naphthol derivatives. In this reaction, both of the carbene substituents, a carbonyl ligand and an alkyne are incorporated into an aromatic ring (eq 1).
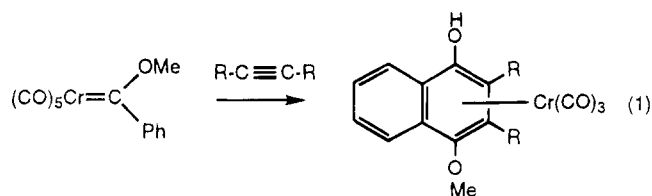
The naphthol fragment can be separated from the metal under mild conditions, and the resulting carbocycles are very useful precursors in the synthesis of natural products such as vitamin K. This methodology has been successfully extended to more complex organic molecules.

Closely related to metallacarbenes are complexes containing a metal to carbon triple bond, called metallacarbynes or alkylidyne complexes. The word "metallacarbynes" will be used throughout this text. Fischer and co-workers isolated the first example in 1973, and since then, their synthetic basis has been substantially broadened. However, the chemistry of metallacarbynes is not as well developed as is the chemistry of metallacarbenes, probably because the synthesis and the reactivity of metallacarbynes is complicated.
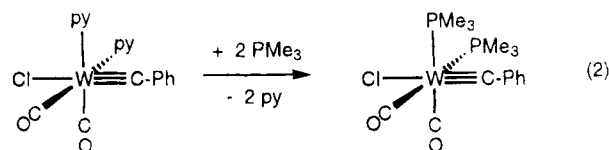
A. Reviews on Metallacarbynes

Three general reviews by H. Fischer,[3] Kim and Angelici,[4] and Mayr and Hoffmeister[5] have comprehensively covered the synthesis, characterization, and reactivity of metallacarbynes up until 1990. Other smaller reviews have dealt with more specialized subjects: low valent group 6 metallacarbynes (Mayr,[6] E. O. Fischer,[7] Fischer and Schubert[8,9]), bridging carbyne ligands (Jeffery and Went,[10] Stone[11]), metallacarbynes with carbaborane ligands (Stone[12]), metallacarbynes of ruthenium and osmium (Gallop and Roper[13]), the photochemistry of alkylidyne complexes (Pourreau and Geoffroy[14]), the chemistry of high oxidation state alkylidyne complexes (Schrock,[15-17] Buhro and Chisholm[18]), and a recent survey of the coupling reactions of π-ligands including carbyne ligands by Mayr and Bastos.[19] The latter review extensively treats the formation of ketenyl and monometallic alkyne complexes from metallacarbynes. The corresponding sections in our text will therefore be limited to a few examples.
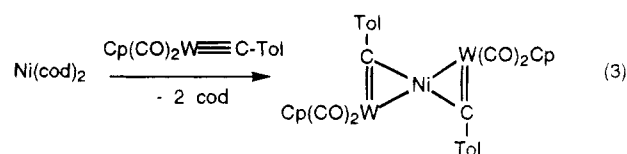
B. Inorganic Chemistry of Metallacarbynes

In a number of reactions of metallacarbynes, no new carbon–carbon or carbon–heteroatom bonds are formed. In these inorganic reactions, the metal–carbon triple bond acts merely as a ligand, and the carbyne carbon is only involved in the formation of metal–carbon bonds. Two typical examples are given below.

The metal center of low-valent metallacarbynes is often surrounded by ligands like carbon monoxide, nitrogen donor ligands (e.g. pyridine), or halogenide

groups. Strongly coordinating ligands as tertiary phosphines frequently react with the metal centre to substitute these labile ligands (eq 2).[20]

The use of metallacarbynes as two or four electron donor ligands in the synthesis of polymetallic complexes is well known, and these reactions have been reviewed by Stone.[21] Often, a metallacarbyne can be used to substitute a labile ligand on a metal center, such as ethylene or cyclooctadiene (cod) (eq 3).[22] Alternatively, metallacarbynes may simply add to certain complexes with metal–metal triple bonds, a reaction that is also observed for alkynes.[23]

More important for organometallic and organic synthesis are reactions in which the carbyne carbon does form new carbon–carbon or carbon–heteroatom bonds. The number of these reactions of metallacarbynes is increasing, but there is no general review dedicated exclusively to this type of reactivity. Since future developments may lead to a broad application of metallacarbynes in organometallic and organic chemistry, a comprehensive review on C–C and C–X coupling reactions seems timely (X = groups 13–16).

C. Organometallic Chemistry of Metallacarbynes

In the three general reviews, the reactions of metallacarbynes have been classified on the type of reagent employed (e.g. electrophiles, nucleophiles, unsaturated organic substrates). For chemists interested in the use of metallacarbynes in synthesis, this classification is not very helpful. Reactions with a certain type of reagent often lead to very different final products, as is the case for the reaction with protons. For example, the protonation of the metallacarbyne $Cp(CO)_2W\equiv C-R$ can either lead to the metallacarbene $Cp(I)(CO)_2W=C(H)R$ or to the μ_2-alkyne complex $[\mu_2\text{-}RC\equiv CR][\mu_2\text{-}H]$ $[Cp_2(CO)_4W_2][BF_4]$ (eq 4).
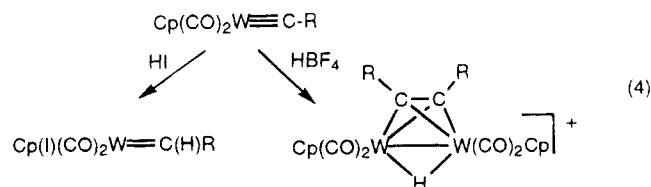
An interesting point in synthesis is the relation between the type of metallacarbyne used and the type of reactivity observed. When these relations can be established, it becomes possible to predict the use of a certain metallacarbyne for the synthesis of a target molecule. Classifying the reactions on the type of reagent however, brings together metallacarbynes of

a very different nature, with each their specific reactivity. In this setup, the relations between the nature of the metallacarbynes and their reactivity are not easily recognized.

The present review presents a solution to most of these inconveniences, by means of a different classification of the reactions of metallacarbynes. First of all, only reactions that lead to new carbon–carbon and carbon–heteroatom bonds that include the carbyne carbon are covered. These selected reactions have been classified according to the nature of the product obtained (e.g. metallacarbenes, alkyne complexes). Within these product sections, metallacarbynes of the same type are brought together as much as possible. This approach demonstrates the use of metallacarbynes in the synthesis of a certain target molecule or a certain molecular fragment. It also becomes easier to predict the applications in the synthesis of a new metallacarbyne, since relations between the nature of the metallacarbynes and their reactivity are more easily recognized (section XIII).

Most metallacarbynes can be classified according to the oxidation state of the metal center, and according to the ligands surrounding this metal. Fischer-type metallacarbynes possess low-valent metal centers surrounded by ligands with clear π-acceptor properties, such as carbon monoxide (e.g. $Cp(CO)_2$-$W\equiv C-Tol$, $Cl(CO)_4Cr\equiv C-Ph$ and $[Cp(CO)_2$-$Mn\equiv C-Ph][BCl_4]$). The carbyne carbon in $Cp(CO)_2$-$W\equiv C-Tol$ is often considered to be weakly nucleophilic, whereas it is more electrophilic in the other two metallacarbynes.

High-valent metal centers stabilized by strong donor ligands as alkoxides and chlorides are typically found in Schrock-type metallacarbynes (e.g. dme-$(Cl)_3W\equiv C^tBu$ and $(^tBuO)_3W\equiv C^tBu$). In these complexes, the carbyne carbon is distinctly nucleophilic.

This classification is useful, but also rather limited. Several theoretical studies[3-5] point out that the reactivity of a metallacarbyne depends both on the partial charges of the atoms and on the ordering and localization of its frontier orbitals. Small changes in the metal valency or the metal ligands may strongly influence these two characteristics, and this may result in a dramatic change in the reactivity of the metallacarbyne. Still, this crude classification will serve as a guide to recognizing the most important relationships between the nature of the metallacarbynes and their reactivity.

A few limitations of this review have to be mentioned here. Schrock-type metallacarbynes have proved their value as catalysts in reactions like the metathesis and polymerization of alkynes, and in the ring opening metathesis polymerization of cyclic alkenes and alkynes (ROMP). In this chemistry, the carbyne carbon is only temporarily incorporated into a new molecule, since the reactions use a catalytic quantity of metallacarbyne. Catalytic reactions of metallacarbynes are considered too different from stoichiometric reactions to be included in the present review. However, an overview of the types of metallacarbynes active in alkyne metathesis is given in section XII.A.

Complexes in which a carbyne ligand bridges two or three metals have become more accessible in

synthesis, and their interesting reactivity certainly merits a comprehensive discussion. However, the presence of more than one metal significantly adds to the complexity of their reactions with respect to their monometallic counterparts. These reactions will be excluded from the present text for reasons of clarity, and the interested reader is referred to other reviews.[10,11]

The present work has been based upon the references given in the existing reviews on metallacarbynes (refs 3–19), which have been completed with new references up to the beginning of the year 1995. In the following sections, the formation of acyclic metal complexes is first discussed. The formation of metallacyclic and carbocyclic complexes is then addressed, and, finally, the formation of free organic molecules.

II. Metallacarbenes

The formation of metallacarbenes is an important reaction of metallacarbynes possessing an electrophilic carbyne carbon atom. Metallacarbenes are useful synthetic species themselves, and their synthesis via metallacarbynes provides an alternative route to metallacarbenes that are perhaps not easily accessible. This section is limited to products in which a clearly defined metal–carbon double bond is present. So-called metallaazacyclic or metallacyclobutadiene complexes are discussed in section X.

A. Monohapto Metallacarbenes from Cationic Metallacarbynes

Neutral (or anionic) nucleophiles add to the electrophilic carbyne carbon of cationic metallacarbynes to form cationic (or neutral) metallacarbenes. This method is by far the most general one to make carbene ligands from metallacarbynes. A recent example is a highly charged osmium complex that reacts in a classical way with different types of nucleophiles, leading in all cases to a cationic metallacarbene (eq 5).[24]

$$[(NH_3)_5Os\equiv C-Ph]^{3+} \xrightarrow[\text{L}]{\text{Nu}} \left[(L)(NH_3)_4Os\!=\!C\underset{X}{\overset{Ph}{\diagdown}} \right]^{2+} \quad (5)$$

Nu = $PrNH_2$, L = MeCN, X = $NHPr^-$
Nu = NaOMe, L = NH_3, X = OMe^-
Nu = Proton Sponge, L = MeCN, X = NH_2^- (87 %)
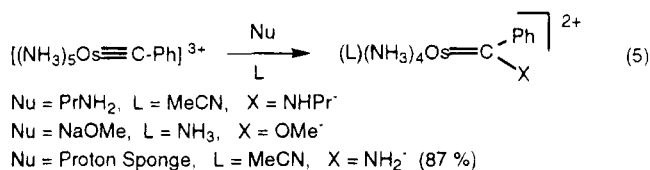
The principle of nucleophilic addition to the carbyne carbon applies to many other metallacarbene formation reactions, and a summary of these examples is presented in eq 6 and Table 1. A given metallacarbyne $[L_nM\equiv C-R]^+$ (M = Cr, W, Mn, Re) reacts with a nucleophile Nu (e.g. PMe_3) or Nu^- (e.g. SPh^-) to afford a metallacarbene $[L_n'M\!=\!C(Nu)R]^+$ or $L_n'M\!=\!C(Nu)R$.[25-56]

Depending on the charge of the incoming nucleophile Nu, the resulting metallacarbene will be neutral or cationic. In some cases, the nucleophile will also substitute one or more of the ligands on the metal center (L becomes L' in eq 6). When amines HNR_2 or alcohols ROH add to the carbyne carbon,

Table 1. Formation of Metallacarbenes [L$_n$M=C(Nu)R] from Cationic Metallacarbynes [L$_n$M≡C−R]$^+$ and Nucleophiles Nu (Eq 6)

metallacarbyne [L$_n$M≡C−R]$^+$	nucleophile Nu (yield metallacarbene)	ref(s)
	M = Cr, W	
[(CO)$_5$Cr≡C−NEt$_2$]$^+$	CN$^-$, NMe$_2$$^-$, HNMe$_2$	25
	NCSe$^-$	26
	NCO$^-$ (35%), NCS$^-$ (83%)	27
	SPh$^-$	28
	TePh$^-$ (65%)	29
	SeR$^-$	30
	R = Ph (47%), Tol (31%),	
	4-C$_6$H$_4$CF$_3$ (59%), 4-C$_6$H$_4$Br (43%),	
	4-C$_6$H$_4$F (46%), 4-C$_6$H$_4$OMe (29%)	
	1-naphthyl (56%)	
	AsPh$_2$$^-$ (12%)	31
[C$_6$H$_6$(CO)$_2$Cr≡C−Ph]$^+$	PMe$_3$ (86%)	32, 33
	HNR$_2$, R = H (84%), Me (93%)	34
[C$_6$H$_5$Me(CO)$_2$Cr≡C−Ph]$^+$	HNR$_2$, R = H, Me	34
[1,4-C$_6$H$_4$Me$_2$(CO)$_2$Cr≡C−Ph]$^+$	PMe$_3$ (91%)	33
	HNMe$_2$, R = H (64%), Me (87%)	34
[1,3,5-C$_6$H$_3$Me$_3$(CO)$_2$Cr≡C−Ph]$^+$	PMe$_3$ (84%)	33
	HNR$_2$, R = H (72%), Me (93%)	34
[(CO)$_5$W≡C−NEt$_2$]$^+$	NPh$_2$$^-$ (4%)	35, 36
	AsPh$_2$$^-$ (29%)	37
	Se(4-C$_6$H$_5$CF$_3$)$^-$ (5%)	38
[Tp'(CO)$_2$W≡C−PMe$_3$]$^+$	Me$^-$	39
	M = Mn, Re	
[Cp(CO)$_2$M≡C−Ph]$^+$	Se(C$_{10}$H$_7$)$^-$, Bu$^-$	40
[Cp(CO)$_2$Mn≡C−Me]$^+$	Me$^-$ (19%)	41
	THF	42
	HN=CPh$_2$	43
	SCN$^-$ (56%)	44
[MeCp(CO)$_2$Mn≡C−Me]$^+$	SCN$^-$ (59%), Cp$^-$ (64%)	44
[MeCp(CO)$_2$Mn≡C−Fc]$^+$	SPh$^-$ (36%), SePh$^-$ (28%), TePh$^-$ (25%)	45
[Cp(CO)$_2$Mn≡C−Ph]$^+$	PMe$_3$ (86%)	33, 46
	SCN$^-$ (38%), CN$^-$ (63%)	47
	CNR	48, 49
	R = Me (78%), cyclo-C$_6$H$_{11}$ (62%), ^{t}Bu (86%)	41
	Me$^-$ (14%)	
	py	46
	OCN$^-$ (66%)	44
	RO$^-$	50
	R = Et (12%), ^{n}Pr (25%), ^{i}Pr (69%), ^{n}Bu (9%), ^{t}Bu (9%),	
	(CH$_2$)$_4$CH$_3$ (15%), (CH$_2$)$_5$CH$_3$ (8%), (CH$_2$)$_7$CH$_3$ (17%),	
	CH(Me)(Et) (62%), CH$_2$CH$_2$^{i}Pr (44%), 4-C$_6$H$_4$OMe (37%),	
	2-C$_{10}$H$_7$ (72%)	
[Cp(CO)$_2$Mn≡C−CH$_2$Me]$^+$	HN=CPh$_2$	43
[Cp(CO)$_2$Re≡C−Tol]$^+$	cyclo-HNCH$_2$C(H)Me (91%),	51
	Ph$_2$C=N−NH$_2$ (71%)	
[Cp(CO)$_2$Re≡C−Me]$^+$	Ph$_2$CdN−NH$_2$ (65%)	51
[Cp(CO)$_2$Re≡C−Ph]$^+$	PMe$_3$ (95%)	33, 46
	SCN$^-$ (35%), CN$^-$ (67%)	47
	C$_2$B$_{10}$H$_{11}$$^-$	52, 53
	Me$^-$ (46%)	54
[[(CO)$_5$Re](CO)$_4$Re≡C−SiPh$_3$]$^+$	MeOH (54%), EtOH (48%), HNEt$_2$	55
	ROH	56
	R = Me (50%), Et (55%), ^{i}Pr (63%), ^{t}Bu (60%)	

they will lose a proton during the C−N or C−O coupling.

$$[L_nM≡C\text{-}R]^+ \xrightarrow{Nu^-} L'_nM=C\overset{R}{\underset{Nu}{\big\langle}} \qquad (6)$$

Metallacarbenes with a phosphine ligand on the carbene carbon are usually considered to be metal ylide complexes of the type L$_n$M−C(R)(=PR$_3$). When the metallacarbynes [(CO)$_5$Cr≡C−NEt$_2$]$^+$ or [Cp(CO)$_2$Mn≡C−R]$^+$ react with an excess of tertiary phosphine, half-ylides may be formed resulting from the reaction between an intermediate metallacarbene and a second molecule of phosphine. These molecules are discussed in the section XII.B.

When the anionic metalate complexes Cp(CO)$_2$-M=C(O)C$_6$H$_4$R]$^-$ are reacted with the cationic metallacarbynes [Cp(CO)$_2$M≡C−C$_6$H$_4$R]$^+$, the negatively charged oxygen attacks the carbyne carbon, and a neutral carbene anhydride complex is formed [M = Mn, R = H (80%); M = Mn, R = CF$_3$ (82%); M = Re, R = H (89%)].[57] The same reaction is observed between the metallacarbyne [(CO)$_5$Cr≡C−NEt$_2$]$^+$ and the complexes [(CO)$_5$M=C(O)R]$^-$ [M = Cr, R = Tol (91%); M = W, R = Me (88%)].[58]

In the reaction between [Cp(CO)$_2$Re≡C−SiPh$_3$]$^+$ and ethanol or dimethylamine, a mixture of two different metallacarbenes is obtained: the expected Cp(CO)$_2$Re=C(X)SiPh$_3$ [X = OEt (64%), NMe$_2$ (69%)] and the metallacarbene Cp(CO)$_2$Re=C(X)H [X = OEt

(29%), NMe$_2$ (24%)], in which the silyl group has been removed.[55] A similar reaction has been observed between the bimetallic carbyne complex [[(CO)$_5$Re]-(CO)$_4$Re≡C—SiPh$_3$]$^+$ and dimethylamine, which leads to a mixture of the two metallacarbenes [[(CO)$_5$Re]-(CO)$_4$Re=C(NMe$_2$)H (30%) and [(CO)$_5$Re](CO)$_4$Re=C-(NMe$_2$)SiPh$_3$].[55]

Ethylene oxide reacts with [Cp(CO)$_2$Re≡C—Tol]-[BCl$_4$] to form an alkoxycarbene complex in which the epoxy ring has been opened by a chloride anion (eq 7, 36% yield).[51] 3,3-Dimethyloxetane reacts in the same way as ethylene oxide (40%).[51]

(7)

In the reaction of the metallacarbyne with either propylene oxide or isobutylene oxide, a mixture of two metallacarbenes is formed in a total yield of 42% (eq 8).[51] Apparently, the chloride anion attacks both

(8)

substituted and unsubstituted carbons of the epoxy ring.

When, in the case of propylene oxide, additional (PPN)Br is added in the reaction mixture, the same metallacarbenes result, now incorporating either a chloride or a bromide group on the alkoxy substituent.

Some strongly reducing nucleophiles do not simply add to the carbyne carbon of cationic metallacarbynes of chromium[59] or tungsten,[35] but, instead, they induce the coupling of two carbyne ligands to form μ-bis-(aminocarbene) complexes (eq 9). The metallacarbyne [(CO)$_5$W≡C—NEt$_2$]$^+$ reacts with KPMePh to give a mixture of a bis(metallacarbene) (19%) and two terminal metallacarbenes, (CO)$_5$W=C(NEt$_2$)(PMePh) and PMePhH(CO)$_4$W=C(NEt$_2$)(PMePh) (8%).

(9)

M = Cr; M'ER$_2$ = LiAsMe$_2$ (30 %)

M = W; M'ER$_2$ = KPEt$_2$ (18 %), KPPh$_2$ (22 %),
                    NaSbPh$_2$ (25 %), NaBiPh$_2$ (9 %)

Triethylphosphine is able to displace the thioether group in the metallacarbyne [Tp'(CO)$_2$W≡C—SMe]$^+$ (section IV.A). When trimethylphosphine is used in this reaction, a second equivalent of phosphine adds to the carbyne carbon of the intermediate metallacarbyne [Tp'(CO)$_2$W≡C—PMe$_3$]$^+$, and the metallacarbene [Tp'(CO)$_2$W=C(PMe$_3$)$_2$]$^+$ is obtained in 80% yield.[39]

Table 2. Yields in the Reaction between the Metallacarbyne [Cp(CO)(PPh$_3$)Mn≡C—C(Me)=CPh$_2$] and RMgX (Eq 10)

nucleophile	vinylidene	carbene
MeMgI	20	56
EtMgCl	24	31
EtMgI	65	35
iPrMgCl	67	

Reacting a manganese vinylcarbyne with Grignard reagents yields mixtures of metallacarbenes and vinylidene complexes (eq 10 and Table 2).[42]

(10)

As expected dimethylamino cyanide (Me$_2$N—C≡N) reacts with [Cp(CO)$_2$Mn≡CPh]$^+$ to give a metallacarbene [Cp(CO)$_2$Mn=C(Ph)N=CNMe$_2$]$^+$ which may react further with MeLi (eq 11, 15%).[60] If (NR$_4$)Cl or (NR$_4$)F is added instead of MeLi, the metallacarbene rearranges, but the final product is similar (eq 11, Cl 6%, F 8%).

(11)

The metallacarbynes [Cp(CO)$_2$Mn≡C—CH$_2$R]$^+$ react with imines in the presence of triethylamine to give metallacarbenes with a cyclic substituent (eq 12).[42,43] With the same reagents, the related complex [Cp(CO)$_2$Mn≡C—Ph]$^+$ gives metallaazacyclic complexes (section X.A).

R = H (85%), Me (62%), Ph (58%)

(12)

When 2 equiv of HN=CPh$_2$ are employed, both metallacarbenes with an acyclic (29%) and a cyclic (50%) substituent are obtained in a similar reaction (eq 13).[43]

(13)

A special case in this series is the reaction with benzalazine, which leads to a bicyclic metallacarbene complex (eq 14, 41%).[42,43]

$$[Cp(CO)_2Mn\equiv C\text{-}Me]^+$$
$$+$$
$$Ph(H)C=N\text{-}N=C(H)Ph$$

(14)

B. Monohapto Metallacarbenes from Neutral Metallacarbynes

Neutral metallacarbynes of the type $X(CO)_4M\equiv CR$ (M group 6) also possess an electrophilic carbyne carbon atom, which reacts readily with nucleophiles. For chromium metallacarbynes (eq 15),[61,62] the reaction is strictly analogous to the reaction of cationic metallacarbynes presented in Table 1.

(15)

R = Me (89 %), CH$_2$Ph (92 %), Ph (92 %)
    Tol (88-92 %), Mes (85 %)
X = Cl, Br, I

When the carbyne metal is tungsten, the same reaction occurs, but an additional substitution of the carbonyl ligands on the metal center by trimethylphosphine takes place.[62-64] Thus, the metallacarbynes $Br(CO)_4W\equiv C\text{-}R$ react at low temperature with trimethylphosphine to give the metallacarbenes Br-$(PMe_3)(CO)_3W=C(PMe_3)R$ [R = Ph (49%), Tol (86%), SiPh$_3$ (76%)], while the reaction at room temperature affords the complexes $Br(PMe_3)_2(CO)_2W=C(PMe_3)R$ [R = Ph (46%), Tol (70%)]. In the presence of an excess of trimethylphosphine, the reaction goes even further to liberate an organic fragment (section XII.B).

Another example involves the bimetallic complex $[(CO)_5Re](CO)_4M\equiv C\text{-}Ph$, which compares to the metallacarbynes in eq 15. Addition of 1 equiv of trimethylphosphine at -50 °C results in the formation of the carbene ligand $\mu_2\text{-}C(PMe_3)Ph$, which bridges both metals in the complex [M = Cr (79%), W (85%)].[65,66] In the presence of an excess trimethylphosphine, carbonyl ligands on the rhenium center will be substituted as well. An entirely different reaction of a high-valent metallacarbyne has been reported recently, in which the aromatic ligand on tantalum is effectively transferred to the carbyne carbon (eq 16).[67] The mechanism of this reaction is not yet understood.

C. Dihapto and Trihapto Metallacarbenes

Electrophilic reagents add to the metal–carbon triple bond of electron-rich metallacarbynes to form dihapto metallacarbenes. The most general route to these products is the addition of a fragment [SR']$^+$

Table 3. Yields in the Formation of Dihaptometallacarbenes from Metallacarbynes $Cp(CO)LM\equiv C\text{-}R$ and Alkylsulfonium Cations [SR']$^+$ (Eq 17)

L	M	R	R'	yield (%)	ref
CO	Mo	Me	Me	91	72
CO	Mo	Tol	Me	95	72
PMe$_3$	Mo	Me	Me	93	72
PMe$_3$	Mo	Ph	Me	91	72
PMe$_3$	Mo	Tol	Me	93	72
CO	W	Me	Et	94	72
CO	W	Me	Tol	76	72
CO	W	Ph	Et	88	72
CO	W	Ph	Tol	81	72
CO	W	Tol	Me	95	68-70
PMe$_3$	W	Me	Me	94	72
PMe$_3$	W	Tol	Me	92	71
CO	W	Me	Me	96	73
CO	W	Ph	Me	91	73
CO	W	Tol	Me	92	73
CO	W^a	Me	Me	92	73
CO	Mo	Ph	Me	93	73

^{a} Metallacarbyne with η^5-C$_5$H$_4$Me ligand instead of η^5-C$_5$H$_5$.

generated in situ

(16)

to complexes of the type $Cp(CO)LM\equiv CR$ (eq 17, Table 3).[68-73]

(17)

Similar examples involve a metallacarbyne with a pyrazolyl ligand (eq 18).[68-70,72]

(18)

The resulting cationic products may react with a second equivalent of "SMe$^+$" to give a (dithiomethyl)-alkyl complex. These reactions are described in the section devoted to other metallacyclic complexes (section X.C).

The electron-rich metallacarbyne $(PPh_3)_2(CO)(Cl)$-$Os\equiv C\text{-}Tol$ reacts with several chalcogenide elements X to give dihapto metallacarbenes, in which X bridges the metal-carbon triple bond (eq 19).[74,75] This reaction is limited to this type of complex, also called "Roper metallacarbyne".

Only one example of a reaction with NaSH has been reported (eq 2a).[76]

$(PPh_3)_2(CO)(Cl)Os\equiv C\text{-}Tol + X_8$

$$\longrightarrow (PPh_3)_2(CO)(Cl)Os\overset{X}{\underset{}{\triangle}}C\text{-}Tol \qquad (19)$$

X = S (96 %), Se (92 %), Te (79 %)

$[Cl_2(PPh_3)_2TolNCOs\equiv C\text{-}C_6H_4NMe_2]^+$

$$\xrightarrow[-\ HCl]{SH^-} Cl(PPh_3)_2(TolNC)Os\overset{S}{\underset{}{\triangle}}C - C_6H_4NMe_2 \qquad (20)$$

One example of a phosphinidene fragment adding to the metal−carbon triple bond is known (eq 21, no yield reported).[77] Supposedly, the reaction with cop-

$$Cp(CO)_2W\equiv C\text{-}Ph \ +$$

$$\xrightarrow[60\ ^\circ C]{CuCl}$$

(21)

per chloride splits the phosphorus complex into the phosphinidene fragment $[P(Ph)W(CO)_5]^-$ and a 4-fold substituted benzene. Attack of the phosphinidene fragment on the carbyne carbon then affords a dihapto metallacarbene ligand.

In the reaction between a metallacarbyne with phosphite ligands and the electrophile trifluoroiodomethane, two different products are formed (eq 22).[78,79] The loss of a proton from the carbyne substituent $CH_2{}^tBu$ together with the addition of iodide to the metal center results in a vinylidene complex.

(22)

P = P(OMe)₃

One of the trimethyl phosphite groups, however, is observed to lose a methyl substituent. Subsequent migration of the modified phosphite ligand onto the carbyne carbon then leads to a dihapto metallacarbene, in which the lone pair of one of the oxygens coordinates to the molybdenum center.

Mayr has developed the synthesis of vinylcarbene complexes starting from metallacarbynes and allyl bromide (eq 23).[80,81] In this process, one of the picoline ligands on the tungsten center is replaced by a bromide. Since the double bond β to the metal−carbon double bond also coordinates to the metal, this complex can be considered as a trihapto metallacarbene.

(23)

R = H (46 %), Me
pic = 4-picoline

Alkynes like diphenylacetylene can also be used to form a vinylcarbene complex (eq 24, 89%).[82,83] Here,

$$Cp(CO)_2W\equiv C\text{-}Tol \ + \ PhC\equiv CPh$$

(24)

a protic acid is required to activate the metallacarbyne. Probably, the carbyne carbon is protonated to form a metallacarbene *in situ*. Then the alkyne may insert into the metal−carbon double bond, a process well known for metallacarbenes. Usually, however, the reaction between these metallacarbynes and alkynes leads to the formation of naphthol complexes (section XI.B).

III. μ-Alkylidene Complexes

When the carbon of a carbene moiety C(R)R′ is bridging two metals, the complex is no longer called a metallacarbene, but a μ-alkylidene complex according to Herrmann.[84] A few of these complexes have been prepared directly from terminal metallacarbynes, and in all cases, one of the carbene substituents is also linked to a metal center. Here we discuss all reactions in which a terminal carbyne carbon is converted into a μ_2-carbene carbon, which possesses two bonds to a main group element (C, B).

Such ligands are obtained in the reaction between the bimetallic metallacarbyne $[(CO)_4Co](CO)_4W\equiv C-R$ and alkynes. Depending on the alkyne employed, the product **1** or its CO insertion product **2** is formed (eq 25 and Table 4).[85,86] In one case, a mixture of both **1** and **2** is obtained $(R^1 = Me$ or Tol, $R^2 = Me$, $R^3 =$ SiMe₃), which are easily interconverted.

$$[(CO)_4Co](CO)_4W\equiv C\text{-}R^1 \ + \ R^2\text{-}C\equiv C\text{-}R^3$$

(25)

1

$R^{1\text{-}3} = Ph, Tol$

2

$R^{1\text{-}3} = Me, Et, Ph$

Another example is the coupling of carbyne and acyl ligands reported by Hart (eqs 26 and 27).[87] It has been suggested that the reaction with the manganese complex $(CO)_5Mn-Me$ should involve the

Table 4. Yields in the Formation of Bimetallic Complexes from Metallacarbynes [(CO)$_4$Co](CO)$_4$W≡C–R^1 and Alkynes R^2–C≡C–R^3 (Eq 25)

R^1	R^2	R^3	yield (%)
complex type 1			
Tol	Tol	Tol	68
Tol	Ph	Ph	69
complex type 2			
Tol	Et or Me	Et or Me	39
Tol	Me	Me	41
Tol	Et	Et	40
Me	Me	Me	62
Me	Ph	Me	40
Et or Me	Et or Me	Et or Me	62

$$Cp(CO)_2W\equiv C\text{-Tol} + Cp_2Ti\overset{CH_2}{\underset{Cl}{\diagup\diagdown}}AlMe_2 \longrightarrow \quad (29)$$

$$2\ Cp(CO)_2W\equiv C\text{-Tol} \xrightarrow[CO]{hv} \quad (30)$$

in which light can be used to promote the reaction (section V). When triphenylphosphine is employed in the reaction instead of carbon monoxide, the usual η^1- and η^2-ketenyl complexes are formed.

The formation of a trimetallic acetylide complex in 30% yield has been reported by Green (eq 31).[93] Labeling experiments have shown that the μ_3-carbon atom has been derived from a carbonyl ligand.

$$Cp(CO)_2M\equiv C\text{-R} + 2\ [Fe_3(\mu\text{-H})(CO)_{11}]^- \xrightarrow[4\ d]{80\ ^\circ C} Cp(CO)_2M\!\!-\!\!Fe(CO)_3 \quad (31)$$

M = W, R = Tol (32 %);
M = W, R = Me (25 %);
M = Mo, R = Me (25 %)

$$(CO)_5Mn\text{-Me} \xrightarrow[\text{toluene, reflux}]{} \quad (26)$$

$$Cp(CO)_2W\equiv C\text{-R}$$

90 %

$$Cp(CO)_3M\text{-Me} \xrightarrow[hv,\ 12\ h]{} Cp(CO)_2W\!\!-\!\!M(CO)_2Cp \quad (27)$$

M = Mo, W
M = Mo, R = 4-Tol (48 %)
M = W, R = 4-Tol (32 %)
M = W, R = 2-C$_6$H$_4$OMe (45 %)

migration of the methyl group onto a carbonyl ligand to form the unsaturated acyl species [(CO)$_4$MnC(O)-Me]. This complex may then coordinate a metallacarbyne, after which a coupling between the carbyne carbon and the acyl fragment can take place.

The cyclic borane BBN reacts with metallacarbynes to give η^3-coordinated ligands. Boron hydride is able of forming a bimetallic μ-alkylidene species, in which two new boron–carbon bonds have been formed with the former carbyne ligands (eq 28).[88,89]

$$2\ L(CO)_2W\equiv C\text{-R} + BH_3\cdot THF \longrightarrow \quad (28)$$

L = MeCp, R = Tol (45 %);
L = Cp, R = Me (80 %), Ph (64 %), Tol (79 %)

The Tebbe reagent is able to transfer its methylene group onto the carbyne carbon of Cp(CO)$_2$W≡C–Tol, thus forming a bimetallic complex with a bridging vinyl ligand in 50% yield (eq 29).[90]

In the presence of light, the reaction between Cp-(CO)$_2$W≡C–Tol and carbon monoxide leads to the coupling between two carbyne ligands and a carbonyl ligand (eq 30, 63%).[91,92] It is clearly related to the nucleophile-induced formation of ketenyl complexes,

Recently, our group has established a novel route to μ-alkylidene complexes from metallacarbynes, which is both general and efficient. The metallacarbynes L$_{OMe}$(CO)$_2$M≡C–Tol react smoothly with the cyclopalladated complexes of N,N-dimethylbenzylamine to give a novel type of μ-alkylidene complexes (eq 32).[94]

$$\xrightarrow{L_{OMe}(CO)_2M\equiv C\text{-Tol}} \quad (32)$$

M = Mo, W
R = OMe

$$L_{OMe} = \left[R_2P\overset{Cp}{\underset{O}{\diagup}}Co\overset{PR_2}{\underset{PR_2}{\diagdown}} \right]^-$$

This reaction has been successfully extended to simple metallacarbynes of the type Cp(CO)$_2$M≡C–R and to a series of different cyclopalladated ligands (eq 33 and Table 5).[95,96] It it clear from the spectral data that all these complexes belong to the same novel class of palladium μ-alkylidene complexes, whose structure is not dependent on the nature of

Table 5. Yields in the Formation of μ-Alkylidene Complexes from Metallacarbynes Cp(CO)$_2$M≡C−R and Cyclopalladated Ligands [Pd(C−Y)X]$_2$ (Eq 33)

R = H: dmba
R = 4-F: F-dmba
R = 4,5-OCH$_2$O: methdmba

pdea   bms   8mquin

bhq   8equin   bzpy   bpdma   bpms

ligand C−Y	X	M	R	yield (%)	ligand C−Y	X	M	R	yield (%)
dmba	Cl	Mo	Tol	93	8mquin	I	W	Tol	59
dmba	I	Mo	Tol	85	8mquin	Cl	Mo	Tol	85
dmba	Cl	W	Tol	93	8mquin	I	Mo	Tol	82
dmba	I	W	Tol	93	bhq	I	Mo	Tol	72
dmba	BF$_4$	W	Tol	96	8equin	I	Mo	Tol	21
dmba	I	W	4-C$_6$H$_4$^{t}Bu	90	bzpy	Cl	Mo	Tol	88
dmba	Cl	W	1-cyclo-C$_5$H$_7$	87	bzpy	I	Mo	Tol	95
F-dmba	Cl	Mo	Tol	81	bzpy	Cl	W	Tol	90
F-dmba	Cl	W	Tol	90	bzpy	I	W	Tol	80
methdmba	Cl	Mo	Tol	79	bzpy	OAc	Mo	Tol	70
pdea	Cl	Mo	Tol	69	bpdma	Cl	Mo	Tol	29
bms	Cl	Mo	Tol	69	bpdma	Cl	W	Tol	29
bms	Cl	Mo	Tol	87	bpms	Cl	Mo	Tol	75
bms	Cl	W	2,6-C$_6$H$_3$Me$_2$	79	bpdms	Cl	W	Tol	86

the cyclopalladated ligand nor on the nature of the metallacarbyne.

(33)

X = Cl, I, OAc, BF$_4$; M = Mo, W
R = Tol, 4-C$_6$H$_4$^{t}Bu, 2,6-C$_6$H$_3$Me$_2$, 1-cyclo-C$_5$H$_7$

IV. Metallacarbynes and Alkyl Complexes

A. Metallacarbynes

A chloride substituent on a carbyne carbon can be easily displaced by aryloxide anions or tertiary phosphines to form metallacarbynes with heteroatom substituents (eqs 34 and 35).[97] This substitution

$$\text{Tp'(CO)}_2\text{M≡C-Cl} \xrightarrow[\text{KCl}]{\text{KOAr}} \text{Tp'(CO)}_2\text{M≡C-OAr} \quad (34)$$

M = Mo; Ar = Ph (34 %), Tol (46 %)
M = W; Ar = Ph (83 %), Tol (94 %),
        4-C$_6$H$_4$OMe (81 %)

$$\text{Tp'(CO)}_2\text{M≡C-Cl} \xrightarrow[\text{- KCl}]{\text{PR}_3 ,\ \text{KPF}_6} \text{[Tp'(CO)}_2\text{M≡C-PR}_3\text{][PF}_6\text{]} \quad (35)$$

PR$_3$ = PMe$_2$Ph (81 %), PPh$_3$ (62 %),
        P(cyclo-C$_6$H$_{11}$)$_3$ (56 %)

reaction has also been observed between Tp'(CO)$_2$-

Mo≡C−Cl and anionic chalcogenide fragments, forming the complexes Tp'(CO)$_2$Mo≡C−ER [ER = SMe$^-$ (70%), SPh$^-$ (100%), SC$_6$H$_4$NO$_2^-$ (70%), SePh$^-$ (100%)] and [Tp'(CO)$_2$Mo≡C−E]$^-$ (E = S, Se, Te, all in about 60% yield).[98]

By using the same principle of chloride substitution, anionic metallacarbynes have been obtained from the reaction between a chlorocarbyne and a series of stabilized carbanions (eq 36, no yields reported).[99] These metallacarbynes can alternatively be considered as vinylidene complexes.

Tp'(CO)$_2$M≡C-Cl + [Na][CHXY]

$$\xrightarrow[\text{- NaCl}]{} \text{Tp'(CO)}_2\text{M≡C—CHXY} \quad (36)$$

M = Mo, W
X = Y = CN, CO$_2$Et

The thioether substituent on the carbyne carbon of Tp'(CO)$_2$W≡C−SMe can be substituted by triethylphosphine to form a cationic metallacarbyne (eq 37, 20%).[39] When a second equivalent of phosphine reacts with the metallacarbyne, a metallacarbene complex is formed (section II.B).

$$\text{Tp'(CO)}_2\text{W≡C-SMe} \xrightarrow[\text{- "SMe"}]{\text{PEt}_3}$$

$$\xrightarrow[\text{MeCN/H}_2\text{O}]{\text{NH}_4\text{PF}_6} \text{[Tp'(CO)}_2\text{W≡C—PEt}_3\text{]}^+ , \text{PF}_6^- \quad (37)$$

B. Alkyl Complexes

A methylene–phosphorane complex is obtained in the reaction between a hydrido metallacarbyne and carbon monoxide (eq 38, 50%).[100] The phosphorane

$$(H)Cl_2(PMe_3)_3W\equiv C\text{-}H \xrightarrow[0\,°C]{CO\ (30\ psi)} Cl_2(CO)_2(PMe_3)_2W(CH_2PMe_3)$$

(38)

complex has not been well characterized since it is unstable in the solid state. The reaction is reminiscent of the nucleophile-induced formation of ketenyl complexes from metallacarbynes (section V).

Exposing the complex $Cp[P(OMe)_3]_2Mo\equiv C\text{-}CH_2$-$^tBu$ to a high carbon monoxide pressure results in the substitution of the phosphite ligands by carbon monoxide to form the metallacarbynes $Cp(L)(CO)$-$Mo\equiv C\text{-}R$ (31%) and $Cp(CO)_2Mo\equiv C\text{-}R$ (26%) (L = $P(OMe)_3$, R = $CH_2{}^tBu$). In the process, also a small amount of another complex is obtained, in which a phosphite ligand and a carbon monoxide have reacted to give an ester substituent (eq 39).[71]

$$Cp(L)_2Mo\equiv C\text{-}CH_2{}^tBu \xrightarrow[3\ d]{CO\ (300\ atm)}$$

(39)

L = $P(OMe)_3$

8%

V. Ketenyl Complexes

Ketenyl complexes are formed via the coupling of a carbyne ligand and a carbonyl ligand on the same metal center. Kim and Angelici[4] and Mayr and Bastos[19] have extensively reviewed these reactions. Therefore, only a few examples from the period before 1991 are given here. The vast majority of these reactions occur in the presence of a nucleophile like a tertiary phosphine. However, the coupling reaction can also be induced by anionic metal complexes or certain Lewis acids.

A. Nucleophile-Induced Ketenyl Formation

Nucleophiles react with relatively electron rich metallacarbynes with carbonyl ligands to give η^1- or η^2-coordinated ketenyl complexes. It is by far the most general method to make ketenyl complexes from metallacarbynes and the first example dates back to 1976 (eq 40, 86%).[101] Since then, this principle has been used successfully in many reactions.

(40)

Most of these examples are known for metallacarbynes of the type $Cp(CO)_2M\equiv C\text{-}R$ (M group 6), but the reaction between $[(CO)_2(dppe)M\equiv C\text{-}R][BF_4]$ and dithiocarbamate ligands also leads to ketenyl complexes (eq 41).[102,103]
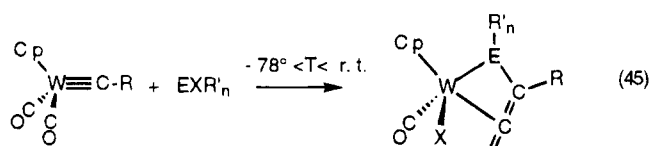
A similar reaction is known between NaS_2CNEt_2 and either $Cl(PMe_3)_2(CO)_2W\equiv C\text{-}Ph$ or $Cl(PMe_3)_2$-$(CO)(CN^tBu)W\equiv C\text{-}Ph$.[104,105] Ketenyl complexes are also formed in the reaction between $Cl(PMe_3)_2$-

Table 6. Yields in the Formation of Ketenyl Complexes from Metallacarbynes $[L(CO)_2M\equiv C\text{-}R]^+$ and Carbonylmetalates $M'(CO)_5^-$ (Eq 44)

L	M	R	M'	yield (%)
Cp	Mn	Tol	Mn	50
Cp	Re	Tol	Mn	40
Cp	Mn	Ph	Re	NR
MeCp	Mn	Ph	Mn	94
MeCp	Mn	Fc	Mn	28

(41)

R = $CHMe_2$, NR'_2 = pyr (79 %)
R = CH_2Ph, NR'_2 = NMe_2 (98 %), NEt_2
N^{i}Pr$_2$ (29 %), pyr (40 %)

$(CO)_2W\equiv C\text{-}R$ (R = Me, Et) and either CN^tBu or PMe_3.[104] An attempt to induce the coupling between the alkylidyne and an isocyanide ligand in $Cl(CN$-$^tBu)_2(CO)_2W\equiv C\text{-}Ph$ in the presence of a nitrogen base resulted again in a ketenyl complex (eq 42).[104]

(42)

Often, irradiation of the reaction mixture promotes the coupling reaction between a carbyne and a carbonyl ligand. In these cases, even relatively weak nucleophiles like acetonitrile may induce the formation of a ketenyl complex (eq 43, 66%).[106]

(43)

B. Other Ketenyl Formation Reactions

When anionic metal carbonyl complexes of manganese[107,108] or rhenium[109] react with metallacarbynes, bimetallic complexes are obtained, in which the ketenyl ligand bridges two metals (eq 44, and Table 6). The X-ray structure of these complexes suggests that the central unit involves a two-electron three-center bonding.

$$[L(CO)_2M\equiv C\text{-}R]^+ + M'(CO)_5^- \longrightarrow L(CO)M\text{---}M'(CO)_4 \quad (44)$$

Certain Lewis acids of the type EXR_n can also induce the formation of ketenyl complexes in high yields (eq 45 and Table 7).[110,111] In the process, a

Table 7. Yields in the Formation of Ketenyl Complexes from Metallacarbynes Cp(CO)$_2$W≡C—R and Lewis Acids EXR′$_n$ (Eq 45)
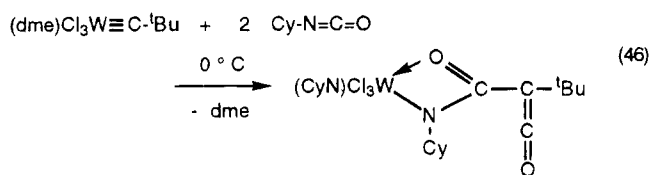
R	EXR′$_n$	yield (%)
Me	PClMe$_2$	93
Me	AsIMe$_2$	86
Me	SCl(4-C$_6$H$_4$NO$_2$)	94
Ph	PClPh$_2$	85
Tol	PClMe$_2$	96
Tol	PClPh$_2$	93
Tol	SCl(4-C$_6$H$_4$NO$_2$)	93

halogenide group is liberated which coordinates to the metal center.

R = Me, Tol, Ph; EXR′$_n$ = PClMe$_2$,
PClPh$_2$, AsIMe$_2$, SCl(4-C$_6$H$_4$-NO$_2$)

In an exceptional reaction, the high-valent metallacarbyne (dme)Cl$_3$W≡C—^{t}Bu reacts with cyclohexyl isocyanate to give a metallacyclic complex in which an isocyanate has been coupled to a ketenyl fragment (eq 46, 85%).[112] The C=O fragment of the ketenyl moiety is not a former carbonyl ligand but it has been provided by the isocyanate ligand. It has been suggested that first a metathesis of the N—C double bond takes place to give the ketenyl complex Cl$_3$-(CyN)WC(^{t}Bu)(=C=O). Insertion of a second isocyanate into the W—C bond of this complex would then lead to the product depicted in eq 46.
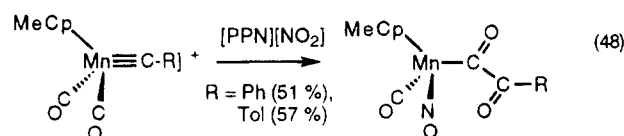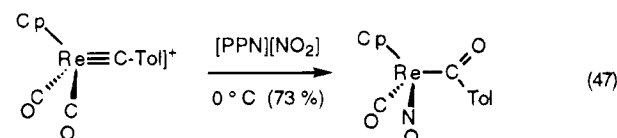

VI. Acyl Complexes

The carbyne ligand C(R) can be converted into an acyl complex in two different ways. Reaction of a metallacarbyne with protic acids induces the coupling between the carbyne ligand and a carbonyl ligand, forming a M—C(O)—CH$_2$R fragment. Alternatively, the carbyne carbon can be oxidized to give a complex containing a M—C(O)—R moiety. In both cases it is sometimes possible to separate the acyl ligand from the metal, to form directly the corresponding organic molecules. These reactions are given in section XII.B.

A. Via Oxidation of the Carbyne Carbon

Geoffroy et al. have demonstrated that the carbyne carbon in rhenium metallacarbynes can be easily oxidized by the nitrite anion (eq 47).[113,114] For the manganese analogue, it has been established at low temperature that the nitrite anion first adds to the electrophilic carbyne carbon to form an intermediate metallacarbene. In this case, the oxidation is accompanied by the insertion of a carbonyl ligand into the metal—carbon bond, thus forming an α-ketoacyl complex (eq 48).[104]
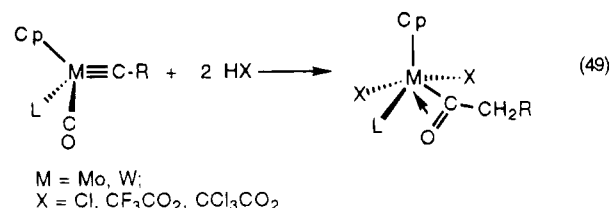
Table 8. Yields in the Formation of Acyl Complexes from Metallacarbynes CpL(CO)M≡C—R and Acids HX (Eq 49)

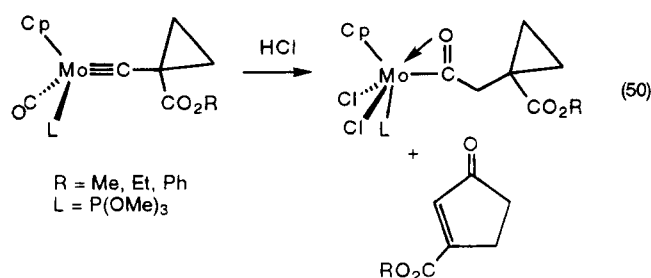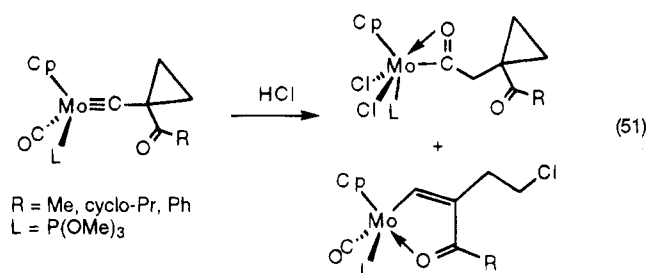| M	L	R	X	yield (%)
Mo	CO	Tol	Cl	89
Mo	CO	Tol	CF$_3$COO	93
W	CO	Me	Cl	96
W	CO	Me	CF$_3$COO	94
W	CO	Ph	Cl	92
W	CO	Ph	CF$_3$COO	95
W	CO	Tol	Cl	93
W	CO	Tol	CF$_3$COO	93
W	CO	Tol	CCl$_3$COO	94
W	CO	cyclo-Pr	CF$_3$COO	92
Mo	P(OMe)$_3$	(Me)cyclo-Pr	Cl	51
Mo	P(OMe)$_3$	(SMe)cyclo-Pr	Cl	58
W	P(OMe)$_3$	cyclo-Pr	Cl	90
W	PMe$_3$	Tol	Cl	95
Mo	P(OMe)$_3$	(CH$_2$)$_2$CH=CH$_2$	Cl	77

B. Via Protonation of the Carbyne Carbon

A series of reactions exists in which the protonation of metallacarbynes with hydrochloric acid or other acids leads to the formation of η^2-coordinated acyl complexes (eq 49 and Table 8).[115-119] A carbonyl ligand is inserted into the metal—carbon bond and the oxygen coordinates via its lone pair electrons to the unsaturated metal center.

M = Mo, W;
X = Cl, CF$_3$CO$_2$, CCl$_3$CO$_2$

Similarly, a metallacarbyne with a substituted cyclopropyl group can react with hydrochloric acid to form an acyl complex. The cyclopropyl ring is found to react as well, as is clear from the presence of small amounts of cyclopentenone (eq 50).[120] The yield of the latter product has been improved by using different reaction conditions (section XI.C).

R = Me, Et, Ph
L = P(OMe)$_3$

When the cyclopropyl ring has a ketone substituent, instead of the ester group shown above, the principal product of the reaction is still an acyl complex. However, the yield has become lower than 50% due to the formation of a new metallacyclic complex in 22 to 46% yield (eq 51). In this case, the cyclopropyl ring has been opened via reaction with the acid, and the carbyne carbon has simply been protonated.
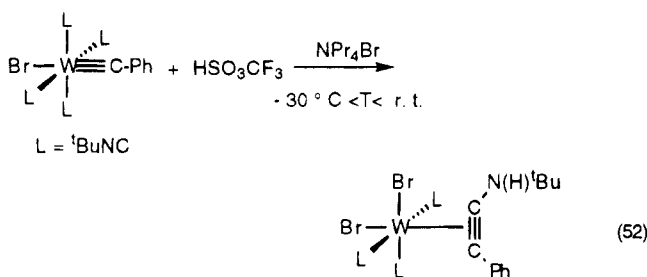

R = Me, cyclo-Pr, Ph
L = P(OMe)$_3$

(51)

VII. Alkyne Complexes

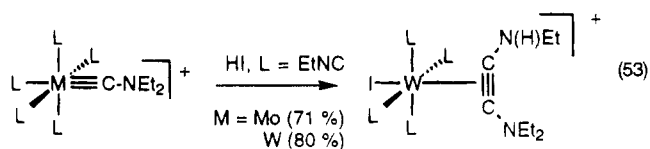### A. Monometallic Complexes with Alkyne Ligands

The coupling reaction between two carbyne ligands on the same metal center affords alkyne or alkyne-type ligands, and these reactions have been reviewed recently.[19] As a consequence, only one example of each type of product is given here. The reader is referred to the review for an exhaustive list of references, although more recent examples have been included in the following text. The formation of monometallic alkyne complexes is related to the formation of ketenyl complexes from metallacarbynes, in which the carbyne ligand is coupled to a carbonyl ligand (section V).

The most successful reaction is the coupling between a carbyne carbon and an isocyanide ligand, leading to ynamine (R—C≡C—NR$_2$), or ynediamine (R$_2$N—C≡C—NR$_2$) complexes. These reactions are usually induced by electrophiles like protons, as demonstrated in eq 52 (86%).[121] In fact, one of the

L = ^{t}BuNC

(52)

isocyanide ligands is transformed into an aminocarbyne moiety via protonation. Coupling of the carbyne and the aminocarbyne ligands then affords the ynamine complex. Recently, evidence has been provided that the first step in these reactions involves the protonation of the metal—carbon triple bond, leading to a reactive cationic metallacarbene.[122]
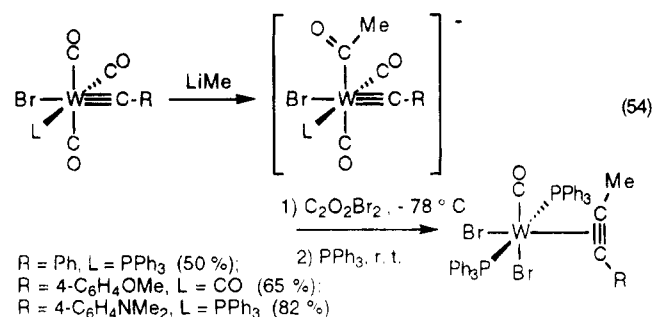
Ynediamine complexes have been prepared in a 40—80% yield from the reaction between the aminocarbyne [(EtNC)$_5$M≡C—NEt$_2$]$^+$ (M = Mo, W) and hydroiodic acid (eq 53).[123] The metallacarbyne is easily prepared in a two steps synthesis, starting from an isocyanide complex. A related example is
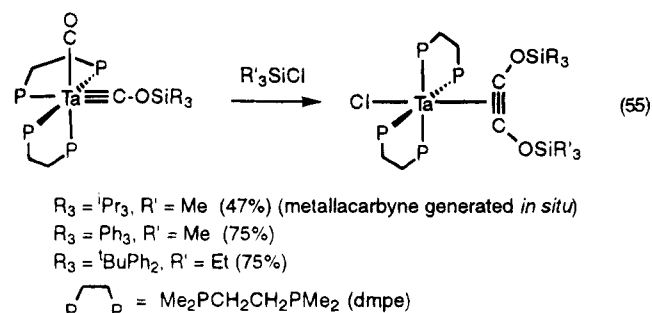

(53)

M = Mo (71 %)
W (80 %)

the conversion of the metallacarbynes [(EtNC)$_5$-M≡C—NEt$_2$]$^+$ into an ynediamine complex, by reacting them successively with [Et$_3$O][BF$_4$] and an excess of NEt$_4$Br [M = Mo (38%), W (36%)].[124]

The metallacarbyne [(trans-dppe)$_2$(CNMe)M≡CN-(H)Me]$^+$ (M = Mo, W) can be transformed into an ynediamine complex as well by reacting it with HBF$_4$.[125]

An alkyne complex can also be formed via the coupling between a carbonyl and a carbyne ligand (eq 54).[126] In this reaction, the carbonyl ligand is converted in two steps into a carbyne ligand (CMe), which then reacts with the initial carbyne moiety (CR).

(54)

R = Ph, L = PPh$_3$ (50 %);
R = 4-C$_6$H$_4$OMe, L = CO (65 %);
R = 4-C$_6$H$_4$NMe$_2$, L = PPh$_3$ (82 %)

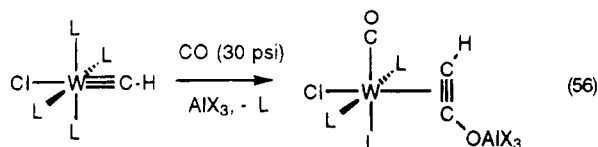1) C$_2$O$_2$Br$_2$, - 78 °C
2) PPh$_3$, r. t.

This transfer of a carbonyl ligand onto the carbyne carbon has been reported for a tantalum metallacarbyne as well. The carbyne complexes react with trialkylsilyl chloride to form alkyne-type ligands (eq 55).[127,128] As for isocyanides, the electrophile reacts with the carbonyl ligand to form an alkoxycarbyne ligand in situ, after which a carbon—carbon coupling between the two carbyne moieties takes place.

(55)

R$_3$ = ^{i}Pr$_3$, R' = Me (47%) (metallacarbyne generated in situ)
R$_3$ = Ph$_3$, R' = Me (75%)
R$_3$ = ^{t}BuPh$_2$, R' = Et (75%)

P⌒P = Me$_2$PCH$_2$CH$_2$PMe$_2$ (dmpe)

Another rare example is the reaction of trichloro - or trimethylaluminum with the tungsten hydridocarbyne Cl(PMe$_3$)$_4$W≡C—H (eq 56).[100,129] The structure of the aluminum trichloride adduct has been reported separately.[130] It is supposed that the Lewis acid AlX$_3$ interacts with the oxygen atom of a carbon monoxide, which would facilitate the coupling between the carbonyl and the carbyne ligand.

The metallacarbyne Cl(OC)$_2$(PMe$_3$)W≡C—R (R = Me, Et) reacts with nucleophiles to give a ketenyl complex, but in the presence of an electrophile like ClCO^{t}Bu, an alkyne complex is formed (eq 57).[104]

(56)

X = Me (83%), Cl (50%)
L = PMe$_3$

(57)

R = Me, Et

B. Bimetallic μ_2-Alkyne Complexes

Metallacarbynes of the type Cp(CO)$_2$W≡C—R are often able to dimerize to the corresponding bimetallic complexes containing a μ_2-bridging alkyne ligand. This intermolecular coupling of two carbyne ligands is usually induced by protic acids, which probably transform the carbyne ligand into a reactive carbene ligand (eq 58).[131,132]

(58)

R = Me (75 %), Tol (95 %)

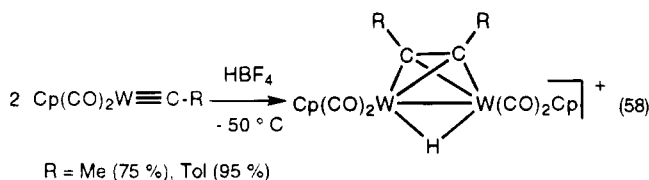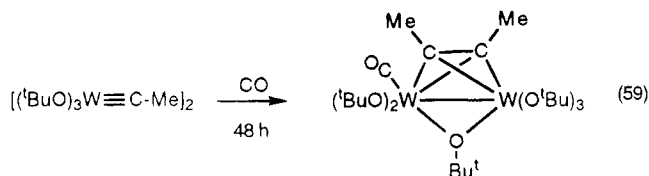The dimerization of the metallacarbyne Cp(CO)$_2$-W≡C—Tol can also be induced by metal complexes containing a metal to metal triple bond, like Cp$_2$-Cr$_2$(CO)$_4$ (100%) and Cp$_2$Mo$_2$(CO)$_4$ (29%),[23] or Cp$_2$-Ni$_2$(μ-CO)$_2$ (50%).[133]

Metallacarbynes with carbaborane ligands like [N(PPh$_3$)$_2$][{η^5-C$_2$B$_9$H$_{11}$}(CO)$_2$W≡C—4-Tol] are related to cyclopentadienyl metallacarbynes, since they also possess a relatively nucleophilic carbyne carbon. The carbaborane complex can undergo a dimerization with HBF$_4$ to form an anionic bimetallic alkyne complex in 47% yield.[134] However, these reactions usually lead to hydroboration products, in which the carbyne carbon has been coupled to the boron cage (section VIII).

The electrophilic metallacarbyne Br(CO)$_4$Cr≡C—Ph is dimerized in the reaction with the complexes Co$_2$(CO)$_8$ (37%) or Cp$_2$Ni (7.5%).[135] In these reactions, complexes with bridging carbyne ligands like (μ_3-CPh)Ni$_3$Cp$_3$ are formed as side products.

The equilibrium between Schrock metallacarbynes and their alkyne-bridged dimers is well known. Sometimes, the addition of a donor ligand like carbon monoxide can push the equilibrium entirely toward the bimetallic complex (eq 59, 100%).[136,137] In the

(59)

reaction between [^{i}PrO]$_3$(py)W≡CNMe$_2$ and carbon monoxide a bimetallic alkyne complex is formed in which the new alkyne ligand is only coordinated to one metal center (60%).[138] In a recent metathesis reaction between (^{t}BuO)$_3$W≡C—^{t}Bu and *tert*-butyl-acetylene, a bimetallic complex is formed, among other products (eq 60).[139] Apparently, the intermediary metallacarbyne (^{t}BuO)$_3$W≡C—H is formed, which then dimerizes to the alkyne complex.

(60)

C. Trimetallic Alkyne Complexes

The reaction between metallacarbynes and the carbonyl complex Fe$_2$(CO)$_9$ leads to the formation of trimetallic complexes with a bridging alkyne ligand (eq 61, 72%).[140,141] It has been proposed to consider the W—μ-C—W bond as a three-center two-electron interaction. Various complexes with μ_3-bridging carbyne ligands are formed at the same time.

(61)

A more general reaction involves metallacarbynes and the trimetallic hydride complex (μ-H)$_2$Os$_3$(CO)$_{10}$ which leads to a mixture of two isomeric trimetallic complexes in 33% yield (eq 62).[142-144] In this reaction, the tetrametallic complexes CpWOs$_3$(CO)$_{11}$(C(O)-CH$_2$—Tol) (21%) and CpWOs$_3$(CO)$_{10}$(4-Tol—C≡C—Tol) (22%) are formed as well. Similar alkyne formation reactions are induced by the complexes (μ-H)$_2$(μ-CH$_2$)Os$_3$(CO)$_{10}$ and Ru$_3$(CO)$_{12}$ (eq 62).[140]

(62)

ML$_n$ = (μ-H)$_2$Os$_3$(CO)$_{10}$, (μ-H)$_2$(μ-CH$_2$)Os$_3$(CO)$_{10}$, Ru$_3$(CO)$_{12}$

VIII. Carbaborane Cage Complexes

Recently, a series of anionic metallacarbynes of the type [B*(CO)$_2$M≡C—R]$^-$ have been prepared by Stone and co-workers, in which B* usually represents an η^5-coordinated carbaborane ligand like η^5-C$_2$B$_9$H$_{11}$ or η^5-C$_2$B$_9$H$_9$Me$_2$. The edges of the polyhedron depicted

below represent either boron or carbon atoms. These six electron ligands are related to the cyclopentadienyl anion Cp^-, which has been commonly used to stabilize metallacarbynes (e.g. $Cp(CO)_2W\equiv C-Ph$). Throughout this review B* will be represented with the following drawing:

The protonation of these carbaborane carbynes has given rise to a variety of different products, and several of these reactions have been reviewed by Stone.[12] It is a rather complex chemistry, in which the choice of the carbaborane ligand and the reaction conditions greatly influence the course of the reaction. For the sake of clarity, it is not desirable to discuss all reactions that have been reported. Rather, one example of each major reaction will be given in an equation, while the other references will be indicated in the text. Whenever the carbaborane ligand of the metallacarbyne is not involved in a B—C coupling reaction, these references will be presented in other sections (IX and X.C).

One of the most general reactions is the low-temperature protonation of a carbaborane metallacarbyne by tetrafluoroboric acid, in the presence of a two-electron donor ligand like carbon monoxide (eq 63). It is assumed that the acid protonates the

R = Me, Tol   3   (63)

carbyne carbon, whereupon the new carbene ligand C(H)R inserts into the B—H bond. This process corresponds to an intramolecular hydroboration of the carbyne carbon. Examples of intermolecular hydroborations are given in section IX.

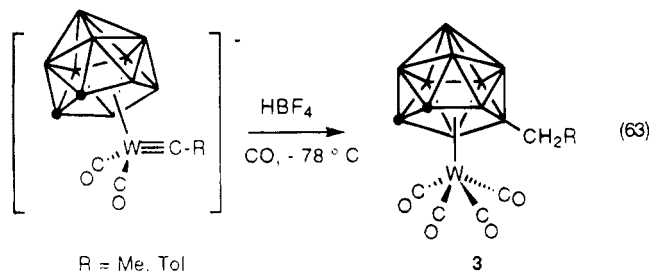A whole series of complexes of type 3 has been obtained according to this principle, using one of the donor ligands being carbon monoxide (80%[145] and 58%[146] yield), tert-butyl isocyanide (92%[145] and 27%[146]), triphenylphosphine (62%[145] and 58%[146]), diphenylphosphine (55%),[146] diphenylacetylene (69 or 86%[145] and 50%[147]) or bidentate phosphines like dppm (78%[146]) and dppe (65 or 90%[147]). In the latter reaction, cyclic ylide complexes may be formed instead of the usual hydroboration product (section X.C). Depending on the donor strength of the ligands, one or more of the carbonyl ligands in 3 will be substituted by this ligand.

When hydrochloric or hydroiodic acid is used instead of hydroboric acid, products of type 3 are also obtained (in 40—50% yield), in which a halogen atom has substituted one of the carbonyl ligands on the

metal center.[130,148,149] These complexes are now anionic species.

A metallacarbyne with a slightly bigger carbaborane cage (C_2B_{10}) does undergo typical transfer reactions in the presence of a donor ligand and HBF_4 as well (eq 64).[150]

R = Tol, L = CO (80% a)
R = Tol, L_2 = PhC≡CPh (80% a)
R = Me, L_2 = PhC≡CPh (70% a)

(64)

A more limited reaction is the protonation of a metallacarbyne with a 2-$C_6H_4CH_2OMe$ substituent on the carbyne carbon (eq 65).[151] In the presence of

R = 2-$C_6H_4CH_2OMe$;
L = CO (53 %), $PHPh_2$ (68 %)   4

(65)

a donor ligand like carbon monoxide or diphenylphosphine, the methoxy group is lost, and a cyclic product is obtained, resulting from a double hydroboration. Other donor ligands like dppm (71%) and diphenylacetylene (59%) or other acids like hydroiodic acid (48%), can also be used. In every case, the metallacarbyne is converted into a complex of type 4.

A platinum hydride complex has been recently used to induce a hydroboration (eq 66).[152] The actual B—C coupling takes place at low temperature, but the product has to be stabilized by the addition of a donor ligand L.

If the protonation reaction is carried out in the absence of donor ligands, the metallacarbyne itself will react with the unsaturated metal center of the hydroboration product. Thus, protonation of the carbaborane carbyne may lead to a bimetallic complex in which one metallacarbyne simply acts as a ligand (eq 67).[153]

Sometimes an additional C—C coupling takes place between the unreacted μ-carbyne carbon and a carbonyl ligand, thus forming a bimetallic ketenyl species. It has also been reported that protonation of a carbyne complex stabilized with a carbaborane cage may lead to a bimetallic alkyne complex, as is

$$\left[\text{Mo}\equiv\text{C-Tol}\right]^{-} \xrightarrow[\text{2. L}]{\text{1. PtH(Cl)(PEt}_3\text{)}_2\text{ / TlBF}_4} \quad (66)$$

L =CO (66 %), PEt$_3$ (65 %), dppm (38 %)

$$\left[\text{W}\equiv\text{C-R}\right]^{-} \xrightarrow{\text{0.5 HBF}_4} \quad (67)$$

R = Me (32 %), Tol (31 %)

observed for related complexes with a cyclopentadienyl ligand (section VII.B). If the protonation is carried out in the presence of a metallacarbyne with a cyclopentadienyl ligand, this metallacarbyne will preferentially coordinate to form a related bimetallic complex (eq 68).[154,155]

$$\left[\text{M}\equiv\text{C-Tol}\right]^{-} \xrightarrow[\text{Cp(CO)}_2\text{M'}\equiv\text{C-R}]{\text{HBF}_4, -78\ ^\circ\text{C} <T <r.t.} \quad (68)$$

M = W, M' = W, R = Me (73 %)
M = W, M' = Mo, R = Tol (62 %)
M = Mo, M' = W, R = Me (60 %)

However when the cyclopentadienyl derivative bears an alkynyl group (e.g. C≡C^{t}Bu), a dimetallacyclopropene is formed instead of a dimetallacyclopropadiene (eq 69).[156]

The protonation of a carbaborane carbyne in the presence of the complex Cp(CO)$_2$W≡C—Tol does not always lead to a bimetallic complex. In one case, a small amount of a double hydroboration product is found.[157] It is an example of the complexity of the chemistry of these carbaborane metallacarbynes.

Another method to obtain hydroboration products is the reaction of anionic carbaborane rhodium complexes with cationic metallacarbynes (eq 70).

$$\left[\text{M}\equiv\text{C-Tol}\right]^{-} \xrightarrow{\text{HBF}_4} \text{Cp(OC)}_2\text{W=C-C}\equiv^t\text{Bu} \quad (69)$$

$$\quad (70)$$

[L(CO)$_2$Re≡C-Tol]$^+$ [MeCp(CO)$_2$Mn≡C-Tol]$^+$

5   6

L = Cp, MeCp;   L' = CO, PPh$_3$

When a rhenium metallacarbyne is used, a bimetallic complex is formed [type **5**, L = Cp (41%), MeCp (37%)], while the manganese metallacarbyne affords a monometallic complex [type **6**, 52%, eq (70)].[158] Similar formations of complexes of type **6** with [MeCp(CO)$_2$Mn≡C—R]$^+$ (R = Tol, 2,6-C$_6$H$_3$Me$_2$, about 50% yield) have been reported.[159] The rhodium complex [(η^5-C$_2$B$_9$H$_9$Me$_2$)Rh(cod)] reacts with the metallacarbyne [MeCp(CO)$_2$Mn≡C—Tol]$^+$ to give a complex of type **6** (14%).[158]

IX. Miscellaneous Metal Complexes

A. η^3-Coordinated Unsaturated Ligands

η^3-Coordinated unsaturated ligands have been obtained from the reaction between the metallacarbyne Cp(CO)$_2$W≡C—Tol and certain metal—alkyl or —aryl complexes which transfer their organic ligand onto the carbyne carbon (eq 71).[160] The aromatic system of the phenyl ring participates in the bonding to the metal, so that an η^3-coordinated ligand is obtained.

On the basis of similar reactions with alkynes, it has been proposed that the metal—carbon triple bond

first inserts into the chromium–carbon bond of CrPh$_3$(THF)$_3$. A γ-hydride shift may then lead to the metal hydride Cp(CO)$_2$W(H)(=C(Ph)Tol)), which rearranges to give the η^3-complex shown in eq 71. The reaction with diethylzinc is different since it leads to the bimetallic olefin complex [Zn[Cp(CO)$_2$W(η^3-Me(Et)C=C(H)(4-C$_4$H$_6$Me)]$_2$] in 72% yield.[160]

$$Cp(CO)_2W \equiv C\text{-Tol} \xrightarrow{MR_n} Cp(CO)_2W \text{---} \quad (71)$$

MR$_n$ = Cr(Ph)$_3$(thf)$_3$ (42 %),
ZnPh$_2$, Zn ^{i}Pr$_2$ (55 %),
Zn(CH$_2$C$_6$H$_4$Me)$_2$ (47 %)

The cyclic borane borabicyclononane is able to convert the metallacarbyne Cp(CO)$_2$W≡C–Tol into another complex with an η^3-coordinated ligand, Cp-(CO)$_2$W(η^3-C(H)(Tol)BC$_8$H$_{14}$) in 88% yield.[88,89] This corresponds to the intermolecular hydroboration of the carbyne carbon, in contrast to the intramolecular process given in section VIII. Two other examples have been reported as well (eq 72).[88,89,161]

$$\xrightarrow{[R'_2BH]_2} \quad (72)$$

R = H, R'$_2$ = 9-BBN (88%)
R = H, R'$_2$ = Et (55%)
R = Me, R'$_2$ = Et (53%)

A rare reaction between a metallacarbyne and 4 equiv of an isocyanide leads to an η^3-coordinated ligand with unsaturated side chains (eq 73).[79,162] Two isocyanide molecules have undergone a coupling with the carbyne carbon, while the other two have substituted the trimethyl phosphite ligands on the metal center. The final product is reminiscent of the half-ylides that are formed in the reaction between metallacarbynes and an excess of trimethylphosphine (section XII.B).

$$Cp[P(OMe)_3]_2M \equiv C\text{-}CH_2R \xrightarrow[- 2 \ P(OMe)_3]{4 \ CNR'} Cp(CNR')_2M \text{---} \quad (73)$$

M = Mo, R = ^{t}Bu (51 %);
M = Mo, R = ^{i}Pr (60 %);
M = W, R = ^{t}Bu (48 %);
R' = 2,6-C$_6$H$_3$Me$_2$

B. Other Metal Complexes

A variety of interesting ligands bridging two or three metals have been obtained from reactions of metallacarbynes. However, they do not form a homogeneous class of compounds, and no general synthetic routes have yet been reported. In a recent publication, the hydridocarbynes Tp'(CO)$_2$M≡C–H have been prepared via the quantitative desilylation of the metallacarbyne Tp'(CO)$_2$M≡C–SiMe$_2$Ph. Upon

Table 9. Yields in the Formation of Vinyl Complexes from Metallacarbynes [DIPP]$_3$W≡C–R and Ketones or Aldehydes R'$_2$CO (Eq 77)

R	R'$_2$CO	yield (%)
^{t}Bu	H$_2$CO	77
^{t}Bu	Me$_2$CO	81
^{t}Bu	Ph(H)CO	NR
^{t}Bu	EtO(H)CO	82
^{t}Bu	NMe$_2$(H)CO	78
Et	Me$_2$CO	78
Et	Ph(H)CO	80
Et	EtO(H)CO	40
Et	NMe$_2$(H)CO	77

standing in solution, this metallacarbyne dimerizes spontaneously to afford a bimetallic complex with a bridging vinylidene ligand (eq 74).[163]

$$Tp'(CO)_2M \equiv C\text{-}SiMe_2Ph \xrightarrow[0\,^\circ C]{NBu_4F} Tp'(CO)_2M \equiv C\text{-}H$$

$$\downarrow r.\,t. \quad (74)$$

$$Tp'(CO)_2M = C \cdots M(CO)_2Tp'$$

M = Mo, W (100 %)

A similar product has been obtained via the spontaneous disproportionation of the cationic metallacarbyne [Cp(OC)$_2$M≡C–Me][BCl$_4$] (M = Mn, Re, eq 75).[42]

$$[Cp(OC)_2M \equiv C\text{-}Me]BCl_4 \underset{- \ BCl_4^-}{\overset{- H^+, \ - 70^\circ C}{\rightleftharpoons}} Cp(OC)_2M = C = CH_2$$
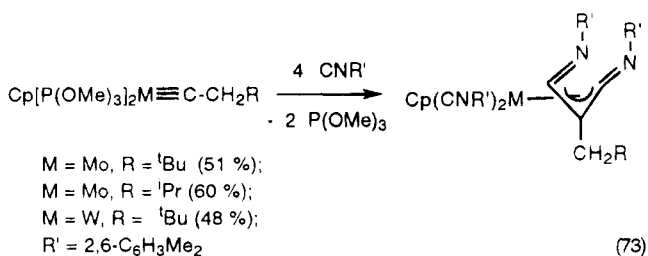
$$M = Mn, Re \xrightarrow{22^\circ C} \quad (75)$$

Mayr et al. have reported a reaction of the metallacarbynes Cl(CO)$_2$(py)$_2$W≡C–R with a thiocarbamate reagent, leading to a ligand analogous to an acyl, a so-called thioaldehyde (eq 76).[164]

$$Cl(CO)_2(py)_2W \equiv C\text{-}R \ + \ 2 \ [H_2NEt_2][S_2CNEt_2] \quad (76)$$

$$\longrightarrow$$

R = Ph (96%), R = Me (62%)

Vinyl complexes are formed in the reaction between the Schrock metallacarbyne [DIPP]$_3$W≡C–R and a series of ketones and aldehydes (eq 77 and Table 9).[165] It has been suggested that the ketone oxygen

$$[DIPP]_3W \equiv C\text{-}R \ + \ R'_2C=O \longrightarrow [DIPP]_3W \quad (77)$$

R = ^{t}Bu, Et
R' = H, Me, Ph, EtO, NMe$_2$

first attacks the electrophilic tungsten center to form an intermediate metallacyclobutene complex, which

then rearranges to a vinyl complex. The vinyl ligand can be separated from the metal as an alkene, by treating the complex with potassium hydroxide.

A similar mechanism has been suggested for the reaction between the metallacarbyne $Cl_3(dme)W \equiv C-$ ^tBu and unsaturated molecules (eq 78).[166]

$$Cl_3(dme)W \equiv C-^tBu \ + \ X=Y \ \xrightarrow{- \ dme} \ \left[Cl_3W \equiv C \substack{^tBu \\ \diagup} \ \Big| \atop X-Y \right] \quad (78)$$

$$Cl_3W-C \substack{^tBu \\ \diagdown \diagup \diagdown} \atop X \diagdown Y$$

$$X=Y \ = \ RN=CHR, \ O=NR, \ RN=C=NR, \ RN=C=O$$

When alkyl isothiocyanates are employed, the reaction goes on to yield a polymeric material, in which the units are bridged by chloride anions (eq 79)).[166,167]

$$Cl_3(dme)W \equiv C-^tBu \ \xrightarrow{R'CH_2-N=C=S} \ \ (79)$$

$$R'CH_2=Et \ (66\%), \ ^nBu \ (66\%), \ Cy \ (60\%)$$

Treatment of a cationic manganese metallacarbyne with $Li(C=S)NMe_2$ affords a trace amount of a coordination complex characterized by an X-ray structure (4%, eq 80).[168]

It is suggested that first, nucleophilic addition to the carbyne carbon gives a thiocarbene ligand, whereafter a sulfur atom is inserted into the metal–carbon double bond. The only other product isolated from this reaction is supposedly $[MeCp(CO)_2Mn]_2(\mu\text{-}S)]$ (6%).

$$\substack{MeCp \\ \diagdown} Mn \equiv C-Ph \ + \ LiC(=S)NMe_2 \ \longrightarrow \ \ (80)$$

Another coordination complex is formed in the reaction between the cationic metallacarbyne $[(CO)_5$-$Cr \equiv C-NEt_2]^+$ and an azide (eq 81, 63%).[169] Probably, the anionic azide adds to the carbyne carbon to form the neutral metallacarbene $(CO)_5Cr=C(N_3)$-NEt_2, which subsequently loses dinitrogen.

$$(CO)_5Cr \equiv C-NEt_2 \ + \ \substack{[NBu_4][N_3] \\ \xrightarrow{\hspace{1.5cm}} \\ - \ N_2} \ (CO)_5Cr \leftarrow N \equiv C-NEt_2 \quad (81)$$

Via a different pathway, the carbyne ligand of [Cp-$(CO)_2Mn=C-CH_2R]^+$ can be transformed into a nitrile ligand (eq 82).[43] To rationalize this, a Beckman-type rearrangement has been proposed by the authors.

Metallacarbynes with a carbaborane ligand on the metal center are well known for their hydroboration reactions induced by protons in the presence of

$$[Cp(OC)_2Mn \equiv C-CH_2R]^+ \ \substack{1) \ Ph_2C=NNH_2 \\ \xrightarrow{\hspace{1.5cm}} \\ 2) \ Et_3N}$$

$$Cp(CO)_2Mn \leftarrow N \equiv C-CH_2R \quad (82)$$

$$R = H \ (62\%), \ Me \ (62\%)$$

nucleophiles (section VIII). In a recent paper, a new bimetallic structure is depicted in which a novel four-carbon ligand has resulted from the coupling of the two carbyne carbons (eq 83).[170] This is reminiscent of the proton-induced coupling reactions which lead to alkyne complexes (section VII.B).

$$(83)$$

$$R = Tol, \ R' = \ ^tBu$$
$$R = \ ^tBu, \ R' = Tol$$

Protonation of a carbyne complex containing a cyclopropyl group leads to a butadiene complex, together with some substituted cyclohexenone (eq 84).[117,119]

$$Cp(CO)(P(OMe)_3)Mo \equiv C \substack{\diagup} \substack{\diagdown} R \ \xrightarrow{HCl} \ \ (84)$$

$$R = Me \ (18\%), \ CH_2CH=CH_2 \ (53\%),$$
$$SMe \ (28\%), \ CH_2Ph \ (24\%)$$

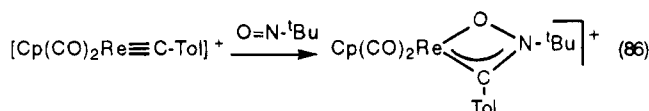## X. Metallacyclic Complexes

A. Metallaazacyclic Complexes

Four-membered metallaazacycles can be obtained from cationic rhenium carbynes and imines, in which the nucleophilic nitrogen atom attacks the electrophilic carbyne carbon (eq 85).[171,172] The new carbene fragment then coordinates intramolecularly to the unsaturated metal center, thus forming a four-membered metallacycle in which the double bond is delocalized ("metallazetine" or "metallaazacyclo-butene").

$$[Cp(CO)_2Re \equiv C-Tol]^+ \ \xrightarrow{Ph(H)C=N-R} \ \ (85)$$

$$R = Me \ 85 \ \%$$
$$R = N=CHPh \ 76\%$$

A closely related reaction is observed with $^tBuN=O$ (eq 86).[172] When the dimeric reagent $[^tBuN=O]_2$ is used, the cycloaddition is followed by an additional insertion of a carbonyl ligand into the $Re-C(Tol)$ double bond (38%).[171,172]

The analogous manganese metallacarbyne also forms a metallacycle with imines, but now the imine

Table 10. Yields in the Formation of *ansa*-Carbene Complexes from Metallacarbynes [(RCp)(CO)₂Mn≡C—Ph]⁺ and Cyanamides N≡CNR′₂ (Eq 88)

R	R′₂	yield (%)	ref
H	Me₂	30	173
H	Et₂	26	60
H	ⁱBu₂	13	60
H	(CH₂Ph)₂	8	60
H	(Me)Ph	21	60
Me	Me₂	20	173
Me₅	Me₂	8	173

$$[Cp(CO)_2Re\equiv C\text{-}Tol]^+ \xrightarrow{O=N\text{-}^tBu} Cp(CO)_2Re\left[\overset{O}{\underset{C\atop Tol}{\diagup\diagdown}}N\text{-}^tBu\right]^+ \quad (86)$$

carbon has been coupled to the cyclopentadienyl ligand (eq 87).[171,172] Surprisingly, the reaction occurs

R = Me : R' =Tol, R" = Me (35 %)
R = H : R' = Ph, R" = Me (45 %);
R = H : R' = Ph, R" = -N=C(H)Ph (56 %)

even with a metallacarbyne bearing a η^5-C₅Me₅ ligand, which implies the loss of one of the methyl groups from the cyclopentadienyl ring. The difference between the manganese and the rhenium metallacarbynes has been explained by the difference in the size of the metal center. When the manganese complex reacts with ᵗBuN=O, initially a four-membered metallacycle is formed, as is observed with the rhenium metallacarbyne. This reaction is followed by an insertion of carbon monoxide into the metal—carbon double bond (overall yield 52%).[172]

Similar metallacyclic complexes have been obtained in the reaction between the manganese metallacarbyne and dimethylcyanamide (eq 88 and Table 10).[60,173,174] In these cases, however, the reagent

formally inserts into the metal—carbon triple bond, while in the reaction with imines, the nitrogen simply adds to the carbyne carbon. If the cyanamide is present in excess, the reaction may go on to the formation of a novel carbocyclic complex: an imidazolium (section XI.D).
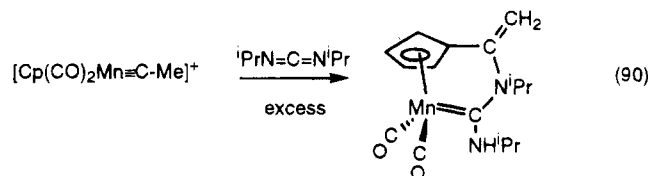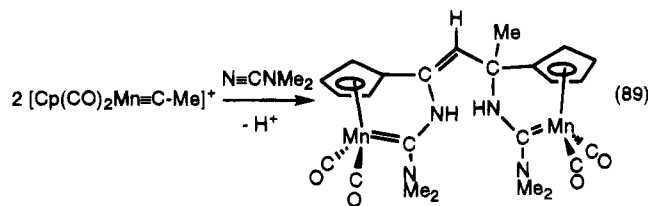
When the carbyne carbon bears a methyl instead of a phenyl group, this reaction leads to the formation of bimetallic *ansa*-metallacarbenes (eq 89, 30%).[175]

Another simple *ansa*-carbene complex is formed in the reaction of [Cp(CO)₂Mn≡C—Me]⁺ with a carbodiimide (eq 90).[43]

cis-Diazoarenes and benzo[c]cinnoline with [Cp(CO)₂Re≡C—Tol]⁺ form new four-membered metal-

Table 11. Yields in the Formation of Metallatriazole Complexes from Metallacarbynes Cp(CO)LM≡C—R and Azides N₃R′ (Eq 92)

M	L	R	R′	yield (%)
Mo	CO	Me	CO₂Me	99
Mo	CO	Ph	CO₂Me	98
Mo	CO	Tol	CO₂Me	98
Mo	PMe₃	Me	CO₂Me	89
Mo	PMe₃	Ph	CO₂Me	97
Mo	PMe₃	Tol	CO₂Me	98
W	CO	Me	CO₂Me	70
W	CO	Ph	CO₂Me	70
W	CO	Tol	CO₂Me	95
W	CO	Me	CH₂CO₂Me	85
W	CO	Ph	CH₂CO₂Me	90
W	CO	Tol	CH₂CO₂Me	85

lacyclic complexes through a formal [2 + 2] cycloaddition of the N=N bond across the M≡C unit.[51]

This reaction depends very much upon the nature of the counteranion associated with the metallacarbyne, since with BCl₄⁻ the obtained compounds evolve to afford different products. Thus CO insertion to give a five-membered acyl ring is obtained in the case of the *cis*-diazoarene reaction, whereas the benzo[c]cinnoline unit was displaced by a chloride from the anion to afford a neutral chlorocarbene compound.[51]

Reaction between the metallacarbynes [Cp(OC)₂₋ₙ(PMe₃)ₙM≡C—R (M = Mo, W) and azides N₃R′ results in a [3+3] cycloaddition leading to metallatriazole complexes in high yields (eq 92 and Table 9).[176] Alternatively, these complexes could be regarded as dihapto metallacarbenes (section II.C).

Table 12. Formation of Metallacyclobutadienes (7) or Their Deprotonated Derivatives (8) from Metallacarbynes $L_nM\equiv C-R$ and Alkynes $R'-C\equiv CR''$ (Eq 93)

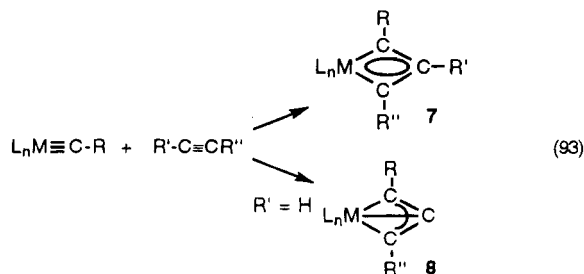| metallacarbyne LnM≡C−R	alkyne R′−C≡C−R″	type of metallacycle obtained	yield (%)	ref
	Metallacyclobutadiene (7)			
[DIPP]₃Mo≡C−ᵗBu	EtC≡CEt	Mo(C₃Et₃)	86	177
(ArN)[(CF₃)₂MeCO]₂ Re≡C−ᵗBu	MeC≡CMe	Re(C₃Me₃)	NR	178
Ar = 2,6-C₆H₃ⁱPr₂	EtC≡CEt	Re(C₃Et₃)	NR	
[ᵗBuO]₃W≡C−Et (+ pinacol)	EtC≡CEt	W(C₃Et₃)	74	179
[DIPP]₃W≡C−ᵗBu	HC≡CᵗBu	W(C₃ᵗBu₂H)	60	180
	EtC≡CEt	W(C₃Et₃)	72	181
	PrC≡CPr	W(C₃Pr₃)	69	
[DIPP]₂(Cl)W≡C−ᵗBu	HC≡CᵗBu	W(C₃ᵗBu₂H)	72	180
CpCl₂W≡C−ᵗBu	MeC≡CMe, EtC≡CEt, ⁱPrC≡CⁱPr, PhC≡CPh	W(C₃ᵗBuR₂) R = Me, Et, ⁱPr, Ph	NR	182
dme[HFIP]₃W≡C−ᵗBu	EtC≡CEt	W(C₃Et₃)	47	183
	PrC≡CPr	W(C₃Pr₃)	58	
dme[HFIP]₃W≡C−Ph	HC≡CᵗBu	W(C₃ᵗBuHPh)	70	180
dme[(CF₃)₂(Me)CO]₃ W≡C−ᵗBu	MeC≡CMe	W(C₃Me₃)	66	183
	EtC≡CEt	W(C₃Et₃)	77	
dmeCl₃W≡C−ᵗBu	MeC≡CMe	W(C₃Me₃)	78	179, 184
	EtC≡CEt	W(C₃Et₃)	57	
thf[DMP]₃W≡C−ᵗBu	HC≡CᵗBu	W(C₃ᵗBu₂H)	69	180
	Deprotio metallacyclobutadiene (8)			
[DIPP]₃Mo≡C−ᵗBu (+ pyridine)	HC≡CPr, HC≡CPh HC≡CᵗBu	Mo(C₃ᵗBuR) R = Pr, Ph, ᵗBu	75−80	177
[(CF₃)(Me)₂CO]₃ Mo≡C−ᵗBu(⁺base)	HC≡CᵗBu	Mo(C₃ᵗBu₂)	87	177
	HC≡CPh	Mo(C₃Ph₂)	88	
(py)₂[HFIP]₃ Mo≡C−ᵗBu	HC≡CᵗBu	Mo(C₃ᵗBu₂)	91	177
dme[(CF₃)₂(Me)CO]₃ Mo≡C−ᵗBu	HC≡CᵗBu	Mo(C₃ᵗBu₂)	94	177
	HC≡CPh	Mo(C₃Ph₂)	86	
	HC≡CⁱPr	Mo(C₃ⁱPr₂)	57	
dme[(CF₃)₃CO]₃ Mo≡C−ᵗBu	HC≡CᵗBu	Mo(C₃ᵗBu₂)	80	177
dme[(CF₃)(O)CO]₃ Mo≡C−ᵗBu	HC≡CᵗBu	Mo(C₃ᵗBu₂)	63	185
	HC≡CPh	Mo(C₃ᵗBuPh)	82	
[DIPP]₃W≡C−ᵗBu (⁺ pyridine)	HC≡CᵗBu	W(C₃ᵗBu₂)	88	180
dme[HFIP]₃W≡C−Ph	HC≡CPh	W(C₃Ph₂)	60	180
dme[HFIP]₃W≡C−ᵗBu (⁺ pyridine)	HC≡CᵗBu	W(C₃ᵗBu₂)	81	180
	HC≡CPh	W(C₃ᵗBuPh)	85	
(ᵗBuO)₃W≡C−ᵗBu	ᵗBuC≡CH	W(C₃ᵗBu₂)	NR	139

B. Metallacyclobutadienes

High-valent metallacarbynes are well known for their reactivity in the metathesis of alkynes (section XII.A). In a number of examples, this reaction stops halfway to afford a stable metallacyclobutadiene complex (eq 93, type **7**), which can be isolated.[177−184] If terminal alkynes are employed, the hydrogen substituent may be lost to give a "deprotonated" or "deprotio" metallacyclobutadiene complex (eq 93, type **8**).[177,180,185] Sometimes, the deprotonation only occurs in the presence of a base-like pyridine or quinuclidine. A summary of the reactions leading to isolated complexes of type **7** or **8** is given in Table 12.

$$L_nM\equiv C-R + R'-C\equiv CR'' \tag{93}$$

The cyclic alkyne cyclooctyne is known to undergo metathesis reactions, but in the reaction with the metallacarbyne [DIPP]₃W≡C−ᵗBu, a dimetallacyclobutadiene complex is formed.[186]

The reaction of CpCl₂W≡C−ᵗBu with *tert*-butylacetylene is believed to form a metallacyclobutadiene which is not isolated. Instead, a mixture of a deprotio metallacyclobutadiene complex and the vinylcarbene complex *trans*-Cp(Cl)₃W=C(Buᵗ)C(H)=C(H)ᵗBu is obtained.[187] The deprotio complex can be converted into the vinylcarbene complex by reacting it with 2 equiv of HCl. This suggests that the two products are the result of a disproportionation reaction of an intermediate metallacyclobutadiene complex. Another argument is the fact that, in the presence of the base triethylamine, only the deprotio complex is formed. It demonstrates why terminal alkynes often cannot participate in normal metathesis reactions, since these disproportionation reactions deactivate the metallacyclobutadiene complex necessary for the metathesis.

C. Other Metallacyclic Complexes

Chalcogenide elements like elemental sulfur or selenium and cyclohexene sulfide may add twice to the metal−carbon triple bond of some metallacarbynes to form metallacyclic complexes (eq 94 and Table 13).[188−190]
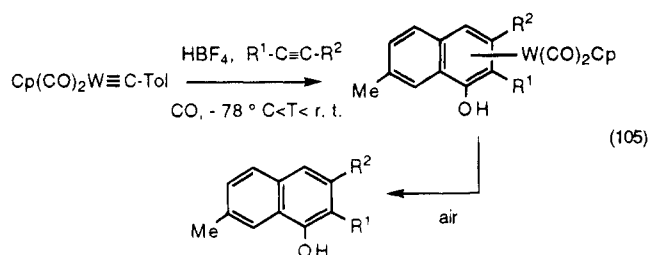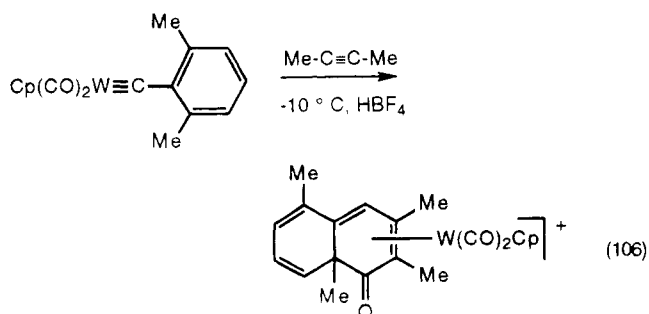
Table 13. Yields in the Formation of Metallacycles from Metallacarbynes L$_n$M≡C−R and Chalcogenides "X" (Eq 94)

L$_n$M≡C−R	"X"	yield (%)	ref
Cp[P(OMe)$_3$]$_2$Mo≡C−CH$_2$^{t}Bu	S$_8$	57	188
Cp(CO)$_2$Mo≡C−CH$_2$^{t}Bu	S$_8$	72	188
	Se$_8$	78	
Cp(CO)$_2$W≡C−Tol	S$_8$	58	188
	Se$_8$	94	
Cp(CO)$_2$W≡C−Me	C$_{10}$H$_8$S	94	189
H$_2$B(pz)$_2$(CO)$_3$W≡C−Me	S$_8$	21	190
[Cp(CO)$_2$Re≡C−Tol]$^+$	cyclo-SCH$_2$CHMe	82	42, 51

Table 14. Yields in the Formation of Dithiomethyl Complexes from Metallacarbynes Cp(OC)LM≡C−R and [Me$_2$SSR']BF$_4$ (Eq 95)

M^a	L	R	yield (%)
Mo	CO	Me	98
Mo	CO	Ph	98
Mo	CO	Tol	96
Mo	PMe$_3$	Me	97
Mo	PMe$_3$	Ph	97
Mo	PMe$_3$	Tol	96
W	CO	Me	97
W	CO	Ph	94
W	CO	Tol	97
W	PMe$_3$	Tol	95
W^b	CO	Me	93
W^b	CO	Ph	88

^{a} R' = Me, except for as indicated. ^{b} R' = Et.

$$L_nM≡C\text{-}R \ + \ "X" \longrightarrow L_nM\diagup\overset{X}{\underset{X}{\diagdown}}C\text{-}R \qquad (94)$$

R = Me, CH$_2$But , Tol
"X" = S$_8$, Se$_8$, SC$_{10}$H$_8$
X = S, Se

Comparable sulfur complexes have been obtained from the reactions between Cp(CO)LM≡C−R (M =Mo, W) and 2 equiv of electrophilic fragments (SR$^+$) (eq 95 and Table 14).[70,191] This reaction proceeds in almost all cases via an intermediary metallacarbene, which can be isolated as well (see also section II.C).

$$[SR']^+ = [Me_2SSR']^+ \qquad (95)$$

A mixture of cyclic complexes resulting from the incorporation of an alkyne and a carbonyl ligand has been presented by Mayr et al. (eq 96, excess of alkyne).[192] It has been suggested that first a metal-

L = PMe$_3$ 26%   13%

lacyclobutadiene and a cyclopropenyl complex are formed, which then react further with a carbonyl ligand. These intermediate complexes would then be similar to those observed in the metathesis of alkynes.

Recently, the formation of a five-membered metallacycle has been observed in the reaction between the metallacarbyne Cl(PMe$_3$)$_4$W≡C−Me and carbon monoxide (eq 97).[193,194] Initially, carbon monoxide

$$Cl(PMe_3)_4W≡C\text{-}Me \xrightarrow[-PMe_3]{CO} Cl(PMe_3)_3(CO)W≡C\text{-}Me \qquad (97)$$

simply substitutes a trimethylphosphine ligand on the metal center, but this intermediate complex quickly reacts further with three other molecules of carbon monoxide. This metallacarbyne also displays alkyne metathesis activity (section XII.A).

Metallacarbynes with carbaborane ligands on the metal center are best known for their hydroboration reactions, induced by protons in the presence of nucleophiles (section VIII). When bidentate phosphine ligands are employed as nucleophiles, sometimes, only a coupling reaction between the carbyne carbon and the phosphine is observed, leading to a cyclic ylide complex (eq 98).[147] Although the boron cage η^5-C$_2$B$_9$R$_2$ (R = H, Me) is a spectator ligand, it influences the overall yields of the reaction.

$$(98)$$

η^5- C$_2$B$_9$H$_9$Me$_2$: R = Tol, L = dppe (89 %);
R = Tol, L = dppm (93 %)
η^5- C$_2$B$_9$H$_{11}$: R = Me, L = dppe (41 %);
R = Tol, L = dppe (77 %)
n = 1, 2

Diphenylphosphine can convert the metallacarbyne Cp(CO)$_2$W≡C−Tol into a mixture of two cyclic alkyl complexes in which the phosphorus lone pair forms a dative bond to the unsaturated metal center (eq 99).[195] The first complex can be obtained in 70% yield, by reacting the metallacarbyne successively with LiPPh$_2$ and NEt$_4$Br.

The reversible formation of a rhenacyclopentene from an alkylidene−alkylidyne complex has been reported recently (eq 100).[196] The intermediate alky-

Cp(CO)₂W≡C-Tol $\xrightarrow[110\,°C]{PHPh_2}$

Cp(CO)₂W ... PPh₂ ... C ... H ... Tol

+   5%

Cp(CO)(PHPh₂)W ... Ph₂ P−O ... C−CO ... H ... Tol

(99)

lidyne—metallacyclobutane can be isolated, but it converts slowly into the metallacyclopentene complex.

H, R' ... C ... Re≡C-ᵗBu + CH₂=CH₂ ⟶ R' ... Re≡C-ᵗBu (100)

RO = ᵗBuO, R' = ᵗBu;
RO = (CF₃)Me₂CO, R' = ᵗBu;
RO = (CF₃)₂MeCO, R' = SPh

⟶ R' ... Re=C ... ᵗBu

Reaction between the cationic metallacarbyne [Cp-(OC)₂Mn≡C−Ph]⁺ and aminoalkynes leads to complex metallacyclic compounds incorporating one or two aminoalkynes (eq 101). The reaction may even go further to yield an organic product (section XII.B).[197]

[Cp(OC)₂Mn≡C-Ph]⁺

$\xrightarrow{MeC\equiv CNMe_2}$ 62%

$\xrightarrow[excess]{MeC\equiv CNEt_2}$

(101)

One example of a cycloaddition of carbon dioxide to a metallacarbyne has been reported (eq 102, 83%).[198] The metallacyclobutene complex obtained is rather similar to rhenacycles discussed above.

(CO)₄Mo ... Ph₂ P ... W≡C-NEt₂]⁻ $\xrightarrow[-10\,°C]{CO_2}$

(CO)₄Mo ... Ph₂ P ... W=C ... CO ... NEt₂]⁻ (102)

XI. Carbocyclic Complexes

A. Pentasubstituted Cyclopentadienyl Ligands

A deactivation route in the metathesis of alkynes is the formation of pentasubstituted cyclopentadienyl ligands from a carbyne carbon and two molecules of an alkyne (e.g. eq 103).

(dme)Cl₃W≡C-ᵗBu $\xrightarrow{R-C\equiv CR}$ [Cl₃W ... ᵗBu ... C−R ... R] (103)

R=Me (99 %)
Et (50 %),
Pr (77 %)

These cyclopentadienyls are formed upon reaction between an initially formed metallacyclobutadiene with a second equivalent of alkyne. It is supposed that a labile metallacyclobenzene ring is formed, which collapses to give the more stable cyclopentadienyl. Equation 103 shows the relation between a metallacyclobutadiene and a cyclopentadienyl complex in the reaction of the metallacarbyne (dme)-Cl₃W≡C−ᵗBu with 2-butyne or 3-hexyne.[179,184] The X-ray structure of the complex W[η⁵-C₅Me₄(ᵗBu)](η²-MeC≡CMe)Cl₂ has been reported separately.[199]

The metallacarbynes (ᵗBuO)₃W≡C−Et[184] and (dme)-[CF₃(O)CO]₃W≡C−ᵗBu (21%)[185] react with an excess of 3-hexyne to give similar cyclopentadienyl ligands.

The reaction has been successfully extended to the tantalum adduct [(dme)Cl₂Ta≡C−ᵗBu][ZnCl₂] and a series of alkynes:[200] 3,3-Dimethyl-1-butyne (82%), RC≡CR [R = Me (70% or 80% with neat alkyne), Et (65%), ⁿPr (67%)] and RC≡CH [R = ᵗBu (75%), ⁱBu (67%)] all react to give complexes with cyclopentadienyl ligands. Dineopentylacetylene reacts to form a cyclopentadienyl complex, but now, two of the neopentyl ligands of the ring are metalated by the tantalum center (70%).

Some tungsten alkyne complexes react with the Fischer metallacarbyne Cp(CO)₂W≡C−R (R = Me, Tol) to give bimetallic complexes with a pentasubstituted cyclopentadienyl ligand, similar to those formed from high-valent metallacarbynes (eq 104).[201] The tris(3-hexyne)tungsten complex reacts with the metallacarbyne to give a similar product, in which an alkyne bridges the two tungsten centers (30%).

Cp(CO)₂W≡C-R $\xrightarrow[heat]{(R'C\equiv CR')_3W(CO)}$ ... W ... W ... Cp ... R' (104)

R = Tol : R' = Ph (26 %), Me and Ph (44 %);
R = Me, R' = Ph (84 %)

B. Naphthols and Related Molecules

A beautiful example of the application of metallacarbynes in organic synthesis is the formation of naphthol ligands from alkynes and metallacarbynes, which has been developed by Geoffroy and co-workers. Protonation of the carbyne carbon of Cp-(CO)₂M≡C−R activates the complex, and it subsequently reacts with alkynes to form a naphthol complex.[82,83] This method has been recently extended to a whole series of alkynes and the resulting

Table 15. Yields in the Formation of Naphthols from the Metallacarbyne $Cp(CO)_2W\equiv C$–Tol and Alkynes R^1–$C\equiv C$–R^2, in the Presence of HBF_4 and CO (Eq 105)

R^1	R^2	yield (%)
Me	Me	62
Et	Et	34
H	^nPr	34
H	^iPr	67
H	^tBu	49
Me	^nPr	33
^nPr	Me	28
Me	^iPr	49
^iPr	Me	16

naphthol ligands can be easily separated from the metal by standing in air for 24 h (eq 105 and Table 15).[202]

(105)

The reaction is very similar to the formation of naphthols from metallacarbenes and alkynes, the so-called Dötz reaction.[1,2] However, the regiochemistry of the naphthols is opposite in the two cases: in the reaction of metallacarbynes, the smallest substituent R is often found next to the hydroxy group, whereas in the Dötz reaction, the opposite is observed. In the reaction of $Cp(CO)_2W\equiv C$–2,6-$C_6H_3Me_2$ with dimethylacetylene, a slightly different complex is formed (eq 106, 73%).[82,83]

(106)

In a reaction related to the formation of naphthols, a metallacarbyne containing a thiophene ligand also undergoes a cyclization reaction to give 4-hydroxy-5,6-dimethylbenzothiophene (eq 107, 33%).[202] Unfortunately, it has not been possible to apply this method to other substituted alkynes.

(107)

When no alkyne is present and a pressure of carbon monoxide is applied to the same metallacarbyne, a diaryl ketone is formed in 21% yield (eq 108).[202]

Table 16. Yields in the Formation of Cyclopentenones from Metallacarbynes $CpL(OC)M\equiv C$–cC_3H_4R by Irradiation (Eq 109)

L	M^a	R	yield (%)
$P(OMe)_3$	Mo	Et	40
$P(OMe)_3$	Mo	Ph	40
$P(OMe)_3$	Mo	Me_2	40
$P(OPh)_3$	W	H	70
$P(OMe)_3$	W^b	H	38

^{a} All reactions from ref 118, except as indicated. ^{b} From ref 203.

(108)

Labeling experiments with ^{13}C-enriched carbon monoxide indicate that the incorporated carbonyl ligand is exogeneous.

C. Cyclopentenones

Irradiation of cyclopropyl metallacarbynes leads to the ring opening of the cyclopropyl ring under formation of a series of cyclopentenones (eq 109 and Table 16).[118,203] Control experiments with $Cp(CO)P(OMe)_3$-$Mo\equiv C$–cC_3H_5 have proven that the cyclization is not catalyzed by HCl from the chloroform.[118]

(109)

Disubstituted cyclopropyl metallacarbynes react to give cyclopentenones as well (40% yield), as does a bicyclic metallacarbyne (10% yield) (eqs 110 and 111).[118,204]

(110)

(111)

The reaction between a related metallacarbyne and hydrochloric acid leads to a mixture of an acyl complex and small amounts of a cyclopentenone ring. If a metallacarbyne of this type is irradiated in chloroform, the cyclopentenones are formed in better yields (eq 112, indicated yields are the yields of the cyclopentenone).[120] In a secondary reaction, however, the carbyne carbon in this complex is simply protonated and a metallacyclic complex is obtained.

(112)

R = Me (15 %), cyclo-Pr (13 %), Ph (21 %),
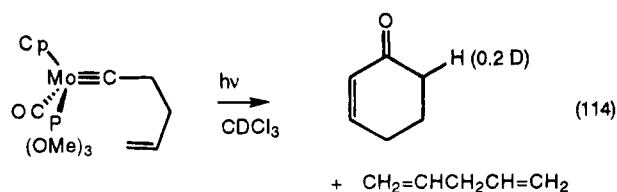OMe (42 %), OEt (38 %), OPh (12 %)

Another five-membered carbocycle is formed upon irradiating a molybdenum metallacarbyne bearing a ketone function (eq 113, 40%).[205] Apparently, one of the methyl groups on the *tert*-butyl substituent can undergo a CH activation reaction with the metal center, after which ring closure occurs.
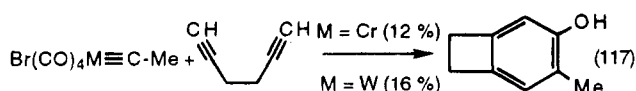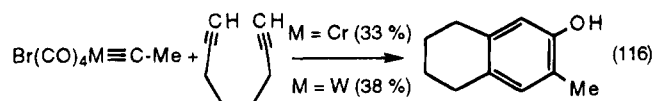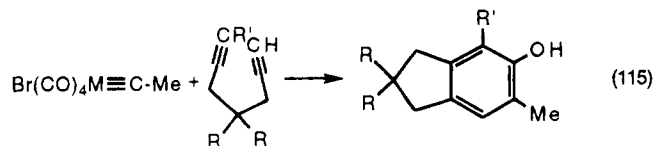

(113)

D. Other Carbocyclic Compounds

A cyclohexenone has been formed in moderate yield (55%) by irradiating a butenyl metallacarbyne in chloroform-*d* (eq 114).[119,204] If the metallacarbyne is protonated, an acyl complex is formed together with a small amount of cyclohexenone (section VI.B).

(114)

+ $CH_2=CHCH_2CH=CH_2$

From the reaction between the carbyne Cl(CO)-$(PMe_3)_3W\equiv C-Ph$ and phenylacetylene, a carbocyclic cyclobutenyl tungsten complex has been obtained. However, since the second product is a metallacyclic complex, this reaction is discussed in section X.

Organic molecules with more than one unsaturated function, like diynes and enynes have proven to be useful in cyclization reactions with metallacarbynes. A series of diynes can be cyclized by the Fischer-type metallacarbynes (eq 115, Table 17, and eqs 116 and 117).[206]

(115)

(116)

(117)

More recently, a similar reaction has been reported involving the 1-alkynyl-1'-vinylbiphenyl (eq 118).[207,208] In all products, the biphenyl ligand is incorporated

Table 17. Yields in the Formation of carboCycles from Metallacarbynes Br(CO)$_4$M≡C—Me and Br(CO)$_4$W≡C—Ph and Various 1,6-Diynes (Eq 115)

metallacarbyne	R	R′	yield (%)
Br(CO)$_4$Cr≡C—Me	H	H	50
	H	Me	46
	H	Ph	31
	CO$_2$Me	H	52
Br(CO)$_4$W≡C—Me	H	H	54
	H	Me	52
	H	Ph	42
	CO$_2$Me	H	60
Br(CO)$_4$W≡C—Ph	H	H	18

into a six-membered cycle. When the terminal methylene group is substituted by CMe_2, the carbyne carbon is no longer incorporated into the final compounds.

(118)

As already mentioned, a common deactivation route in the metathesis of alkynes is the formation of pentasubstituted cyclopentadienyl ligands. A related example is the formation of a molybdenum carbene complex bearing a trisubstituted phenyl ligand (eq 119, 91%).[209] The reaction is thought to go via an intermediate deprotiometallacyclobutadiene complex (section X.B).
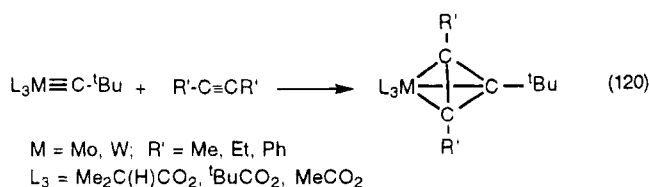

(119)

High-valent metallacarbynes often react with 1 equiv of an alkyne to give a metallacyclobutadiene complex (section X.B). When these planar complexes are not accessible, the reaction may also stop at the stage of stable cyclopropenyl complexes (eq 120 and Table 18).[185]
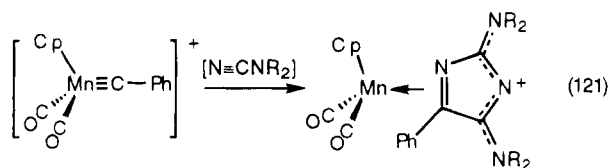
The cationic metallacarbyne $[Cp(OC)_2Mn\equiv C-Ph]^+$ reacts easily with cyanamides to form metallacyclic complexes (section X.A). In the presence of an excess of cyanamide, the reaction goes on to give novel

Table 18. Yields in the Formation of Cyclopropenyl Complexes from Metallacarbynes $L_3M\equiv C-{}^tBu$ and Alkynes $R'C\equiv CR'$ (Eq 120)

$L_3M\equiv C-{}^tBu$	$R'C\equiv CR'$	yield (%)
$[Me_2C(H)CO_2]_3Mo\equiv C-{}^tBu$	$MeC\equiv CMe$	NR
	$EtC\equiv CEt$	NR
	$PhC\equiv CPh$	77
$[{}^tBuCO_2]_3Mo\equiv C-{}^tBu$	$MeC\equiv CMe$	100
	$EtC\equiv CEt$	100
	$PhC\equiv CPh$	70
$[{}^tBuCO_2]_3W\equiv C-{}^tBu$	$MeC\equiv CMe$	62
	$EtC\equiv CEt$	100
$[MeCO_2]_3W\equiv C-{}^tBu$	$EtC\equiv CEt$	60

$$L_3M\equiv C-{}^tBu \ + \ R'-C\equiv CR' \longrightarrow L_3M \overset{\overset{R'}{C}}{\underset{\underset{R'}{C}}{}} C-{}^tBu \quad (120)$$

M = Mo, W; R' = Me, Et, Ph
L_3 = $Me_2C(H)CO_2$, ${}^tBuCO_2$, $MeCO_2$

imidazolinium complexes (eq 121).[60,174] In the case of $NCNMe_2$ and $NCNEt_2$, a certain amount of *ansa*-metallacarbene is formed as well.

$$\left[\begin{array}{c} Cp \\ Mn\equiv C-Ph \\ O^C{}_C{}^C_O \end{array} \right]^+ \xrightarrow{[N\equiv CNR_2]} \begin{array}{c} Cp \\ Mn \\ O^C{}_C \\ O \end{array} \quad (121)$$

XII. Alkynes and Other Organic Molecules

A. Alkynes from the Metathesis of Triple Bonds

The metathesis of alkynes is a typical reaction of high-valent metallacarbynes. Schrock and Chisholm have already discussed many of the details of this reaction.[15-18] The generally accepted mechanism of the metathesis proposes the formation of a metalla-cyclobutadiene complex as the first step (section X.B). Breaking up again this complex generates a new metallacarbyne and a new alkyne (eq 122). Whenever the reaction follows a different pathway, met-allacyclic complexes (metallacyclobutadienes, section X.B) or carbocyclic complexes (cyclopentadienyls and cyclopropenyls, section XI) are formed.

$$L_nM\equiv C-R \xrightarrow{R'-C\equiv CR'} L_nM \overset{\overset{R}{C}}{\underset{\underset{R'}{C}}{}} C-R' \quad (122)$$

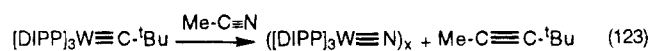$$\downarrow$$

$$L_nM\equiv C-R' \ + \ R'-C\equiv CR$$

The metathesis of alkynes can be a stoichiometric or a catalytic reaction. The carbyne metal is usually molybdenum or tungsten surrounded by bulky alkox-ide ligands. The carbyne substituent is often a bulky alkyl group like *tert*-butyl. An important number of alkynes undergo metathesis reactions and it seems therefore not useful to review these reactions com-prehensively. For our purpose, a summary of the

Table 19. Metallacarbynes $L_nM\equiv C-R$ Active in the Metathesis of Internal Alkynes $R'-C\equiv C-R'$ (Eq 122)
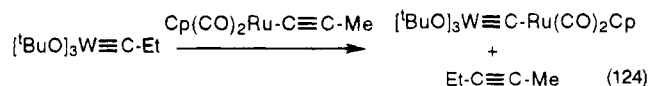
$L_nM\equiv C-R$	ref
$[{}^tBuO]_3Mo\equiv C-{}^tBu$	177
$[DIPP]_3Mo\equiv C-{}^tBu$	210
$[HFIP]_3Mo\equiv C-{}^tBu$	177
$[(CF_3)(Me)_2CO]_3Mo\equiv C-{}^tBu$	210
$[(CF_3)_2(Me)CO]_3Mo\equiv C-{}^tBu$	177
$dme[HFIP]_3Mo\equiv C-{}^tBu$	177, 210
$dme[(CF_3)_2MeCO]_3Mo\equiv C-{}^tBu$	177, 210
$dme[(CF_3)_3CO]_3Mo\equiv C-{}^tBu$	210
$(ArN)[(CF_3)_2(Me)CO]_2Re\equiv C-{}^tBu$	178
$Ar = 2,6-C_6H_3{}^iPr_2$	
$[{}^tBuO]_3W\equiv C-{}^tBu$	211
$(py)_2[HFIP]_3W\equiv C-Et$	183
$(py)_2[HFIP]_3W\equiv C-{}^tBu$	183
$(py)_2[(CF_3)_2MeCO]_3W\equiv C-{}^tBu$	183
$(thf)_2[(CF_3)_2MeCO]_3W\equiv C-{}^tBu$	183
$dme[HFIP]_3W\equiv C-{}^tBu$	180, 183
$dme[(CF_3)_2(Me)CO]_3W\equiv C-Et$	183
$dme[(CF_3)_2(Me)CO]_3W\equiv C-{}^tBu$	183
$Cl_3(PEt_3)(O=PEt_3)W\equiv C-{}^tBu$	211
$Cl_3(PMe_3)_3W\equiv C-{}^tBu$	211
$Cl_3(O=PEt_3)W\equiv C-{}^tBu$	211

different metallacarbynes active in alkyne metathesis will be sufficient; see Table 19. Thus, a given metallacarbyne $L_nM\equiv C-R$ (M = Mo, W; R = ${}^tBu$, Et) will react with an alkyne $R'-C\equiv C-R'$ (R' = Me, Et, Ph, etc.) to afford the metallacarbyne $L_nM\equiv C-R'$ and the alkyne $R'-C\equiv C-R$, usually in high yield.[177,178,180,183,210,211]

When polyenynes such as *trans*-5-decene-3,7-diyne are used as substrates instead of simple alkynes, normal metathesis products are obtained and these reactions have been reviewed by Mayr (50-80% yield).[212] One example is known, in which a triple carbon—nitrogen bond undergoes a quantitative me-tathesis reaction with the metallacarbyne $[DIPP]_3$-$W\equiv C-{}^tBu$, giving rise to a tungsten—nitrido complex (eq 123).[165]

$$[DIPP]_3W\equiv C-{}^tBu \xrightarrow{Me-C\equiv N} ([DIPP]_3W\equiv N)_x + Me-C\equiv C-{}^tBu \quad (123)$$
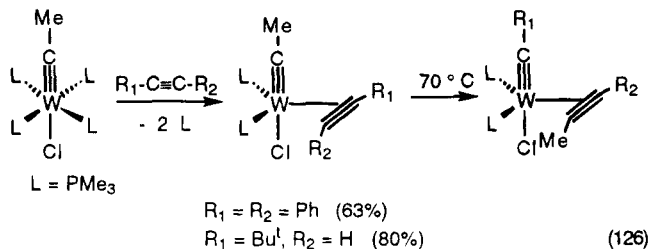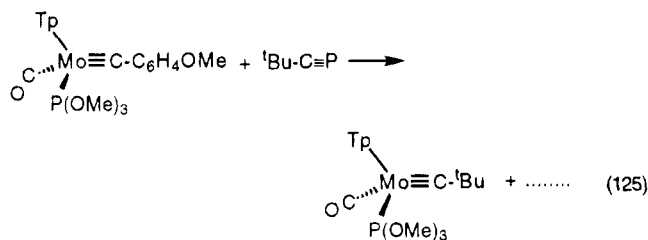
Although $Cp(CO)_2Ru-C\equiv C-Me$ is an acetylide complex, it reacts with metallacarbynes as would be expected for a normal alkyne (eq 124, 55% isolated bimetallic complex).[213] It suggests that the alkyne metathesis reaction can be extended to other com-plexes with a triply bonded carbon.

$$[{}^tBuO]_3W\equiv C-Et \xrightarrow{Cp(CO)_2Ru-C\equiv C-Me} \begin{array}{c} [{}^tBuO]_3W\equiv C-Ru(CO)_2Cp \\ + \\ Et-C\equiv C-Me \end{array} \quad (124)$$

A metathesis reaction involving the Fischer met-allacarbyne $Tp(CO)[P(OMe)_3]Mo\equiv C-2-C_6H_4OMe$ has been reported by Stone et al. (eq 125, 84%).[214] The phosphaalkyne apparently reacts as a simple alkyne, although it is not clear if the expected second product $P\equiv C-2-C_6H_4OMe$ has actually been isolated.

Recently, the metallacarbyne $Cl(PMe_3)_4W\equiv C-Me$ has been found to undergo a stoichiometric metath-esis reaction with diphenylacetylene (eq 126).[193,194] Clearly, the carbyne ligand and the alkyne ligand have exchanged their substituents. The initially formed alkyne complex can also be prepared with the

$$\text{(125)}$$

$$R_1 = R_2 = Ph \quad (63\%)$$
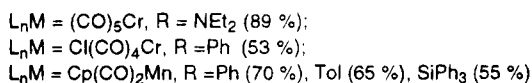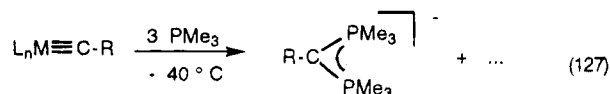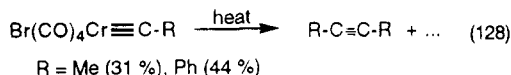$$R_1 = Bu^t, R_2 = H \quad (80\%) \quad \text{(126)}$$

alkyne *tert*-butylphenylacetylene. Upon standing in solution at room temperature this complex gives a mixture of products, in which the known metallacarbyne Cl(PMe$_3$)$_4$W≡C—^{t}Bu could be recognized. Again, the carbyne and alkyne substituents have been exchanged.

B. Other Organic Products

Tertiary phosphines such as trimethylphosphine add to electrophilic carbyne carbons to give metallacarbenes, also called metal—ylide complexes (section II). In the presence of 1 equiv of phosphine, the reaction may go further to give anionic half-ylides (eq 127).[215,216]
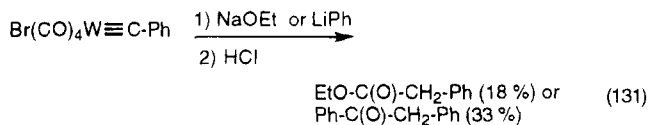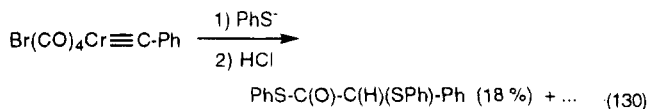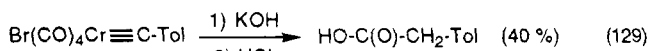

$$\text{(127)}$$

L$_n$M = (CO)$_5$Cr, R = NEt$_2$ (89 %);
L$_n$M = Cl(CO)$_4$Cr, R =Ph (53 %);
L$_n$M = Cp(CO)$_2$Mn, R =Ph (70 %), Tol (65 %), SiPh$_3$ (55 %)

In Fischer metallacarbynes of the type X(CO)$_4$-M≡C—R, the carbyne ligand can be separated from the metal to give free alkynes, corresponding to the coupling of two carbyne ligands. Simply heating the metallacarbyne may be sufficient to liberate the organic molecule (eq 128).[217] When the metallacar-
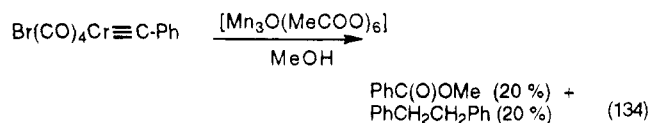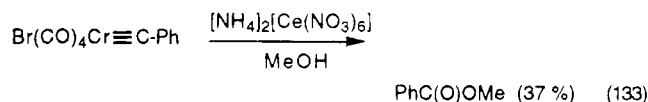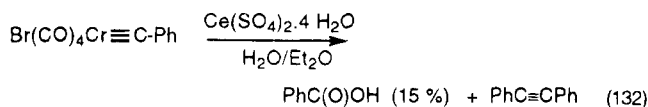
$$Br(CO)_4Cr≡C-R \xrightarrow{\text{heat}} R-C≡C-R + ... \quad \text{(128)}$$

$$R = Me \ (31 \ \%), Ph \ (44 \ \%)$$

bynes Br(CO)$_4$Cr≡C—Ph and Br(CO)$_4$Cr≡C—Tol are heated together, a mix of three different alkynes is obtained (total yield 37%).[217] Apparently, different carbyne ligands are as easily combined to form alkynes as is the case with identical carbyne ligands.
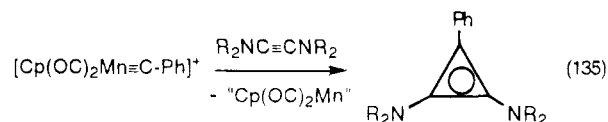
The successive action of an anionic nucleophile like OH⁻, OEt⁻ and Ph⁻ [218] or PhS⁻ [219] and hydrochloric acid upon the metallacarbynes X(CO)$_4$Cr≡C—R results in the liberation of the carbyne ligand in the form of an organic product. The reaction is believed to involve first an attack of the nucleophile on a carbonyl ligand, followed by a migration of the acyl fragment onto the carbyne carbon (eqs 129—131).
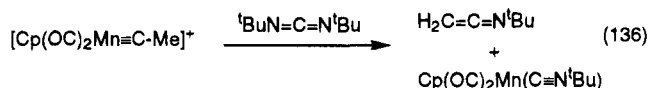
$$Br(CO)_4Cr≡C-Tol \xrightarrow[\text{2) HCl}]{\text{1) KOH}} HO-C(O)-CH_2-Tol \quad (40 \%) \quad \text{(129)}$$

$$Br(CO)_4Cr≡C-Ph \xrightarrow[\text{2) HCl}]{\text{1) PhS}^-}$$

$$PhS-C(O)-C(H)(SPh)-Ph \ (18 \%) + ... \quad \text{(130)}$$

$$Br(CO)_4W≡C-Ph \xrightarrow[\text{2) HCl}]{\text{1) NaOEt or LiPh}}$$

$$\begin{array}{l} EtO-C(O)-CH_2-Ph \ (18 \%) \text{ or} \\ Ph-C(O)-CH_2-Ph \ (33 \%) \end{array} \quad \text{(131)}$$

The oxidation of the metallacarbyne Br(CO)$_4$-Cr≡C—Ph by Ce(IV) or Mn(III) complexes affords the formation of the organic molecules Ph—C(O)OMe and Ph—CH$_2$—CH$_2$—Ph (eqs 132—134).[220]

$$Br(CO)_4Cr≡C-Ph \xrightarrow[\text{H}_2\text{O/Et}_2\text{O}]{\text{Ce(SO}_4\text{)}_2.4 \text{ H}_2\text{O}}$$

$$PhC(O)OH \ (15 \%) + PhC≡CPh \quad \text{(132)}$$

$$Br(CO)_4Cr≡C-Ph \xrightarrow[\text{MeOH}]{[\text{NH}_4]_2[\text{Ce(NO}_3\text{)}_6]}$$

$$PhC(O)OMe \ (37 \%) \quad \text{(133)}$$

$$Br(CO)_4Cr≡C-Ph \xrightarrow[\text{MeOH}]{[\text{Mn}_3\text{O(MeCOO)}_6]}$$

$$\begin{array}{l} PhC(O)OMe \ (20 \%) + \\ PhCH_2CH_2Ph \ (20 \%) \end{array} \quad \text{(134)}$$

The metallacarbyne [Cp(OC)$_2$Mn≡C—Ph]⁺ reacts with diaminoalkynes to give cyclopropenium compounds in moderate yields, thereby liberating the organic ring fragment (eq 135).[174,197]

$$\text{(135)}$$

A metathesis reaction between the metallacarbyne [Cp(OC)$_2$Mn≡C—Ph]⁺ and a carbodiimide leads to the incorporation of the carbyne carbon into a ketenimine (eq 136, 49%).[42,43]

$$[Cp(OC)_2Mn≡C-Me]^+ \xrightarrow{^tBuN=C=N^tBu} \begin{array}{c} H_2C=C=N^tBu \\ + \\ Cp(OC)_2Mn(C≡N^tBu) \end{array} \quad \text{(136)}$$

XIII. Conclusions

The previous sections demonstrate that metallacarbynes may be used to form a large variety of different products, mainly acyclic metal complexes. Unfortunately, many reactions have found limited application in synthesis so far, and only a few general reactions have been reported. The classification used in the present review allows for an evaluation of the application of metallacarbynes in synthesis. In order to recognize the relations between the nature of the metallacarbynes and their reactivity, the results have been classified by the type of metallacarbyne involved (Table 20).

The terms "electrophilic" and "nucleophilic" carbyne carbon are formal and they are exclusively used

Table 20. Overview of the Most Important Products Obtained from the C–C or C–X Coupling Reactions of a Certain Metallacarbyne (Type–Reactivity Relationships)

metallacarbyne	reagent used	product (section)
	Electrophilic carbyne carbon	
$[Cp(CO)_2Mn{\equiv}C{-}R]^+$	nucleophile	metallacarbene (II.A)
	imine, N-oxide	metallaazacycle (X.A)
$Cl(CO)_4Cr{\equiv}C{-}R$	nucleophile	metallacarbene (II.B)
	metal complex	alkyne complex (VII.B)
	diyne, enyne	carbocycle (XI.D)
	nucleophilic carbyne carbon	
$Cp(CO)_2W{\equiv}C{-}R$	nucleophile	ketenyl complex (V)
	Pd complex	μ-alkylidene (III)
	electrophile	metallacarbene (II)
	protons	acyl complex (VI.B)
		alkyne complex (VII.B)
	protons/alkynes	naphthols (XI.B)
$[C_2B_9H_{11}(CO)_2W{\equiv}C{-}R]^-$	protons	carbaborane complex (VIII)
$Cl(RNC)_4W{\equiv}C{-}R$	electrophile	ynamine and ynediamine complexes (VII.A)
$[{}^tBuO]_3W{\equiv}C{-}R$	alkynes	alkyne (XII)
		metallacyclobutadiene (X.B)
		cyclopentadienyl complexes (XI.A)

on the basis of the reactivity observed. For each type of metallacarbyne only one example has been given here, but generally, several other metallacarbynes will display the same reaction (see related sections).

Low-valent (or Fischer-type) metallacarbynes have been used most extensively in the synthesis of new C–C or C–X bonds from metallacarbynes. A very general reaction is the addition of a nucleophile to an electrophilic carbyne carbon, leading to the formation of metallacarbenes (section II). As long as the metallacarbynes are of the type $[Cp(CO)_2Mn{\equiv}C{-}R]^+$ or $Cl(CO)_4Cr{\equiv}C{-}R$, a variety of tertiary phosphines and anionic nucleophiles can be used. It provides an essential synthetic route to metallacarbenes that are not directly accessible.

This electrophilic character has also been exploited in the reaction with organic molecules containing a relatively nucleophilic nitrogen atom (imines, N-oxide, section X). Addition of these reagents to a cationic metallacarbyne affords metallaazacyclic complexes. This is rather recent chemistry, so the possible general potential of this reaction remains to be established.

In the cyclization reactions of diynes or enynes with metallacarbynes like $Cl(CO)_4Cr{\equiv}C{-}R$, these electronic considerations are not so evident (section XI). For the moment, the reaction seems to be limited to this type of metallacarbyne and to rather exotic unsaturated molecules. Finally, these metallacarbynes can be transformed into bimetallic alkyne complexes, although this reaction is not as general as is the case for metallacarbynes of the type $Cp(CO)_2W{\equiv}C{-}R$.

Metallacarbynes of the type $Cp(CO)_2W{\equiv}C{-}R$ seem to be the most versatile in coupling reactions reported so far. Their relatively nucleophilic carbyne carbon does not react directly with nucleophiles. Instead, the coupling between the carbyne carbon and a carbonyl ligand leads to the formation of ketenyl complexes (section V). This is a fairly general reaction, as has been demonstrated in a recent review.[19]

The most important success of these metallacarbynes, however, seems to stem from their ability to be protonated on the carbyne carbon. It activates the complex by forming reactive metallacarbene species

in situ, and a coupling reaction is observed between a carbyne carbon and a carbonyl ligand (acyl complexes, section VI). Alternatively, the protonation can lead to a series of bimetallic alkyne complexes (section VII).

The principle of protonating the carbyne carbon has also been applied in the reaction of anionic metallacarbynes of the type $[C_2B_9H_{11}(CO)_2W{\equiv}C{-}R]^-$ which contain a carbaborane ligand. Systematically, the protonation of these metallacarbynes leads to the hydroboration of the carbyne carbon, which becomes therefore attached to the carbaborane cage (section VIII). It is a rather peculiar reaction that is limited to this special type of metallacarbyne. Only two examples of a hydroboration of another type of metallacarbyne have been reported.

At first sight, metallacarbynes like $Cl(RNC)_4W{\equiv}C{-}R$ seem to be analogues of electrophilic metallacarbynes such as $Cl(CO)_4Cr{\equiv}C{-}R$, but they display an unparalleled chemistry, which is directly related to the presence of isocyanide ligands. Electrophiles like oxonium salts react with the electron-rich isocyanide nitrogen, and ynamine and ynediamine complexes are formed from the subsequent coupling between the carbyne carbon and the transformed isocyanide (section VII).

High-valent (or Schrock-type) metallacarbynes have found their major application in the catalytic metathesis of alkynes, which has been excluded from the present review. The deactivation products of this reaction, however, are interesting complexes, which may have further applications in synthesis. High-valent metallacarbynes all possess a nucleophilic carbyne carbon and a strongly electrophilic metal center. Their reaction with alkynes leads either to new alkynes (section XII), to metallacyclobutadiene complexes (section X), or to complexes with pentasubstituted cyclopentadienyl ligands (section XI).

XIV. Abbreviations

Ar	aryl
BBN	borabicyclononane
bms	benzyl methyl sulfide
bhq	benzo[h]quinoline
bpdma	N,N-dimethyl-2-phenylaniline

bpms	biphenyl methyl sulfide
ᵗBu	*tert*-butyl
bzpy	2-benzylpyridine
cod	cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
d	day
DIPP	2,6-diisopropylphenoxide
dmba	2-[(dimethylamino)methyl]phenyl
dme	1,2-dimethoxyethane
DMP	2,6-dimethylphenoxide
dmpe	(dimethylphosphino)ethane
dppe	(diphenylphosphino)ethane
dppm	(diphenylphosphino)methane
Et	ethyl
ex	excess
8equin	8-ethylquinoline
Fc	ferrocenyl
h	hour
HFIP	hexafluoroisopropoxide
Me	methyl
MeCN	acetonitrile
MeCp	methylcyclopentadienyl
Mes	mesityl
8mquin	8-methylquinoline
methdmba	4,5-dioxomethylene-2-[(dimethylamino)-methyl]phenyl
NR	not reported
OAc	acetate
pdea	1-phenyl-*N,N*-dimethylethylamine
Ph	phenyl
pic	γ-picoline
PPN	$N(PPh_3)_2^+$
Pr	propyl
Proton Sponge	1,8-bis(dimethylamino)naphthalene
py	pyridine
r.t.	room temperature
tmeda	tetramethylethylenediamine
Tol	*p*-tolyl
Tp	hydridotris(pyrazolyl)borate
Tp′	hydridotris(3,5-dimethylpyrazolyl)borate
Xyl	2,6-xylyl

XV. Acknowledgments

XVI. References

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