Chem. Rev. **2000,** *100,* 3591–3637 **3591**

Di- and Polymetallic Heteroatom Stabilized (Fischer) Metal Carbene Complexes

Miguel A. Sierra*

Departamento de Química Orgánica I, Facultad de Química, Universidad Complutense, 28040-Madrid, Spain

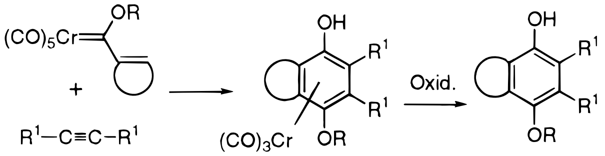
Received March 9, 2000

Contents

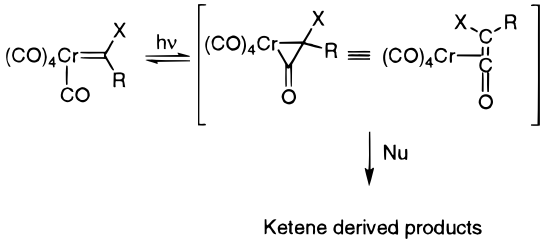
I. Introduction

The preparation by Fischer and Maasböl of complex **1**, the first fully characterized heteroatom stabilized metal carbene complex,[1] was the starting point for the rapid development of the synthesis of these types of organometallic compounds. Their applications in organic synthesis were early recognized, and the last 30 years have been witness of their evolution, from the first exploratory carbene transfer reaction to olefins[2] to the wide array of synthetically useful methodology based on these compounds that is known today. Reactions such as Dötz benzanulation (eq 1)[3] or Hegedus metal carbene based photochemistry (eq 2)[4] are now standard tools in synthetic organic chemistry. As a consequence, the different aspects of the chemistry of Fischer carbenes and their

Miguel A. Sierra studied chemistry at the Universidad Complutense de Madrid (UCM) and received his doctorate (honors) in 1987. He was appointed Profesor Ayudante at UCM in 1987, and after a postdoctoral stay (1988–1989) at the Colorado State University with Prof. Louis S. Hegedus, he returned to Madrid where he was promoted to Profesor Titular in 1990. His research encompasses the development of new processes based on catalytic and stoichometric reactions of transition metal complexes, especially those derived from homo- and hetero-dimetallic systems and their use in organic synthesis as well as the design and synthesis of new chelating agents for supplying trace elements to plants and soil and water decontamination.



(1)



(2)

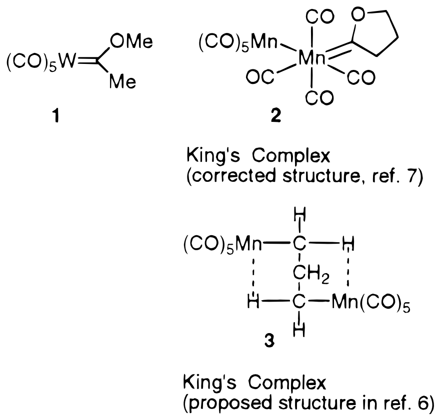
---

* E-mail address: sierraor@eucmax.sim.ucm.es.

10.1021/cr9804137 CCC: $35.00

synthetic applications have been thoroughly and repeatedly reviewed.[5]

Strictly speaking, the first dimetallic heteroatom stabilized carbene complex **2** was synthesized by King in 1963, 1 year before Fischer reported the synthesis of complex **1**.[6] The structure **3** initially assigned to this compound was further corrected by Casey (Figure 1).[7] The history of homo- and hetero-di- and polymetallic Fischer carbenes parallels that of monometallic carbene complexes, and many of these compounds have been synthesized during the last 30 years. Nevertheless, the applications of these complexes in synthesis fall well behind their mononuclear cousins. In fact, the first examples of the use of di- and polymetallic carbenes in organic synthesis have been reported only during the last 10 years. These efforts may be fostered by the growing interest in the development of di- and polymetallic reagents and catalysts for organic synthesis. The awareness that two or more metals can cooperate in catalytic transformations more efficiently than if they were isolated as well as the ability to promote new processes unknown for the metals alone have drawn an enormous interest in these compounds.[8] The present review will survey the synthesis of di- and polymetallic metal carbenes having a heteroatom bonded to the carbene carbon (Fischer carbenes) and their application to organic synthesis.



1

2

King's Complex
(corrected structure, ref. 7)

3

King's Complex
(proposed structure in ref. 6)

Figure 1.

There are, in principle, three possibilities to join new metal centers on a metal carbene double bond (Figure 2). The first mode is on the carbene carbon, either directly joined to it (A) or through a carbon chain (B); the second is through the heteroatom attached to the carbene carbon (C and D); and the third is directly to the metal center, either by a metal–metal bond (E) or by using a bidentate ligand joining both metal centers (F). There are also a few examples of complexes that may be included in more than one group.

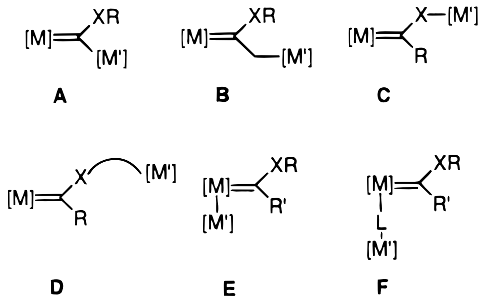


Figure 2.

II. Class I Di- and Polymetallic Metal Carbene Complexes

Class I polymetallic metal carbenes (except when otherwise stated, to avoid repetitive long names, the term metal carbene complex or carbene complex will refer to heteroatom stabilized metal carbene complexes) have the metal centers joined through C–C bonds on the carbene carbon (structures A and B in Figure 2), and they represent the larger class of these compounds. Their synthesis is made by one of the following methods, which are mainly based on the standard synthetic procedures developed for the preparation of mononuclear carbenes:

(i) From metal complexes lacking a preformed carbene ligand

(ii) By the alkylation or acylation of a carbanion generated α to the carbene carbon of a mononuclear metal carbene complex

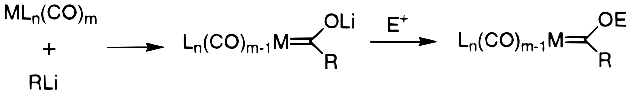
(iii) By attaching the additional metal center on the double or triple bond of metal carbene complexes having unsaturated substituents

(iv) From allenyl complexes

(v) By addition of a metal nucleophile to a carbyne complex

A. Synthesis of Di- and Polymetallic Metal Carbenes by Building the Carbene Ligand

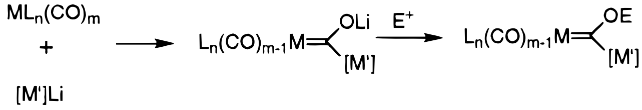
This approach to di- and polymetallic metal carbenes follows the original method reported by Fischer, namely, the addition of a nucleophile reagent (usually an organolithium) to a metal carbonyl (eq 3).



(3)

$ML_n(CO)_m$ = $Cr(CO)_6$; $Mo(CO)_6$; $W(CO)_6$; $Fe(CO)_5$; $Cp(CO)_3Mn$; $Cp(CO)_2RuAr$;$Cp(CO)_2(NO)Mo$;$Tp'Mo(CO)_2(NO)$ ....
R = Alkyl, cycloalkyl, aryl, vinyl, ethynyl....

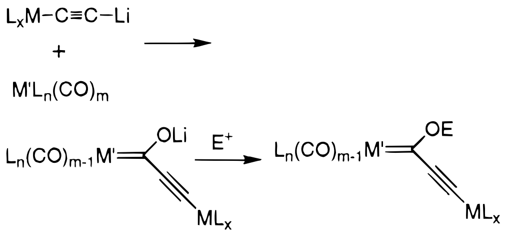
This first addition reaction forms an ate complex that is subsequently alkylated. Evidently, the use of an organolithium reagent having an additional metal center would give, at the end of the process, a dimetallic carbene complex (eqs 4 and 5).



(4)

$ML_n(CO)_m$ = $Cr(CO)_6$; $Mo(CO)_6$; $W(CO)_6$; $Fe(CO)_5$; $(C_5H_4Me)Mn(CO)_3$; $(C_4H_4N)Mn(CO)_3$; $Re(CO)_5Cl$
[M'] = Cp_2Fe; Cp_2Ru; $(C_6H_5)Cr(CO)_3$; $(C_4H_3S)Cr(CO)_3$; $(C_8H_5S)Cr(CO)_3$;$CpMn(CO)_3$; $Cp(CO)_2Fe(Me)$; $RC_2B_{10}H_{10}$

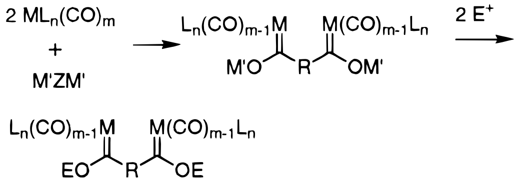
On the other hand, the reaction of a dilithium reagent



(5)

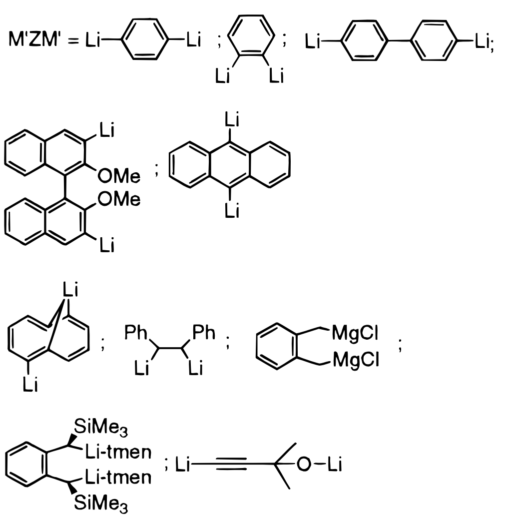
$L_xM = Cp^*Re(NO)PPh_3$; $Cp^*(NO)PPh_3ReCC-$
$M'L_n(CO)_m = W(CO)_6$; $Fe(CO)_5$; $(\eta^5-C_5H_{5-n}Cl_n)Mn(CO)_3$; $Re_2(CO)_{10}$; $Os_3(CO)_{12}$

with two equivalents of metal carbonyl would form a bis-carbene, once the dilithium salt obtained in the first term is alkylated (eq 6).

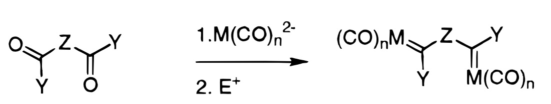


(6)

$ML_n(CO)_m = Cr(CO)_6$; $Mo(CO)_6$; $W(CO)_6$

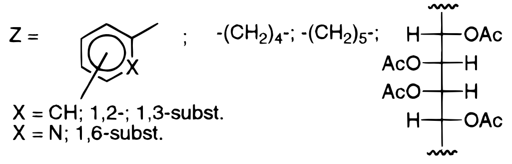


Alternatively, dianions of group 6−8 metal carbonyls may be reacted with diamides or diacid−dichlorides to yield dimetallic bis-carbene complexes (eq 7).



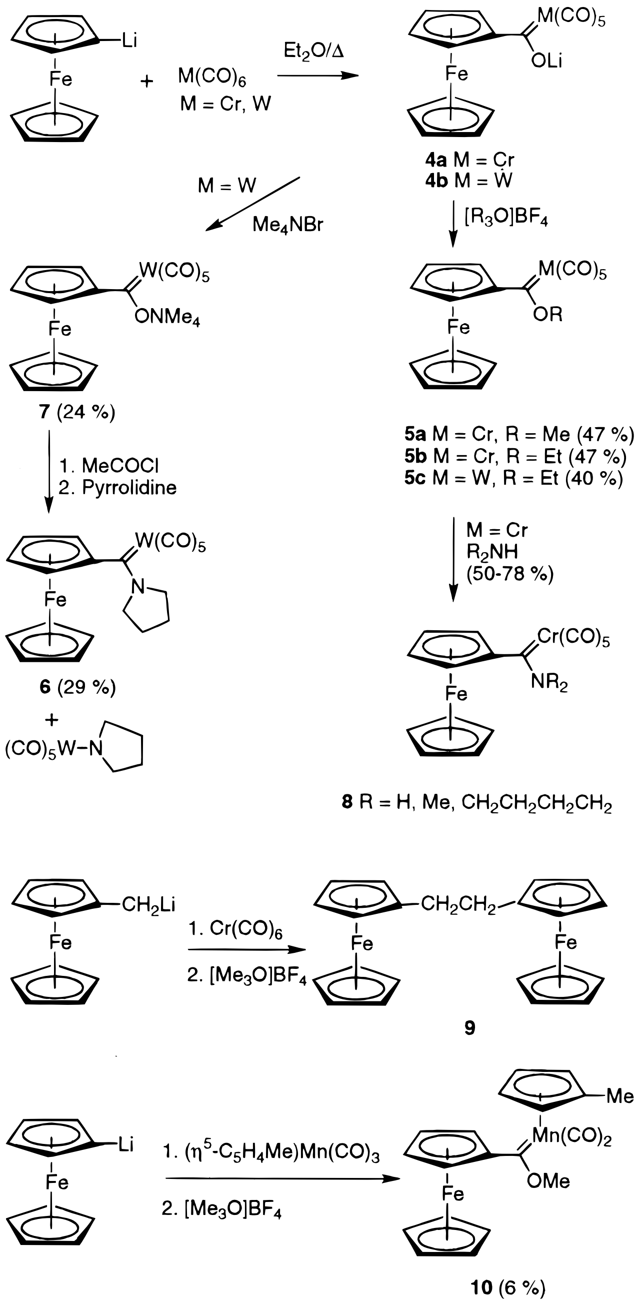
(7)

M = Cr, Fe; Y = Cl, Me_2N



The first example[9] of the synthesis of heterodimetallic carbene complexes following the route depicted in eq 4 was the addition of ferrocenyl lithium (FcLi) to [$M(CO)_6$] (M = Cr, W) to yield the ate complexes **4a,b** that were alkylated with [Me_3O]BF_4 or [Et_3O]BF_4 to yield complexes **5a**−**c**. Alternatively, the lithium salt **4b** was transformed into the amino derivative **6** via its tetramethylammonium salt **7** by sequential reaction with acetyl chloride and pyrrolidine. Chromium aminocarbene complexes **8** were obtained by standard alkoxy−amine interchange. Attempts to prepare the analogous pentacarbonyl[(ferrocenylmethyl)(methoxy)carbene]chromium(0) from $FcCH_2Li$ and $Cr(CO)_6$ followed by alkylation were fruitless. Dimer **9** was the sole reaction product (Scheme 1). Analogously, attempts to prepare the complexes [$(\eta^5$-$C_5H_5)Co(CO)C(Fc)OR$] and [$(\eta^5$-$C_5H_5)$-$V(CO)_3C(Fc)OR$] from the reaction of FcLi with [$(\eta^5$-$C_5H_5)Co(CO)_2$] and [$(\eta^5$-$C_5H_5)V(CO)_4$], respectively, were also unsuccessful. In each case, ferrocene was recovered together with unreacted starting material.

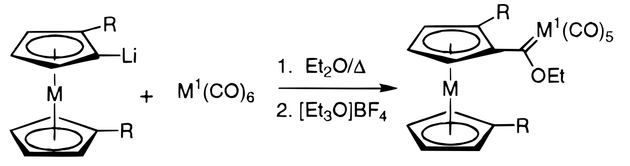
Scheme 1



However, [(η^5-C_5H_4Me)Mn(CO)$_3$] reacted with FcLi followed by alkylation to yield [(η^5-C_5H_4Me)Mn(CO)$_2$C(Fc)OMe], **10**.

Lithiated ruthenocene, [(η^5-C_5H_5)$_2$Ru], and 1,1′-dimethylferrocene, [(η^5-C_5H_4Me)$_2$Fe], were also converted to heterodimetallic complexes **11** by the standard addition to [M(CO)$_6$] (M = Cr, Mo, W) followed by alkylation with Et_3OBF_4 (Scheme 2).[10]

Scheme 2

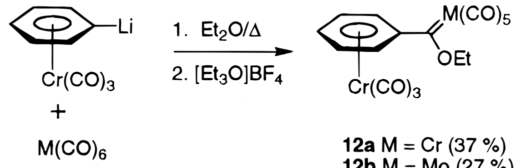


R = H, M = Ru
R = Me, M = Fe
M^1 = Cr, Mo, W

11a M = Ru, M^1 = Cr (14 %)
11b M = Ru, M^1 = W (17 %)
11c M = Fe, M^1 = Cr (32 %)
11d M = Fe, M^1 = Mo (27 %)
11e M = Fe, M^1 = W (30 %)

η^6-Arene and heteroarene complexes have been converted to homo- and heterodimetallic complexes following the standard Fischer procedure (Scheme 3). Thus, [(η^6-C_6H_6)Cr(CO)$_3$] was lithiated and reacted with [M(CO)$_6$] (M = Cr, Mo, W) to yield the corresponding dimetallic derivatives **12** (Scheme 3).[11]

Scheme 3

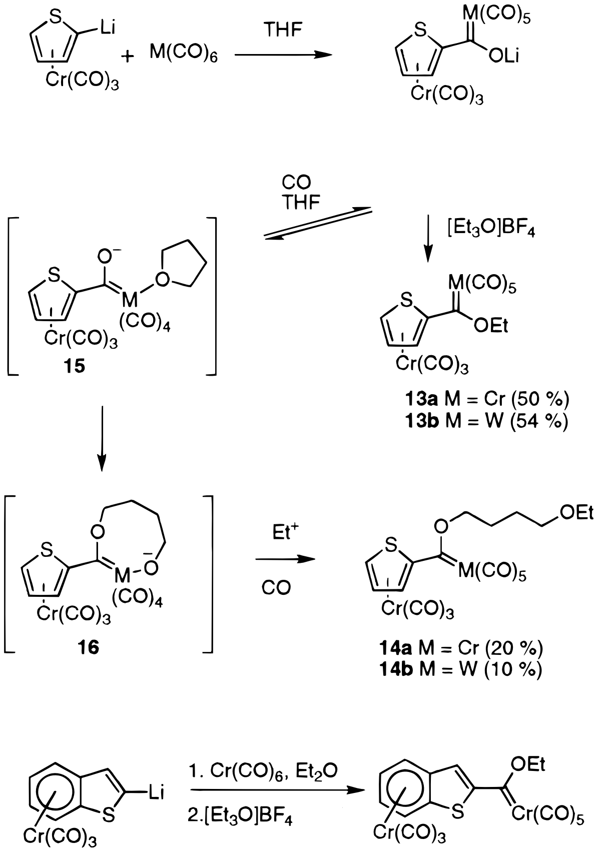


M = Cr, Mo, W

12a M = Cr (37 %)
12b M = Mo (27 %)
12c M = W (39 %)

The analogous reaction of lithium [(η^6-C_4H_4S)Cr(CO)$_3$] with [M(CO)$_6$] (M = Cr, W) followed by methylation with [Et_3O]BF_4 produced a mixture of the expected dimetallic carbene complexes **13** and new carbene complexes **14**.[12] Formation of complexes **14a,b** represents the cleavage and inclusion of THF into the ethoxy substituent of the dimetallic carbene complex. This unexpected reaction is proposed to occur by coordination of the solvent to the initially formed acylmetalate, followed by nucleophilic attack of the acylate oxygen to the carbon α to the oxygen on the coordinated THF on **15** to produce the new intermediate **16**. Finally, ethylation of the intermediate **16** would lead to the observed product **14** (Scheme 4). However, products such as **14a,b** were not formed during the reaction of lithium [η^6-benzo[*b*]thiophene-Cr(CO)$_3$] and [Cr(CO)]$_6$ to yield complex **17**.

Scheme 4

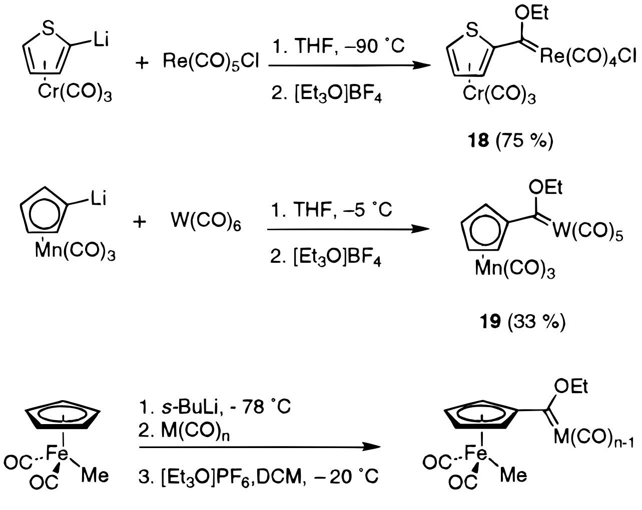


13a M = Cr (50 %)
13b M = W (54 %)

14a M = Cr (20 %)
14b M = W (10 %)

17 (95 %)

Scheme 5



18 (75 %)

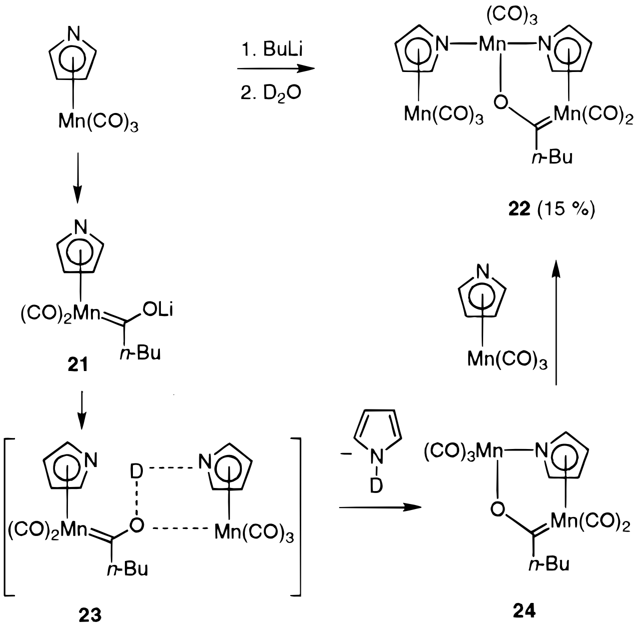
19 (33 %)

20a M = Cr, n = 6 (38 %)
20b M = Mo, n = 6 (35 %)
20c M = W, n = 6 (25 %)
20d M = Fe, n = 5 (23 %)

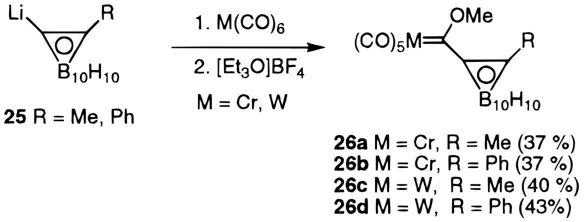
The reaction of lithium [(η^6-C_4H_4S)Cr(CO)$_3$] with [Re(CO)$_5$Cl] followed by ethylation yielded the dimetallic Re carbene **18** as the sole product.[13] Complex **18** is stable in air for short periods of time, but it losses the Cr(CO)$_3$ fragment in polar solvents. The related reaction of the lithium derivative of [(η^5-C_5H_5)Mn(CO)$_3$] and [W(CO)$_6$] followed by alkylation to give complex **19** has been also reported (Scheme 5).[14] Analogously, [CpFe(CO)$_2$Me] is lithiated by *sec*-BuLi and reacts with different group 6 and group 8 metal carbonyls to yield the dimetallic complexes **20a–d**.[15]

A more bizarre transformation occurred when η^5-pyrrolyltricarbonylmanganese is reacted with *n*-BuLi. After the initial formation of the ate complex **21**, quenching with D_2O formed trinuclear carbene complex **22**. The proposed mechanism for the forma-

Scheme 6



Scheme 7



tion of compound **22** involves the elimination of deuteriopyrrole from deuterated **23** by action of a new molecule of η^5-pyrrolyltricarbonylmanganese, followed by reaction of intermediate **24** with, again, a new molecule of η^5-pyrrolyltricarbonylmanganese (Scheme 6).[16]

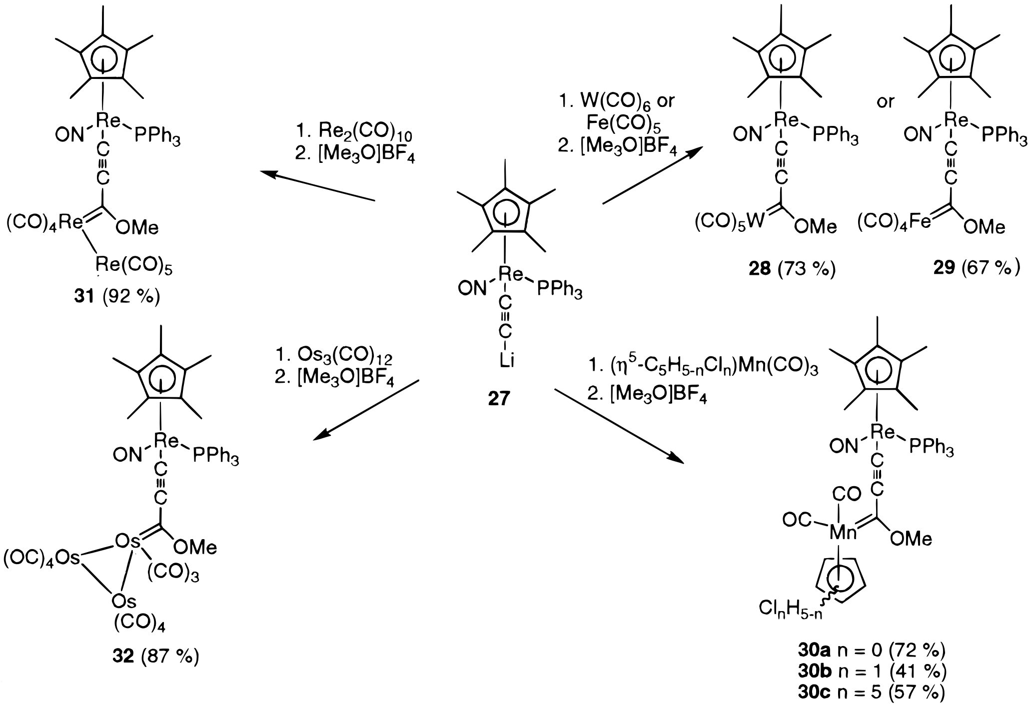
Lithium-*o*-carboranes **25** have been reacted with $[M(CO)_6]$ (M = Cr, W) followed by alkylation to yield a new class of dimetallic Fischer carbenes having an *o*-carboranyl substituent in their structures, namely, the [(*o*-carboranyl)methoxycarbene]metal complexes **26a**−**d** (Scheme 7). [17]

The preparation of heterodimetallic carbenes by addition of a lithium acetylide bearing a metal nucleus has been widely used to prepare heterodimetallic mono-carbene complexes in connection with the search for lineal forms of carbon, a chemistry that has been reviewed.[18] The general approach to this kind of complexes is represented in eq 5. Thus, the Re/Li−C$_2$ complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)-(CC)Li]$, **27**, prepared from $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)-(CCH)]$ was reacted with carbonyl complexes $[W(CO)_6]$, $[Fe(CO)_5]$, and $[(\eta^5\text{-}C_5H_{5-n}Cl_n)Mn(CO)_3]$ ($n = 0, 1, 5$), and the lithium ate complexes formed were alkylated with $[Me_3O]BF_4$ to yield complexes **28**−**30**.[19,24] The analogous reaction of acetylide anion **27** with $[Re_2(CO)_{10}]$ formed the trinuclear carbene complex **31**,[20] while tetranuclear complex **32** was obtained from **27** when $[Os_3(CO)_{12}]$ was used (Scheme 8).[21,22]

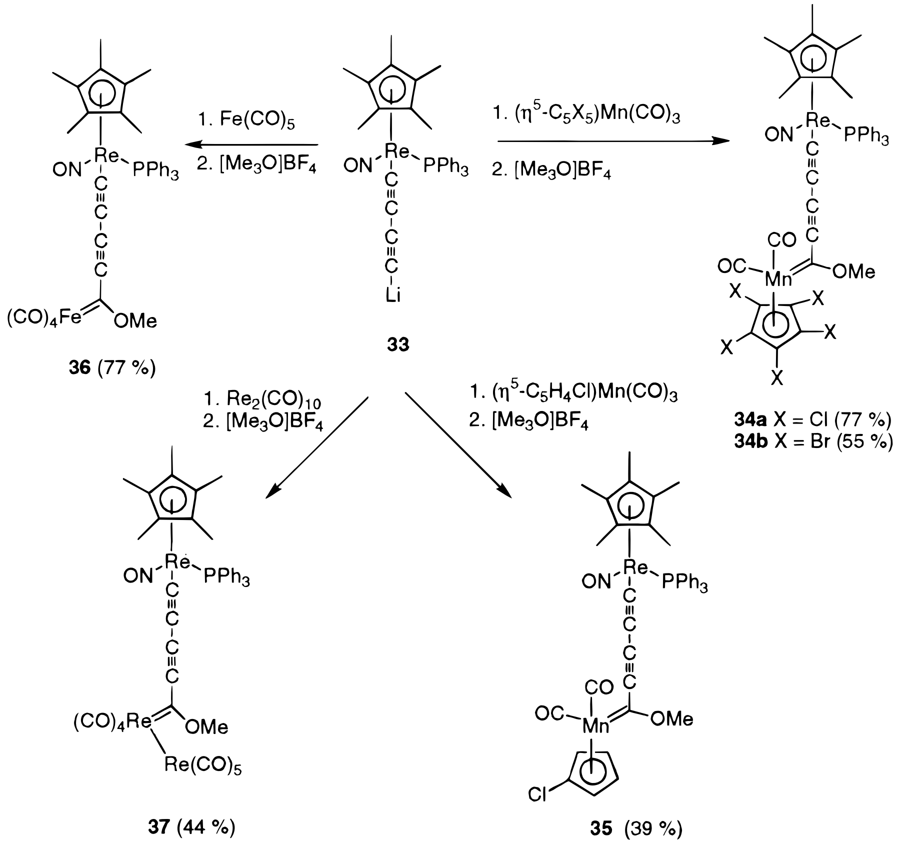
The homologous diethynyllithium derivative **33** prepared from $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CC-CCH)]$ was analogously reacted with $[(\eta^5\text{-}C_5X_5)Mn(CO)_3]$ (X = Cl, Br) and $[(\eta^5\text{-}C_5H_4Cl)Mn(CO)_3]$ to form, respectively, complexes **34** and **35**.[23,24] Iron derivative **36** was prepared in the same manner. Trinuclear complex **37** was obtained from the reaction of **33** and $[Re_2(CO)_{10}]$ (Scheme 9). [21]

A different approach to dimetallic carbenes is the addition of a dilithium derivative to two equivalents of a metal carbonyl (eq 6). The alkylation of the obtained dilithium bis-acylate would yield the desired dimetallic bis-carbene. This approach leads by its

Scheme 8



Scheme 9



own nature to homodimetallic bis-carbenes. No examples of the sequential preparation of a heterodimetallic bis-carbene complex by this method have been reported to date. Aromatic dilithium reagents have been the most extensively used dinucleophile reagents. Thus, the reaction of *p*-phenylenedilithium with [M(CO)$_6$] (M = Cr, W) followed by alkylation with Et$_3$OBF$_4$ yields bis-carbene complexes **38a,b**, together with the corresponding mononuclear carbene complexes **39a,b**, the latter arising from the reaction of PhLi with bromobenzene to form biphenyllithium. This lithium reagent generated in situ reacts, successively, with [M(CO)$_6$] and the alkylating agent to yield the observed compound **39b** (Scheme 10).[25] In contrast, the analogous reaction with *o*-phenylenedilithium led to monuclear 1,4-chelated bis-carbene complexes **40a**−**c**.[25] *p*-Biphenylenedilithium reacts with [M(CO)$_6$] (M = Cr, W) to form the dimetallic bis-carbene complexes **41a,b**,[26] while the analogous reaction with *o*-biphenylenedilithium does not lead to the desired bis-carbene complexes but to the corresponding monocarbene complexes. Treatment of complexes **41a,b** with ammonia yielded the expected amino bis-carbenes **42**. Binaphthyl bis-carbene **43** was prepared by the reaction of dilithium derivative of racemic 1,1′-dimethoxybinaphthyl with [Cr(CO)$_6$] followed by alkylation. A mixture of bis-carbene **43** and monocarbene **44** resulted from this reaction. Axial chiral (*R*)- and (*S*)-**43** were prepared starting from enantiomerically pure naphthyl derivatives.[27]

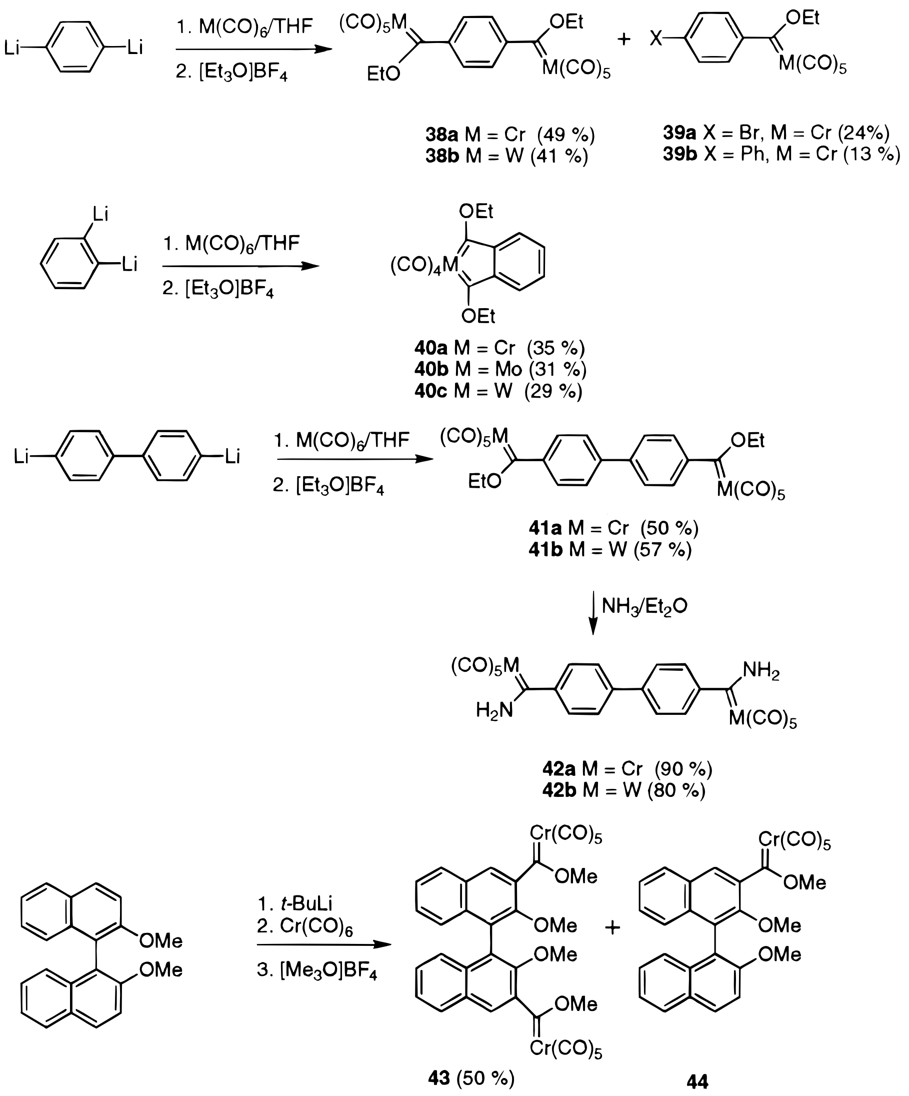
Complex **43** showed broad signals corresponding to the MeO groups in its ^{1}H NMR spectrum. This fact may be explained in terms of hindered rotation of the carbene MeO groups, which evidently influences the aromatic MeO substituents. Variable temperature NMR studies suggested that there is a cooperative mobility of the MeO groups, namely, the orientation of the carbene MeO group controls the conformation of the aromatic MeO group, as consequence of the *E*−*Z* configuration of the C$_{\text{carbene}}$−O bonds. Additionally, the dihedral angle θ between the two naphthyl rings [C(2)−C(1)−C(1′)−C(2′)] decreases from 110° (free 2,2′-dimethoxybiphenyl) to 75°. These results reflect the balance of steric interaction between the bulky M(CO)$_5$ moieties on one side and both naphthyl systems on the other side. However, the C(1)−C(1′) bond is only slightly longer (1.507 (6) Å) than the free binaphthyl (1.488 (7) Å).

Other examples of the formation of bis-carbenes from aromatic dilithium derivatives are the preparation of tungsten bis-carbene complex **45** from 9,10-dilithium anthracene[28] and complex **46** from 1,6-dilithiomethano[10]annulene (Scheme 11).[29] The analogous reaction of 2,10-dilithiomethano[10]annulene gave only monocarbene **47**. Neither bis-carbene **48** nor chelated mononuclear bis-carbene **49** were obtained.

Aliphatic dilithium derivatives have been sparingly used in the preparation of bis-carbene complexes. Thus, 1,2-diphenyl-1,2-dilithioethane was reacted with [M(CO)$_6$] (M = Cr, W) to give low yields of the corresponding bis-carbene complexes **50a,b** together with mononuclear bis-carbenes **51a,b** as the major products (Scheme 12).[25]

The analogous reaction of di-Grignard reagent **52** with [M(CO)$_6$] (M = Cr, Mo, W) gave the stable magnesium ate bis-carbene complexes **53a**−**c**. Com-

Scheme 10



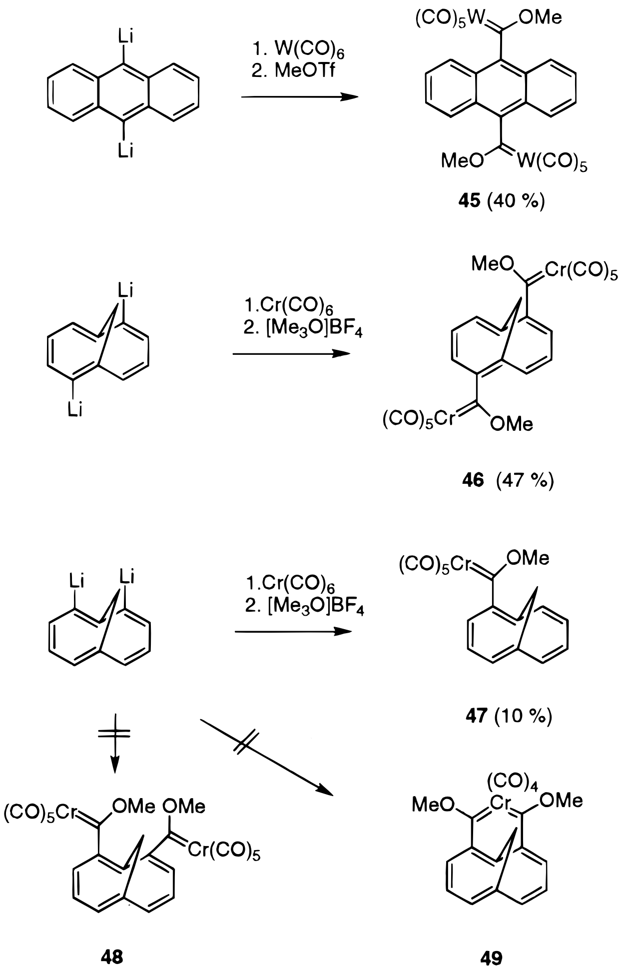
plexes **53a** and **53c** were methylated to yield complexes **54a,b** while compound **53b** decomposed to a mixture of unknown compounds. It is noteworthy that bis-carbenes **53a**–**c** having an OMg bond are thermally stable, but they did not undergo further transformation to yield a chelating bis-carbene, as might have been expected by analogy with the reaction with $Li_2(o\text{-}C_6H_4)$ (see above). Dilithium reagent **55** gave complexes **56a,b** by reaction with $[M(CO)_6]$ (M = Cr, W).[30] Ligand interchange by Et_3P on **54a** gave the new dimetallic bis-carbene complex **57** (Scheme 13).

Carbon–oxygen dianion **58** reacted with $Cr(CO)_6$ in the usual way to yield the ate complex **59**. This compound upon treatment with acetyl chloride formed dimetallic complex **60**. The reaction is thought to occur through the intermediate **61**, formed by acylation of the oxygen bonded to the carbene carbon. The intramolecular 1,4-addition of the alkoxide to the alkyne triple bond on intermediate **61** would lead to **62**, which by reaction with a new molecule of acylate **59** would form a new dimetallic complex **63**. Complex **63** would yield **60** by a cascade cyclization promoted by the intramolecular attack of the oxygen alkoxide to the extreme of the ylidene carbon (Scheme 14).[31]

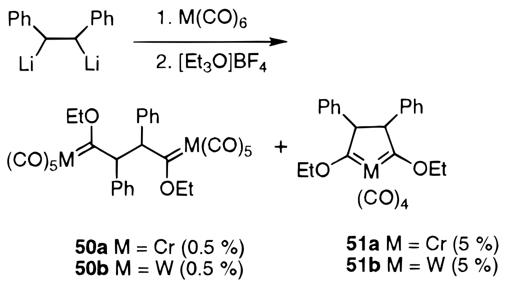
An alternative and efficient approach to the Fischer synthesis of metal carbenes is the reaction of $M(CO)_n^{2-}$ with tertiary amides in the presence of TMSCl.[32] The use of a diamide would lead evidently to a homodimetallic bis-carbene complex. Thus, a series of Cr and Fe dimetallic bis-carbene complexes **64** were prepared by reacting bis-amides **65** with $[M(CO)_n]^{2-}$ (M = Fe, Cr; n = 4, 5), followed by quenching with TMSCl.[33] These reactions produced also monocarbene **66**, the main reaction product when M = Fe. Heterodimetallic bis-carbene complex **67** was prepared sequentially from amide **68** through monocarbene **69**. This approach was also used to prepare bis-carbenes **70a,b** having the metallic nuclei joined by an aliphatic chain. Aliphatic diamides **71** were the starting materials in these cases. Diamides derived from oxalic and malonic acids failed to give any isolable carbene product. This failure may be due in the latter case to deprotonation of the acid diamide protons by the strongly basic $[Cr(CO)_5]^{2-}$ (Scheme 15).

Carbohydrate-bridged bis-carbene complexes **72a,b** were prepared from the corresponding anionic carbonylmetalates and aldaric acid dichlorides, following the method reported by Semmelhack.[34] Thus, 2,3,4,5-tetra-*O*-acetyl-D-galactaryl dichloride, **73**, was re-

Scheme 11



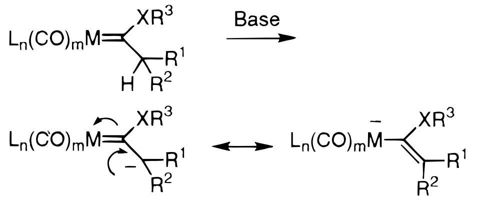
Scheme 12



acted with $K_2M(CO)_5$ (M = Cr, W) to yield after alkylation Cr and W bis-carbenes **72a,b** (Scheme 16).[35]

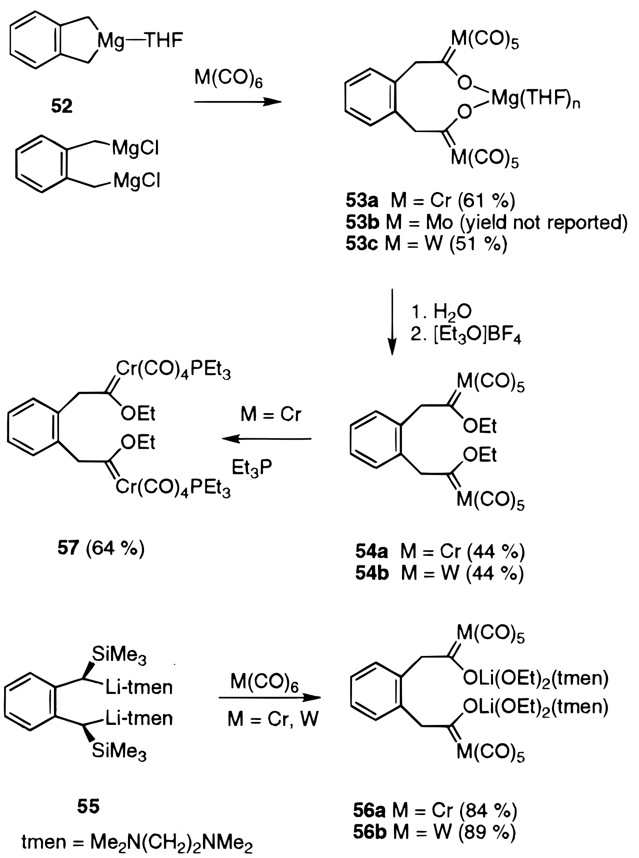
B. Di- and Polymetallic Metal Carbene Complexes from Carbanions α to a Preformed Carbene Ligand

Hydrogens bonded to the carbon α to the carbene ligand in metal carbene complexes are acidic (eq 8).[36]



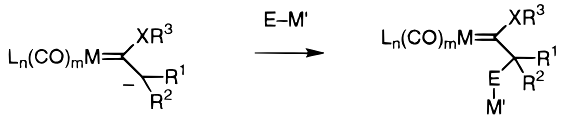
(8)

Scheme 13



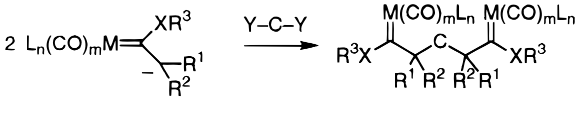
The resulting carbanions can react with different electrophiles to produce new carbene complexes. There are, in principle, three possibilities to prepare di- or polymetallic metal carbene by using these carbanions:

(i) Capture with an electrophile having a metal nucleus (eq 9).



$L_n(CO)_mM = (CO)_5Cr, (CO)_5W; (C_5H_4Me)(CO)_2Mn$ (9)
X = O, N
E-M' = $[(C_2H_4)Re(CO)_5]^+$; $[(C_7H_7)Cr(CO)_3]^+$; $[(C_7H_7)Mo(CO)_3]^+$; $[(C_2H_4)FeCp(CO)_2]^+$; $[(C_6H_7)Fe(CO)_3]^+$; $[C_7H_9Fe(CO)_3]^+$; $[(C_7H_7)Fe_2(CO)_6]^+$; $[(C_6H_6)Mn(CO)_3]^+$; $[(C_6H_5Me_2)Fe(CO)_3]^+$; $C_5H_5Fe(C_5H_4$-Y-CHO)

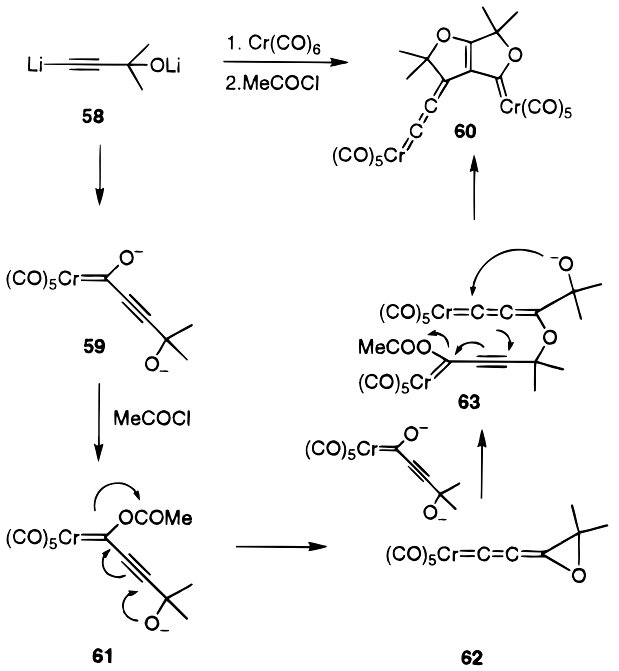
(ii) Capture with a carbon bidentate electrophile. This reaction will lead to an homodimetallic bis-carbene complex (eq 10).



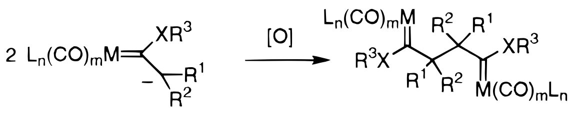
(10)

$L_n(CO)_mM = (CO)_5Cr, (CO)_5W; (C_5H_4Me)(CO)_2Mn$
X = O, N
Y-C-Y = m-$C_6H_4(CHO)_2$; p-$C_6H_4(CHO)_2$; $OHCC_6H_4FeC_6H_4CHO$; I-$(CH_2)_n$-I; ClCOCH=CHCOCl; Cl_4C_3

Scheme 14



(iii) Oxidative dimerization of the carbanion. This process would form a symmetric homodimetallic bis-carbene complex (eq 11).

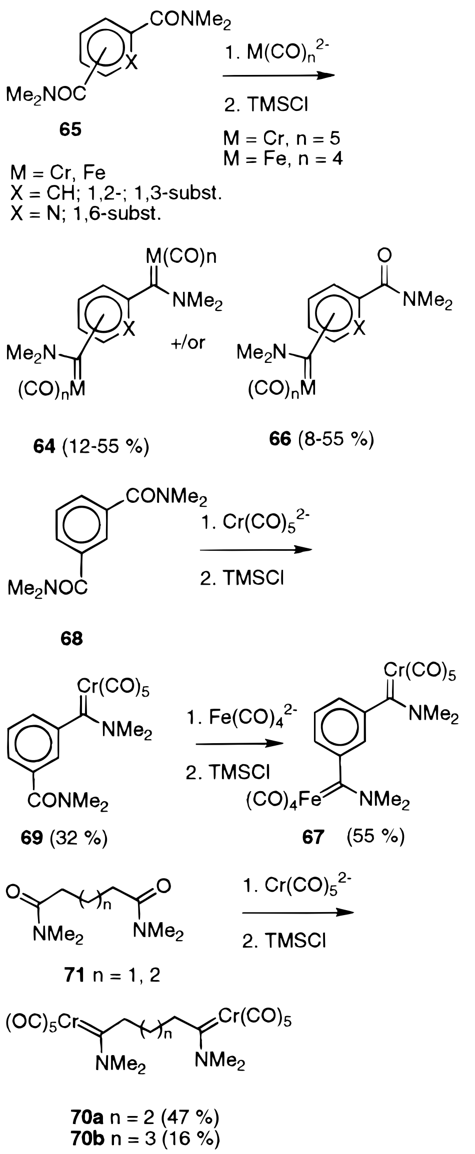
 (11)

$L_n(CO)_mM$ = $(CO)_5Cr$, $Cp^*(CO)PR^4{}_3Fe$; $(C_5H_4Me)(CO)_2Mn$;
XR^3 = OMe; OEt; -NPh

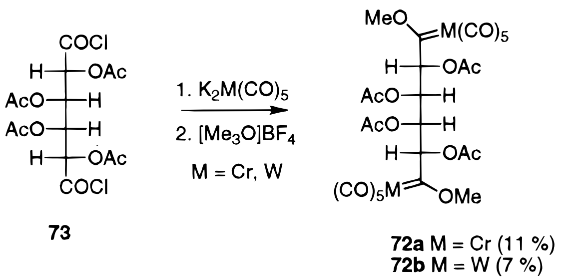
The first example of the synthesis of a homodimetallic bis-carbene **74** following the approach represented in eq 9 was the reaction between the anion derived from cyclic carbene **75** and formaldehyde. This reaction failed to produce the desired exo-methylene carbene complex **76**, and the only isolated product was the bis-carbene **74**. This complex arises from Michael addition of the carbene anion of **75** to the initially formed exo-methylene carbene complex **76**. The analogous reaction of the carbene anion derived from **75** and the formaldehyde equivalent $ClCH_2OMe$ gave also bis-carbene **74** in good yields together with dialkylated complex **77** (Scheme 17).[37]

A general procedure for the synthesis of (μ-bis-carbene)ditungsten complexes **78** was developed by the Michael addition of anions **79** to α,β-unsaturated carbenes **80**, followed by the capture of the lithium enolates **81** by different electrophiles (Scheme 18).[38,39] The process outlined in Scheme 18 is quite general for both the anion and the Michael acceptor. Polymerization was observed when the anion derived from the parent complex was used. It was also observed that, as the number of substituents on the α-lithio carbanion increased, their reactivity toward a given α,β-unsaturated carbene decreased. Organometallic Michael acceptors **80** behave similarly to standard organic Michael acceptors. Substitution at the terminal carbon decreases its reactivity, and only complexes having an *E* configuration are reactive. The reagents used to quench the carbanions **81** formed after the Michael addition, were triflates, benzyl and allyl bromides, and trimethylsilyl chloride. Monoalkylated products **78** were consistently obtained together with variable amounts of carbenes **82** arising from the protonation of the carbanion **81**. Methyl triflate showed a increased tendency to form dialkylated products. These reactions were also moderately diastereoselective.

Scheme 15

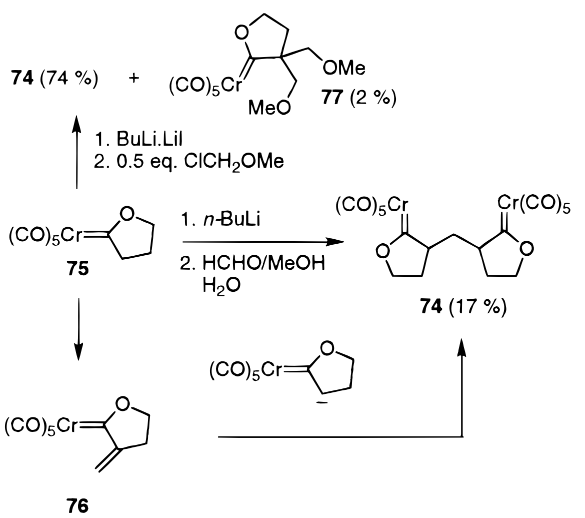


Scheme 16

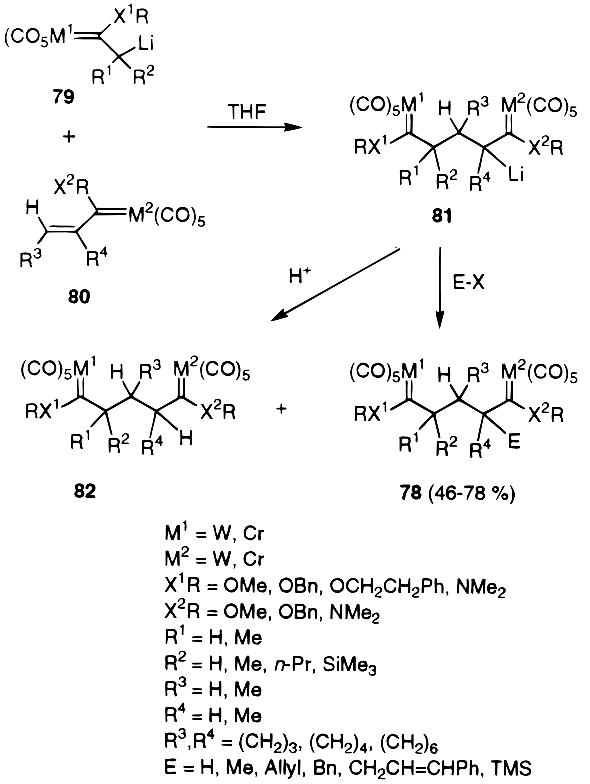


Capture of anions by cationic metal complexes produced the corresponding dimetallic monocarbene

Scheme 17

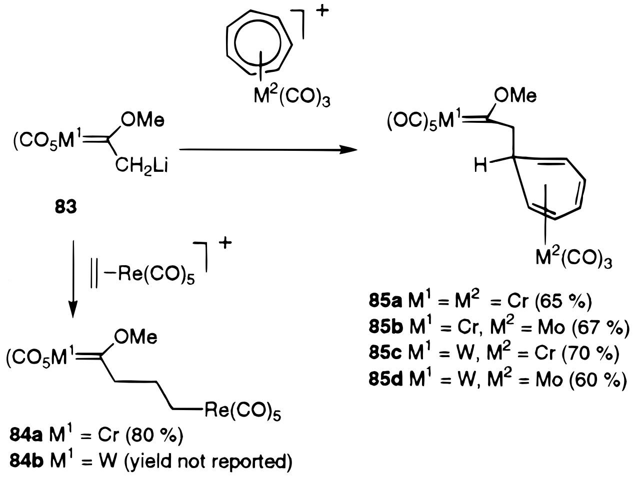


Scheme 18



complexes. Thus, the addition of anion **83** to the cationic complexes $[(CO)_5Re(C_2H_4)]^+$ and $[(CO)_3M(\eta^7\text{-}C_7H_7)]^+$ (M = Cr, Mo) affords the dimetallic hydrocarbon-bridged complexes **84** and **85**, respectively (Scheme 19).[40]

Scheme 19



The addition of carbanion **86** to $[(\eta^2\text{-ethenyl})Fe(CO)_2Cp]^+$ **87** and $[\eta^5\text{-cyclohexadienyl})(CO)_3Fe]^+$ has been reported to yield the expected complexes **88** and **89**, respectively. The reaction of **86** with $[(\eta^5\text{-cyclohexadienyl})(CO)_3Fe]^+$ lead also to the trimetallic complex **90**.[41] The last compound can be also obtained by reaction of the lithium anion derived from **89** with a new equivalent of $[(\eta^5\text{-cyclohexadienyl})(CO)_3Fe]^+$. A diastereomeric mixture of complexe **90** was obtained in this way. Similarly, treatment of complex **1** with Et_3N and coordinated olefins **91** yielded the corresponding dimetallic carbenes **92**. Dialkylation occurs in complexes **92a**–**c** by treatment with Et_3N and a new mole of the coordinated olefins **91** to form compounds **93a,b** as diastereomeric mixtures (Scheme 20).[42]

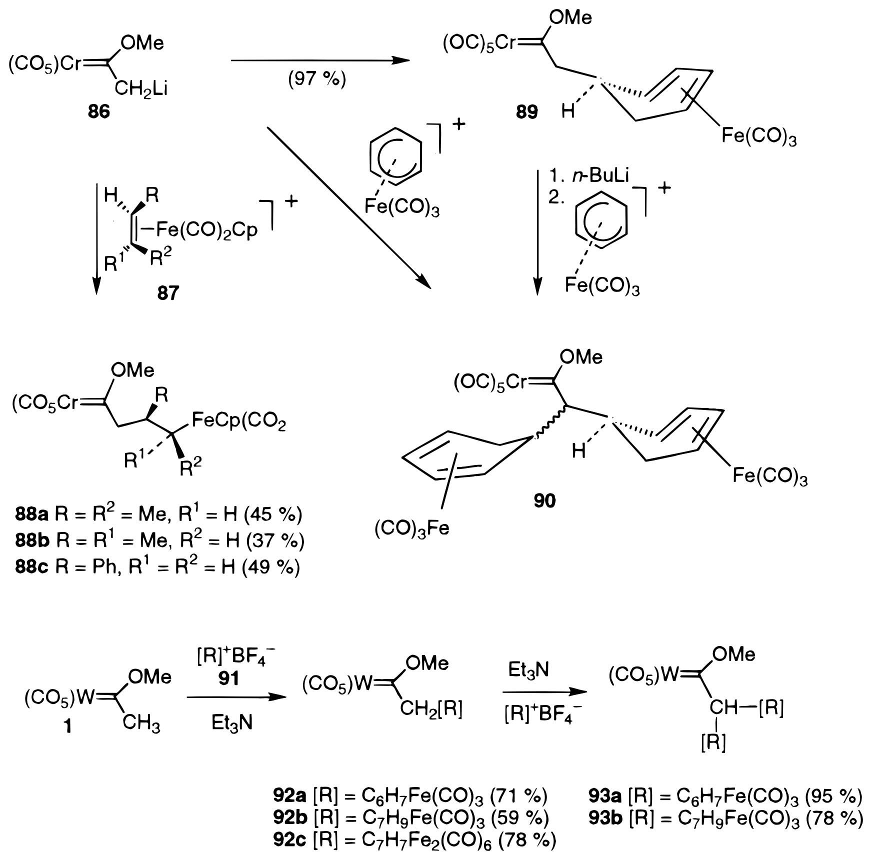
Anions **94a**–**e** reacted with $[(C_6H_6)(CO)_3MnPF_6]$ complexes to yield dinuclear (η^5-cyclohexadienyl)-manganese tricarbonyl carbene complexes **95**. Both, alkoxy- and aminocarbene complexes gave satisfactory results. The reaction of cyclic carbenes **96** with cationic tricarbonyliron(η^5-cyclohexadiene) complex **97** gave the expected neutral heterodimetallic complexes **98a,b** as diastereomeric mixtures (Scheme 21).[43,44]

Heteroanions **99** and **100** generated in situ by treatment of **101** with BuLi and CS_2 were quenched with organometallic Lewis acids to form diverse heterodimetallic carbenes. Thus, treatment of heterodianion **99** with $[(CO)_5ReBF_4]$ or $[cis\text{-}MCl_2(PR_3)_2]$ (M = Pd, Pt) gives complexes **102** and **103**, respectively. Heteroanion **100** forms complexes **104a,b** when reacted with $[XRe(CO)_5]$ or $[XAuPPh_3]$. The behavior of heteroanion **100** toward coordinated ethene or allyl ligands is analogous to that of the parent carbanion derived from **101**, yielding hydrocarbon-bridged dimetallic carbenes **105** and **106** (Scheme 22).[45]

Chromium carbene **107** reacts with ferrocenylcarbaldehyde under the conditions tuned up by Aumann to prepare α,β-unsaturated carbene complexes[46] to form heterodimetallic monocarbene **108** (Scheme 23).[47a] An analogous process using benzaldehyde tricarbonyl chromium gave homodimetallic monocarbene complex **109**.[47b] Ferrocenylcarbaldehyde and 1,1′-bis-formylferrocene formed dimetallic carbene complexes **110a,b** by reaction with the Mn carbene complex anion **111**,[47c] while polyconjugated monocarbenes **112a,b** were obtained from 9-ferrocenyl-2,7-dimethylnonatetraenal and complexes **1** and **113** following essentially the Aumann procedure.[48]

As was exemplified in eq 10, the capture of a carbene α-anion with a bidentate electrophile would lead to a homodimetallic bis-carbene complex. This methodology was implemented originally by reacting two equivalents of complex **113** with aromatic di-

Scheme 20



aldehydes **114** and **115** to form bis-carbene complexes **116** and **117** (Scheme 24).[46] Trimetallic bis-carbene **118** was formed when an excess of Mn carbene anion **111** was reacted with 1,1′-ferrocenedicarbaldehyde.[47c] Diverse di- and trimetallic bis-carbene complexes with structures analogous to **119** were accessed from the Peterson olefination reaction of tungsten carbene **120** and different polyene dialdehydes.[48] The sequential reaction of the anion derived from complex **121** with α,ω-dihalogenoalkanes yields in first instance complexes **122** and finally bis-carbenes **123a**−**c**.[49]

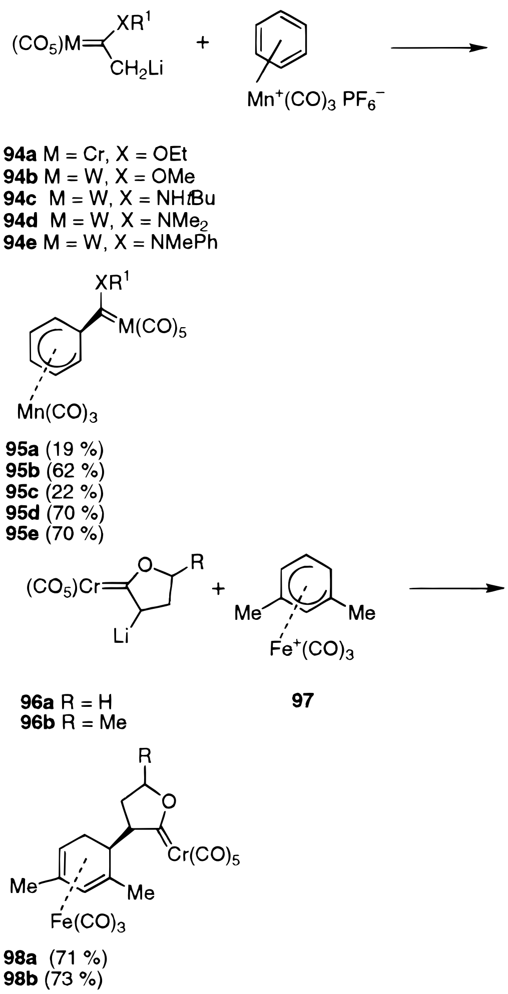
The reaction of anions derived from complexes **124** and fumaryl dichloride gave results different from those expected. In this case bis-carbene complex **125**, having a lactone nucleus in its structure, were obtained. Apparently, after the acylation of the carbanion had occurred to yield a new carbene complex **126**, a second molecule of **124** preferred the addition to **126** in a conjugated fashion rather than to the carbonyl group of the acid chloride moiety. The enolate oxygen of intermediate **127** is hence intramolecularly acylated by the acid chloride to yield **128**. This intermediate finally yields **125** by 1,3-H shift (Scheme 25).[50]

bis-Carbene complex **129** connected by a conjugated ammonium pentadienide bridge has been obtained by reacting **113** with tetrachlorocyclopropene **130** in the presence of Et_3N. This reaction involves the elimination of 4 equivs of HCl and the formation of the nitrogen ylide complex. The actual mechanism of the process is unknown (Scheme 26).[51]

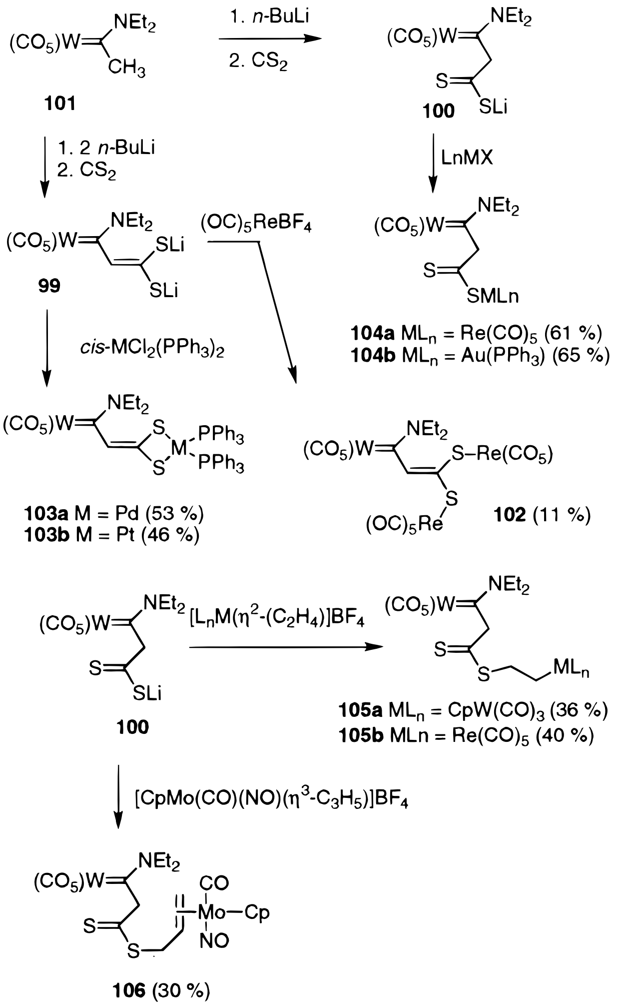
The oxidative dimerization of a carbene anion to yield a dimetallic carbene complex (eq 11) was initially observed when $TiCl_4$ was used to activate an oxirane ring toward the nucleophilic attack of a chromium carbene anion. Thus, the anion **86**, derived from **113**, was reacted with propylene oxide in the presence of $TiCl_4$ to form the expected complex **131** together with bis-carbene complex **132**. This last compound was formed probably by the oxidation of anion **86** by Ti(IV) to yield a radical species that undergoes dimerization to the carbene **132**. No improvement in the yield of complex **132** was observed when the reaction was carried out in the absence of the oxirane (Scheme 27).[52] A controlled oxidation of carbanion **86** was achieved by using $AgBF_4$.[53] These conditions lead to complex **132** in 50−80% yields that was, in turn, converted to α,β-unsaturated bis-carbene complex **133** through the sequence deprotonation, to form the carbene dianion **134**, followed by $AgBF_4$ oxidation. This dianion was also reacted with $[(CO)_5Re(C_2H_4)BF_4]$ and $[(CO)_3Fe(C_6H_7)BF_4]$ to yield the tetranuclear complexes **135** and **136**, respectively.[53]

Iron bis-carbene **137** was obtained following an analogous approach from cationic complexes **138**, which were transformed to the neutral vinyl complex **139** by deprotonation with KO*t*Bu at −80 °C. The reaction of complex **139** with an stoichiometric amount of $[Fe(\eta^5\text{-}C_5H_5)_2PF_6]$ gave a mixture of **137** as two pure diastereomers (Scheme 28).[54] The dimerization should occur through a 17-electron radical cation **140** generated from **139** that is stable at −80 °C. Dimerization of **140** occurs upon warming in the solid state. When **140** remained in solution, abstraction of an hydrogen from the solvent favorably competes with

Scheme 21



Scheme 22

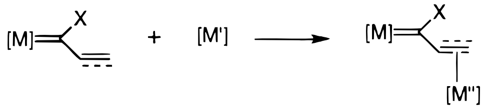


the dimerization to produce starting materials **139**. Dimerization of two 17-electron species having a CO ligand is rather interesting, since this ligand is exceptionally labile in these compounds, and often evolves with decoordination of CO that leads to decomposition.

The oxidation of the anions derived from Mn carbene complexes **141** and **142** with CuI and O_2 yields bis-carbene complexes **143** and **144**, respectively. Complex **143b** has two stereogenic centers, and it is formed as a 1:1 mixture of diastereomers. Complex **144** was formed as a mixture (66:33) of two of the six possible diastereomers. Finally, the transformation of **143a** into complex **145** can be achieved by either electroxidation or by oxidation of its dianion with $CuCl_2$ and O_2. The dianion derived from **143a** behaves as expected when reacted with MeI, yielding compound **143b** in quantitative yield as a 60:40 mixture of diastereomers (Scheme 29).[55]

C. Synthesis of Di- and Polymetallic Metal Carbenes from α,β-Unsaturated Metal Carbenes

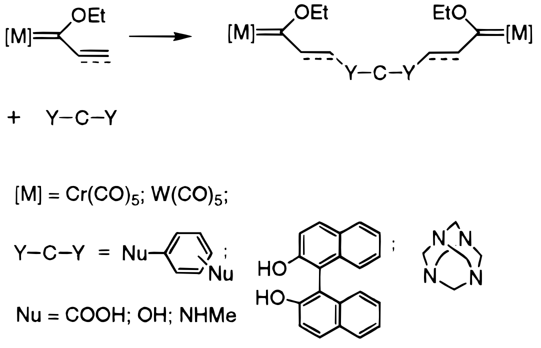
Due to the different possibilities of reaction in the conjugated unsaturation, this approach leads to structurally diverse complexes. The simplest way to di- and polymetallic metal carbenes is to gain advantage of the coordination chemistry of the double or triple bond or to introduce the new metal center or centers (eq 12).



(12)

[M] = $Cr(CO)_5$; $W(CO)_5$;
[M'] = $Co_2(CO)_8$; $Fe_2(\mu\text{-}EE')(CO)_6$; $B_{10}H_{10}(NCMe)_2$

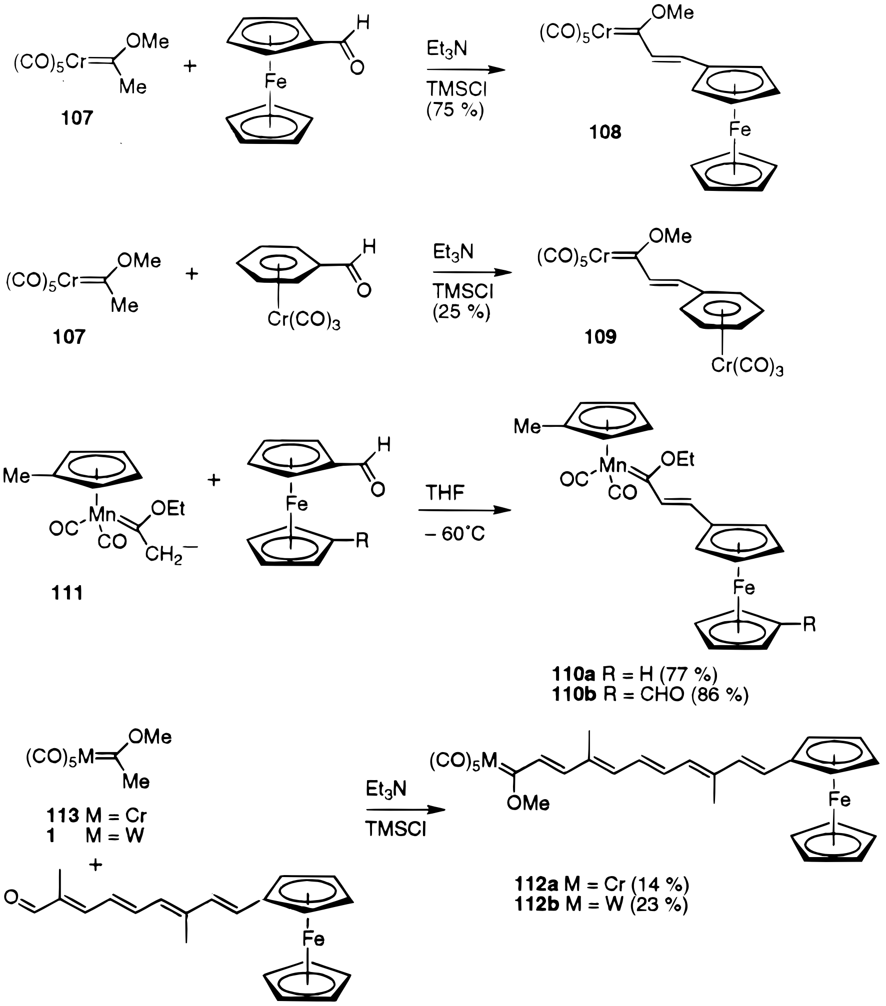
Alternatively, the conjugated double addition of a bidentate dinucleophile to 2 molecules of carbene would lead also to dimetallic complexes (eq 13).



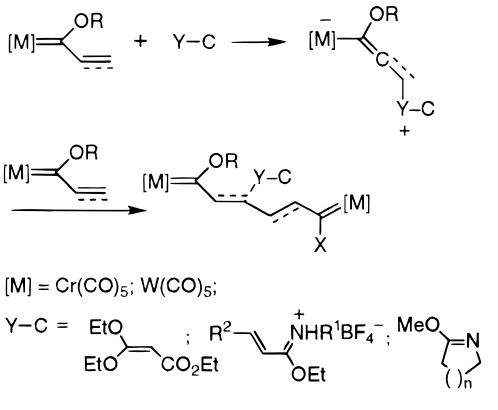
(13)

In the same way, the compound obtained from the

Scheme 23



Michael addition may react with a new molecule of the unsaturated carbene to yield to a new dimetallic complex (eq 14).



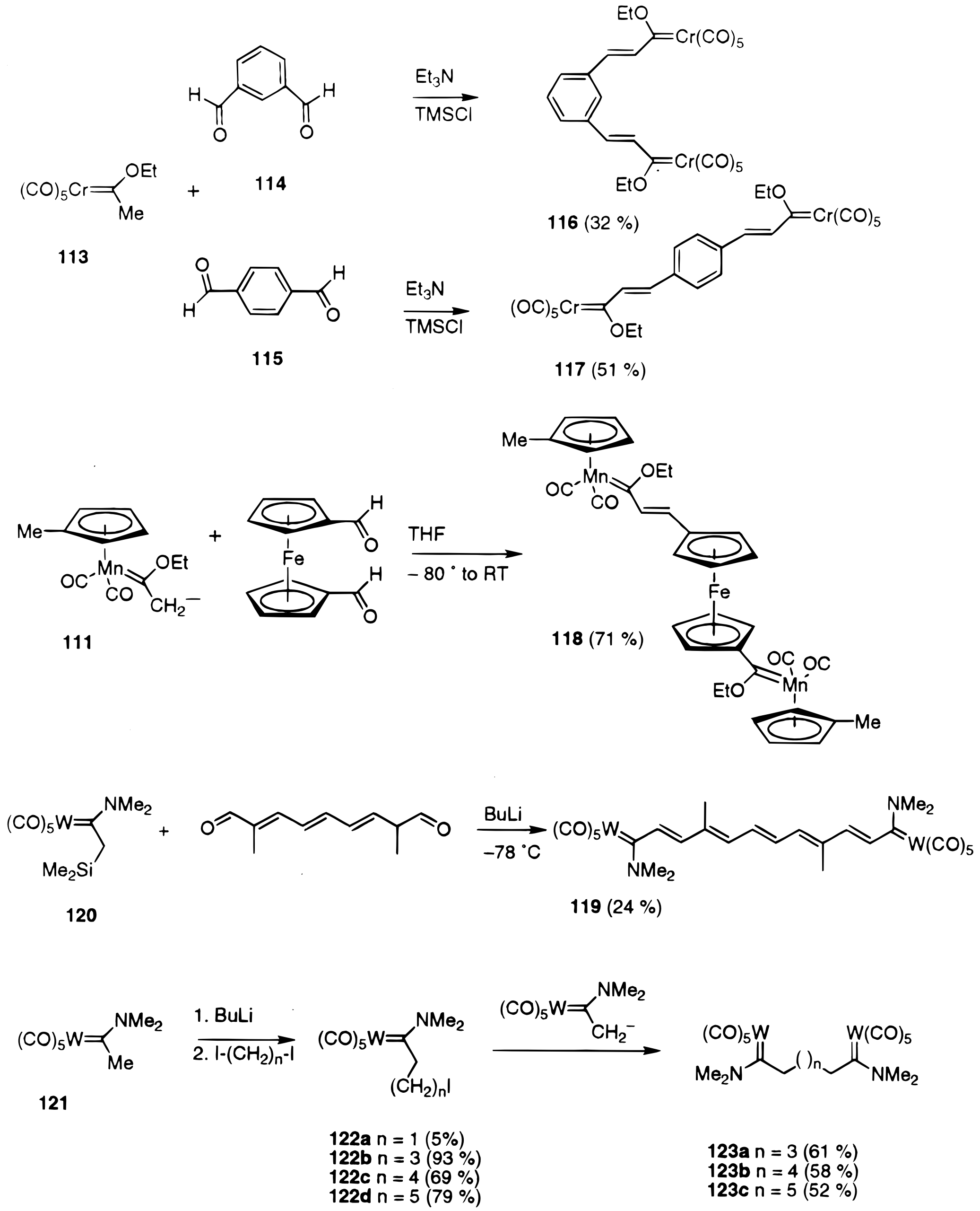
(14)

By far, the most profusely used route to di- and polymetallic carbenes starting from α,β-unsaturated metal carbene complexes is represented in eq 12, namely, the coordination of new metal centers to an α,β-unsaturated bond. α,β-Alkynyl carbenes react with $Co_2(CO)_8$ to yield the corresponding heterodimetallic trinuclear complexes. These complexes are reacted, in general without isolation, with different olefins to yield the corresponding cyclopentenones in a Pauson−Khand (P−K) reaction.[56] The synthetic applications of these dicobalt hexacarbonyl metal carbenes will be discussed below. The first examples of isolation of trinuclear monocarbene complexes by this approach were reported almost simultaneously by three different groups. Complex **146** prepared by reaction of complex **147** with $Co_2(CO)_8$ was the first example (Scheme 30).[57] Other alkoxy trinuclear carbene complexes, **148**, were also prepared from the corresponding monuclear carbenes **149** and some (**148**, M = Cr, R = Me) characterized by X-ray difraction.[58,59]

These preliminary reports were promptly followed by the isolation of complex **150** by reaction of tungsten carbene complex **151** and $Co_2(CO)_8$ (Scheme 31).[60] Complex **150** was formed by an alternate evolution of the first intermediate of the P−K reaction **152**, after the initial formation of cobalt−tungsten complex **153**. Instead of a reductive elimination of the first cobalt atom, intermediate **152** evolves by replacing the tungsten at the carbene center by a Co. The steric hindrance of the bulky TMS group was claimed to be the responsible for this unexpected result.[60]

The P−K chemistry of trinuclear complexes such as the above-mentioned has been thoroughly studied since these preliminary results were reported (see below).[57−64] However, only a few complexes have been isolated and characterized. Thus, complexes **154a,b**

Scheme 24



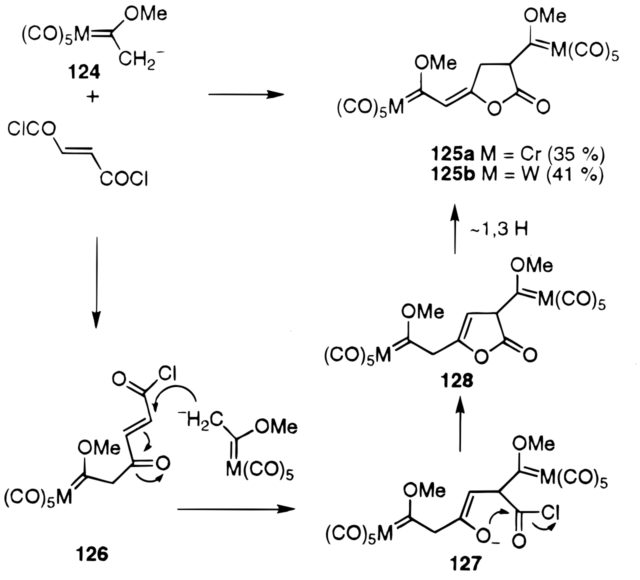
were prepared by the reaction of carbenes **155** and $Co_2(CO)_8$.[61] The reaction of carbene complexes **156** and $Co_2(CO)_8$ produced complexes **157** as side products.[62,63] The analogous reaction of carbenes **158a,b** formed complexes **159a,b** (Scheme 32).[64]

Chalcogenide and mixed chalcogenide iron carbonyl cluster metal carbenes **160a**–**k** were prepared also by the addition of $[Fe_2(\mu\text{-}EE')(CO)_6]$ (E = S, Se, Te; E′ = S, Se, Te) to alkynylcarbene complexes **161**. The reaction was clean and, together with the polynuclear complexes **160**, new mononuclear carbene complexes **162a,b**, produced by the conjugated addition of MeOH to the starting **161**, were obtained as traces. The analogous aminocarbene polynuclear complexes **163a**–**f** were obtained by aminolysis of the corresponding alkoxy complexes **160** (Scheme 33).[65,66] The reactivity of these complexes as well as their preliminary synthetic applications have been also studied (see below).[67,68]

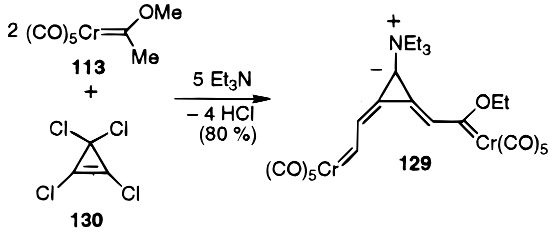
The transformation of the carbon–carbon triple bond of carbene complex **164** into an *o*-carborane framework was achieved by reaction with $B_{10}H_{12}(MeCN)_2$. Compounds **165a**–**d** were obtained in high yields from the direct two carbon insertion reaction of the alkynylcarbene complex.[17] Formation of dinuclear complex **166** occurred upon standing complex **167** in solution at room temperature.[69] Complex **166** is very stable in solution and only regenerated the starting complex **167** after heating for long periods of time (Scheme 34).

As stated earlier, the addition of a bidentate dinucleophile to 2 molecules of an α,β-unsaturated carbene will lead to an homodimetallic carbene complex (eq 13). Analogously, the Michael addition of a nucleophile to an α,β-unsaturated carbene may lead to a new complex that also can react as a nucleophile with an additional molecule of starting material, leading again to a homodimetallic carbene

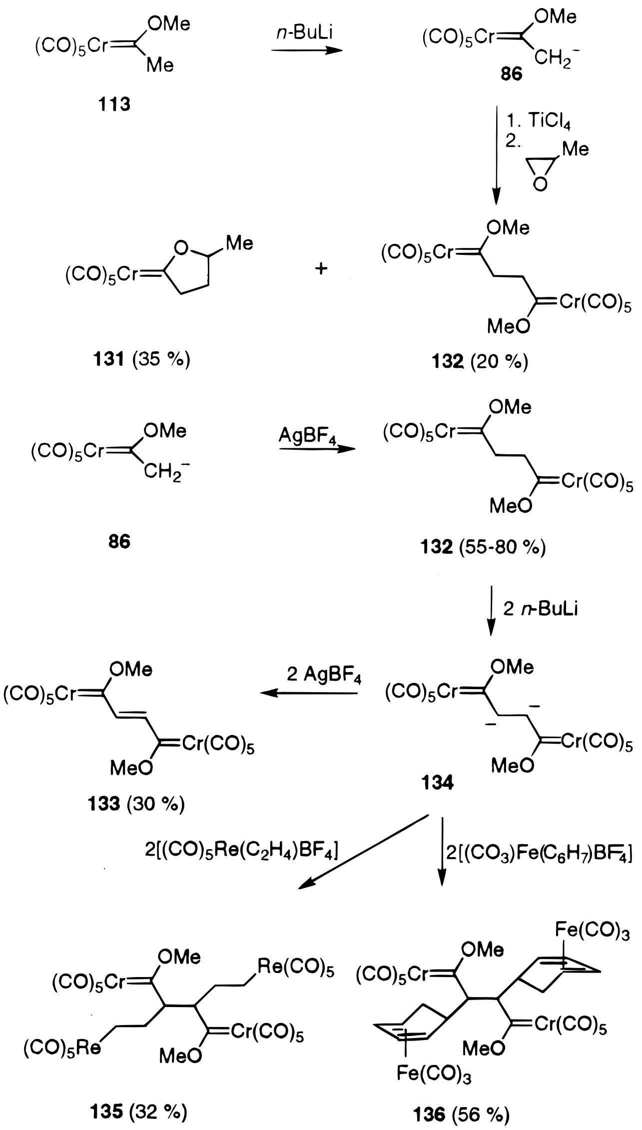
Scheme 25



Scheme 26



Scheme 27



(eq 14). The first example in which an homodimetallic chromium complex, namely, bis-carbene **168**, was prepared through a double Michael addition route was the reaction of tungsten complex **169** with terephthalic acid. This reaction yields complex **168** as single *Z*,*Z*-isomer. The sequential reaction of equimolar amounts of complex **169** and *p*-*N*-methylaminobenzoic acid yielded the *E*-complex **170** that was converted to *E*,*Z*-homo bis-carbene **171** by the addition of a new molecule of **169**. This last addition requires the presence of Et_3N as the catalyst (Scheme 35).[70]

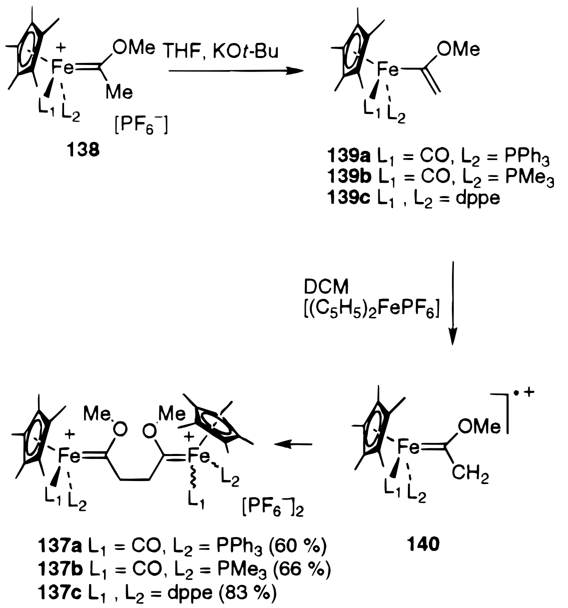
Dinuclear carbene complexes **172** and **173** were analogously prepared by the reaction of *m*- and *p*-diphenols and 1,1′-binaphthol and metal complexes **161a,b**. Complexes **172**−**174** were obtained exclusively as their *E*,*E*-isomers. However, while **172** was configurationally stable, complex *E*,*E*-**173** slowly isomerizes in solution to the *Z*,*Z*-isomer, and *E*,*E*-**174** formed a mixture of *E*,*Z*- and *Z*,*Z*-isomers when solved (Scheme 36).[71]

The reaction of aqueous urotropine with metal carbene **175** leads to symmetric complex **176** having a quinuclidin nucleus, with extrusion of formaldehyde in the process. This is a striking result since the reaction of urotropine with other carbenes, including α,*β*-alkenyl derivatives **177**, leads to destruction of the metal complex with formation of the corresponding aldehyde and [$(CO)_5Cr$(urotropine)]. The formation of **176** was explained by the initial conjugated addition of the base to the complex **175** to yield the allenyl zwitterion **178**. Fragmentation of the urotopine nucleus yields a new intermediate **179** that is hydrolyzed to complex **180** with the loss of 1 molecule of formaldehyde. Complex **180** adds to a new molecule of the starting complex to give the observed product **176** (Scheme 37).[72]

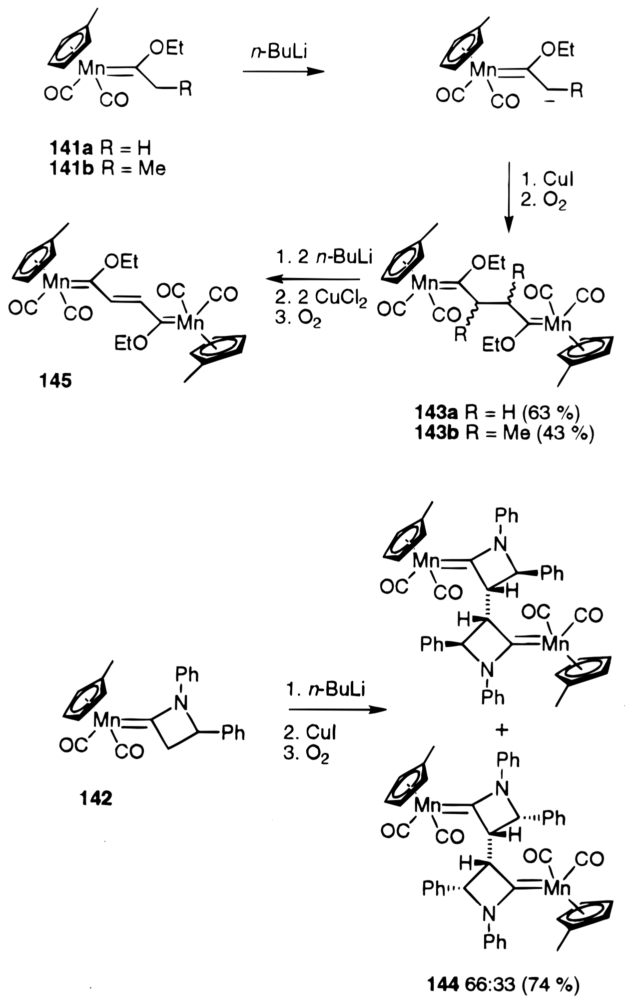
The generation of a nucleophilic carbene intermediate that is able to react with a new molecule of the starting material is exemplified by the reaction in Scheme 38, and it has been successfully used to prepare different classes of compounds. The reaction of complex **175** with 3,3-diethoxy acrylate leads to bis-carbene complex **181** when a limited amount of ester is used. Formation of complex **181** was explained by the initial formation of zwitterionic intermediate **182**. The intramolecular cyclization of **182** forms pyranylidene complex **183** that adds to a new molecule of the starting material to finally yield **181** (Scheme 38).[73]

A beautiful cascade [4+2]-[2+2] cycloaddition between complex **175** and alkenyl imidates **184** has been used to prepare bicyclic bis-carbenes **185a**−**c**. These complexes in turn rearranged to monocyclic bis-carbenes **186a**−**c** after acid treatment. Formation

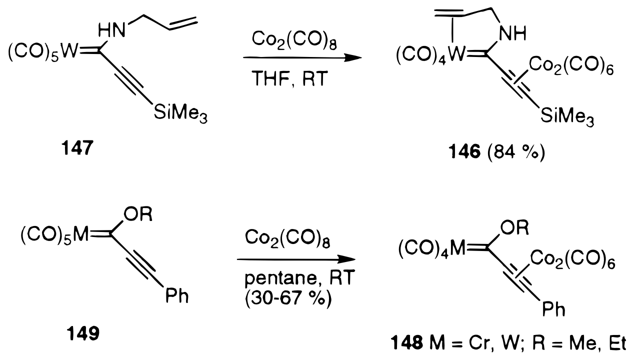
Scheme 28



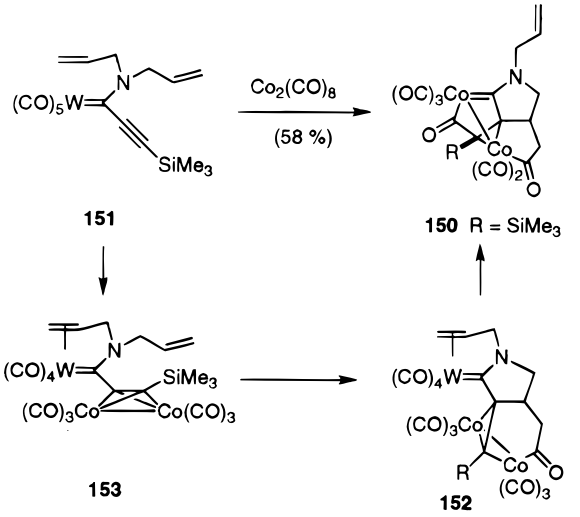
Scheme 29



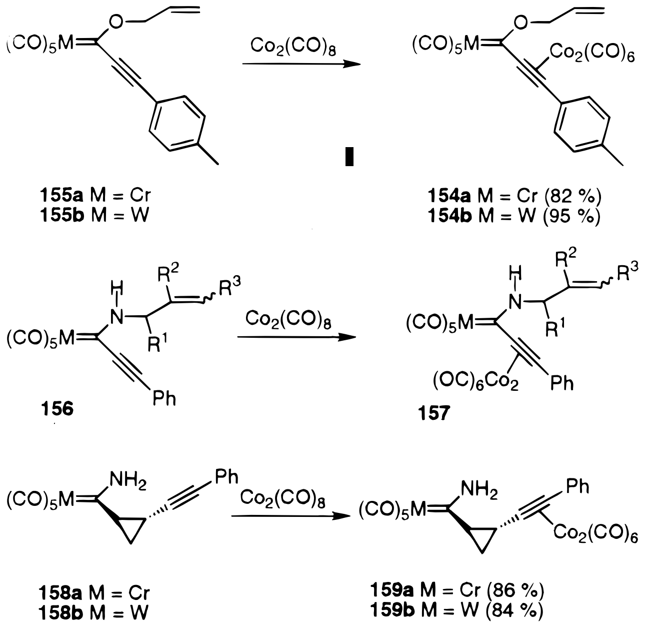
Scheme 30



Scheme 31

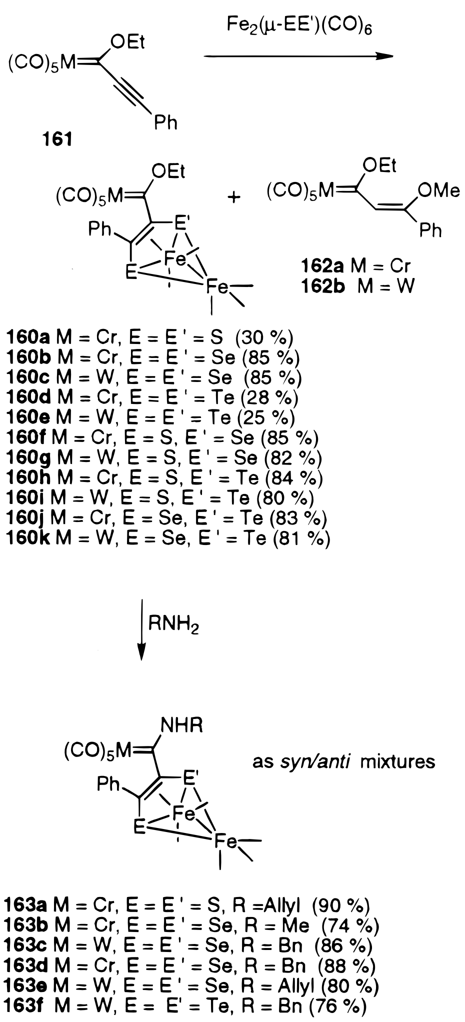


Scheme 32

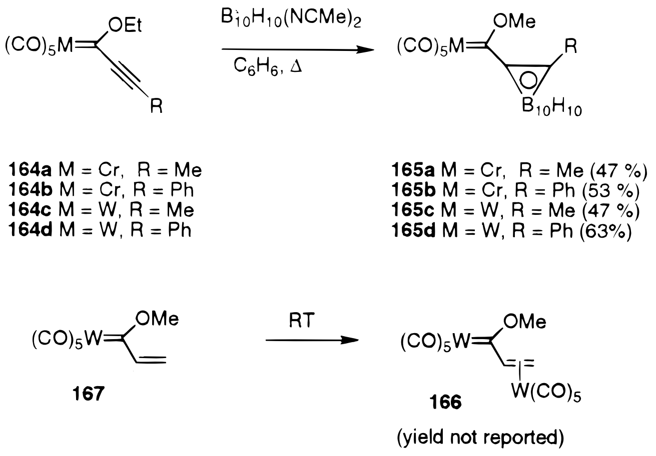


of complexes **185** is explained by the initial conjugate addition of the imidate nitrogen to the carbene complex **175** followed by the ring closure of the intermediate zwitterion **187** to yield the new complex **188**. This reactive intermediate undergoes a [2+2] cycloaddition with a second molecule of **175** to yield the observed compound **185**. Complex **185** is stable in the solid state but rearranges to the monocyclic compounds **186a**–**c** upon acid treatment. The regioselective breakage of the cyclobutane ring generates a new zwitterionic complex **189**, which evolves to the

Scheme 33



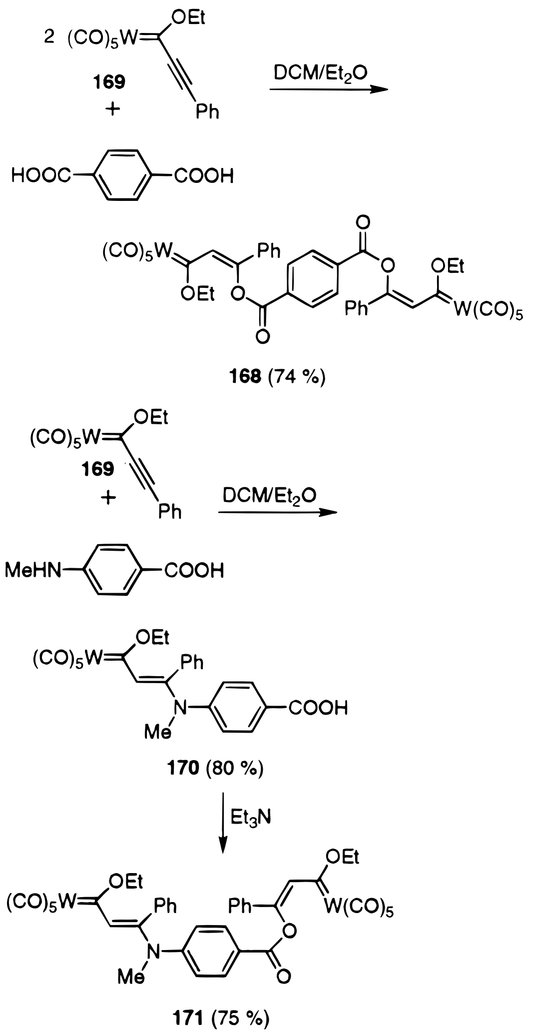
Scheme 34



final products by successive protonation–deprotonation (Scheme 39).[74]

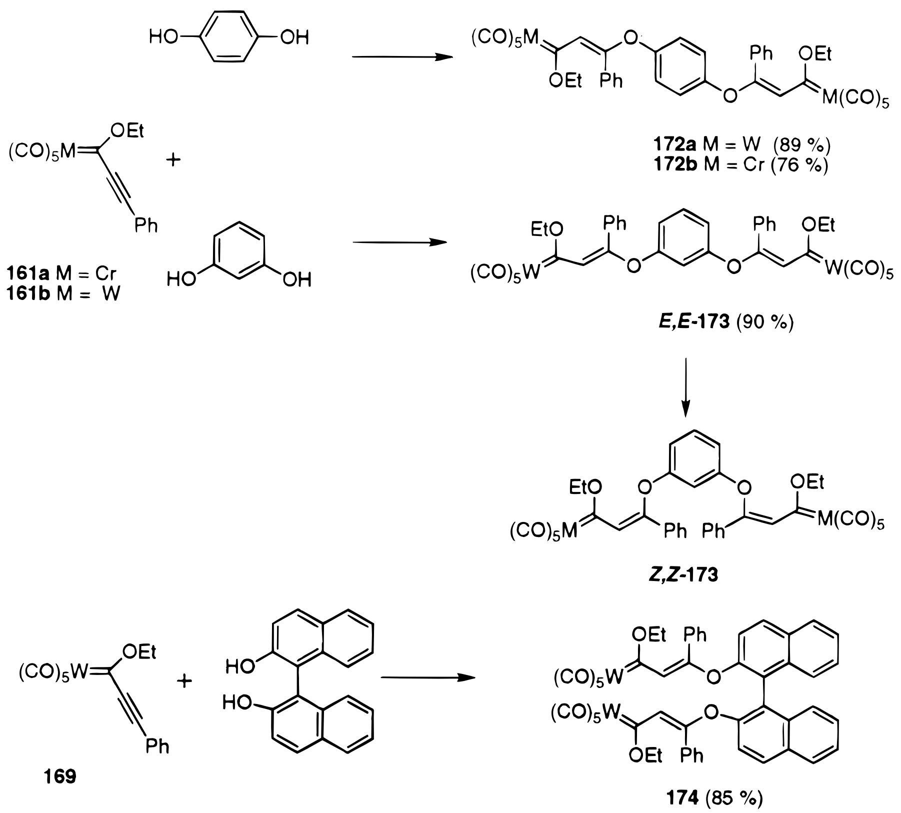
Five- and six-membered cyclic imidates (lactims) gave also dinuclear complexes referable to **185**.[75] Thus, five-membered *O*-methyl lactim **190a** reacted with (1-alkynyl)carbene complexes **161a,b** in a 1:2 ratio to afford dinuclear carbene complex **191a** in excellent yields. Mononuclear complexes **192a–f** could not be detected as intermediates, even when the lactim was used stoichiometrically. The reaction of complexes **161** with six-membered *O*-alkyl lactim **190b** gave by analogy complex **191b**. On the contrary seven- and eight-membered lactims gave exclusively mononuclear complexes **192a–f**. Formation of complexes **191a–c** was explained by the initial addition of the lactim nitrogen to the β-carbon of the complex to yield allenyl complex **193**. This complex undergoes a spontaneous 1,5-hydrogen shift to give the enamine derivative **192**. The obtained dinuclear complexes **191a–c** are then formed by [2+2] cycloaddition of the triple bond of a new molecule of the starting complex to the electron-rich C=C(OMe)N bond of **192**. Probably, in the case of five- and six-membered lactims the second step of the reaction, the [2+2] cycloaddition between **192** and **161**, is faster than the first one; hence, complexes **192a–f** could not be isolated in these cases (Scheme 40).

Scheme 35

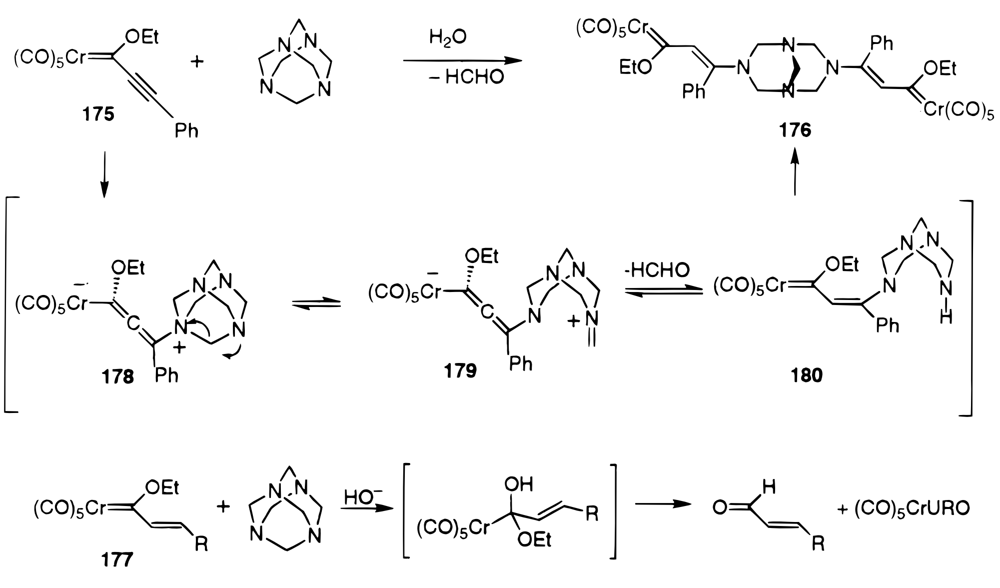


Other homodimetallic bis-carbene complexes could be obtained from **191b**. This complex was not stable in solution and undergoes fast transformation, especially in acidic media, to give three different products after chromatography, two of them containing a bis-carbene moiety. Then, complex **194** was formed by a (1-cyclobutenyl)carbene → metallatriene rearrangement[74] that involves a 1,3-H migration on the initially formed intermediate **195**. Compound **196** was formed from **195** by hydrolysis. Cyclization of the metalla-

Scheme 36



Scheme 37

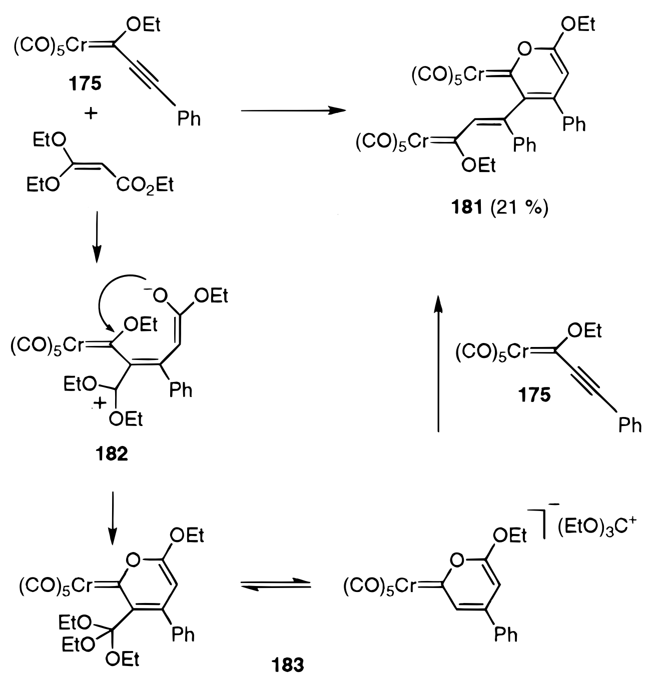


triene unit of **194** formed **197**, which evolves to the final product **198** by the hydrolysis of the enol ether moiety of intermediate **199** (Scheme 41).[75]

An intringuing case occurred during the reaction of complex **200** with sodium teramilate ($C_2H_5(CH_3)_2$-CONa). This reaction leads to a mixture of compounds from which monuclear carbenes **201** and **202**, dinuclear carbene **203**, and finally trinuclear complex **204** were isolated and characterized. A mechanism for the formation of these compounds involves the conjugate addition of sodium teramilate to **200**. Complex **201** would be formed by protonation of the resulting anion **206**. The conjugated addition of anion **206** to a new molecule of complex **200** results in **207**, which by protonation would lead to **202** (protonation at tungsten) and **203** (protonation at carbon). The formation of **204** is a consequence of two successive conjugate additions of α-carbene anions to **200** forming sequentially **208** and **209**. Protonation of (μ-tetrakis(carbene)) complex **209** at tungsten followed by reductive elimination would yield the observed complex **204** (Scheme 42).[76]

Polymeric tungsten carbene complexes have been also reported. In fact, during the synthesis of complex **167**, an insoluble orange solid was invariably produced when the standard Fischer procedure was

Scheme 38



followed.[77] Compound **167** could be obtained when purification of the crude reaction mixture was effected immediately and was stable at −30 °C. However, it evolves to the same orange insoluble material upon standing 7 days at room temperature (see Scheme 43). This orange material was identified as polymer **210** on the basis of spectroscopic data and by its oxidative conversion to poly(methyl acrylate). Together with this material, a soluble copolymer **211** could be obtained by partial oxidation of **210**. The mechanism of formation of polymer **210** under bulk conditions is not known, but both radical and anionic pathways appear possible. The radical polymerization of monomer **167** occurred in the presence of AIBN. Likewise, monomer **167** can be homopolymerized by using many anionic initiators including TMEDA, PPh_3, *t*-BuLi, etc.

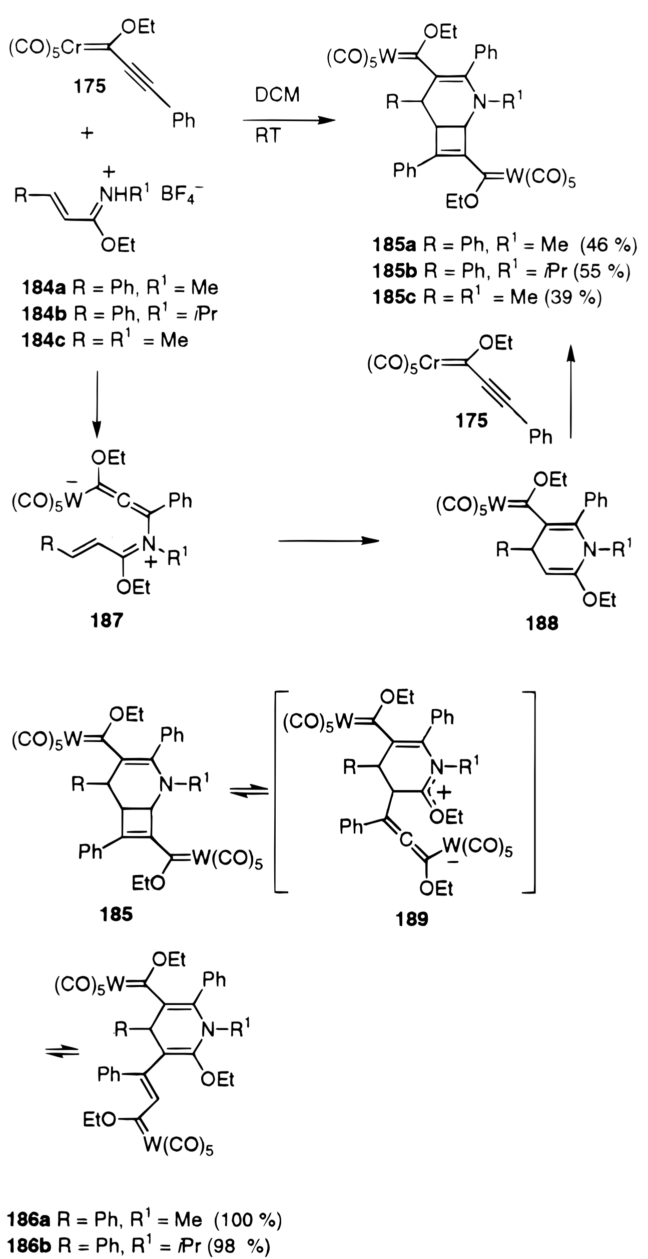
A totally different approach to di- and polymetallic carbene complexes, starting from ethynyl mononuclear metal carbenes, makes use of the acidity of the terminal ethynyl hydrogen to anchor the new metal/s center/s (eq 15).

(15)

[M] = $Cr(CO)_5$; $W(CO)_5$;
[M'] = *trans*-$Pd(PEt_3)_2Cl$; *trans*-$Fe(dmpe)_2Cl$; $ClPd(PEt_3)_2(CCH)$; $Cl_2Ni(PEt_3)_2$; $Cl_2Pd(PEt_3)_2$; $Cl_2Pt(PEt_3)_2$; $Cl_2Fe(dmpe)_2$; Cl_2Hg; Cl_2TiCp_2; BBr_3; PCl_3; $SiCl_4$; $GeCl_4$; $SnCl_4$

Moreover, this approach allows us to attach more than 1 molecule of the ethynyl carbene to the new metal center.[78−81] Ethynyl carbene complexes **212a,b** react with metal mono-, di-, tri-, and tetrachloride derivatives leading to di-, tri-, tetra-, and pentanuclear carbene complexes, **213**−**216**, respectively.

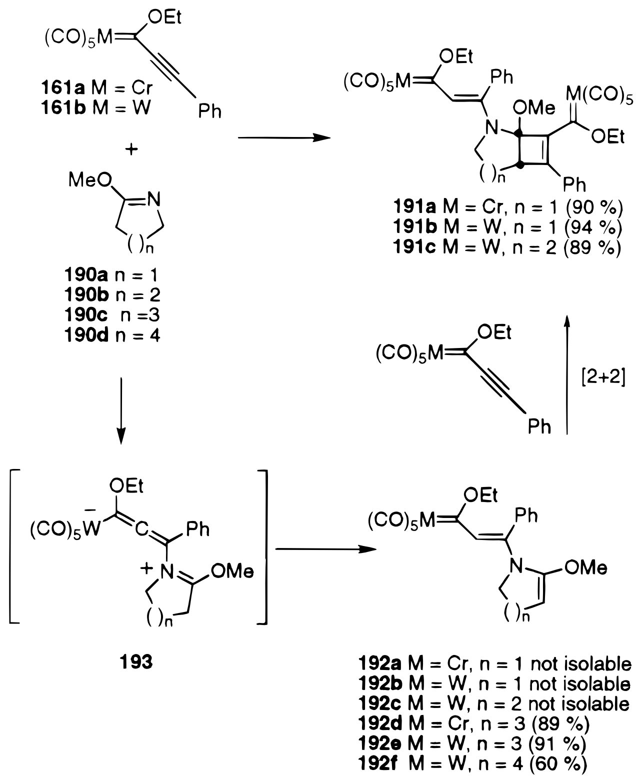
Scheme 39



Spectroscopic and structural data for these complexes suggest only a weak interaction between the carbene fragments and the central metal nucleus (Scheme 44).[78]

The homologous diinyl carbene complex **219a** was obtained from **212a** by reaction with BuLi, followed by quenching with CuI and $BrCCSiMe_3$ and desilylation by KF.[79] Triinyl carbene complex **219b** was obtained from the Pd-catalyzed coupling of dimetallic carbene **217** and $ICC{-}CCSiMe_3$, followed by desilylation by fluoride.[80] Complex **219a** formed dinuclear complex **220** by deprotonation of the acetylenic hydrogen followed by treatment with $[IFe(CO)_2Cp]$. Analogously, deprotonation of **219** followed by quenching with $ClSnBu_3$ yielded complexes **221a,b**. Treatment of such complexes with $[ClRu(CO)_2Cp]$ in the presence of $[Cl_2Pd(CH_3CN)_2]$) yielded diynyl and triynyl dinuclear carbene complexes **222a,b**.

Scheme 40

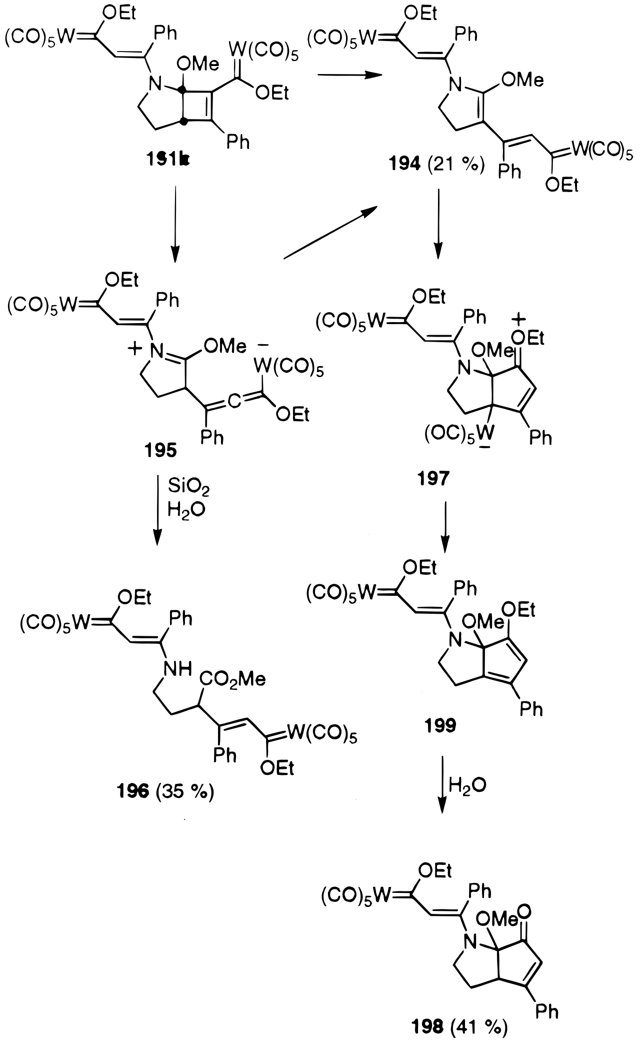


Trinuclear bis-carbene complexes **223a,b** were obtained by successive treatment of monuclear carbenes **219a,b** with BuLi and $HgCl_2$ (Scheme 45).[79,80]

Dimetallic bis-carbene complexes having conjugated C4, C6, C10, and C14 bridges were efficiently synthesized from ethynyl complexes **224** following two alternative routes (see Scheme 46).[81] Symmetrically substituted alkynediyl bis-(aminocarbene) complexes **227** were prepared by Pd-catalyzed coupling of two $(CO)_5M{=}C(NR_2)(CC)_xY$ ($Y = I, SnBu_3$) units **225** and **226**. This route allowed for the synthesis of complexes with an even number of ethynyl units. Alternatively, the lithium derivative of **212a** reacted with $W(CO)_6$ followed by methylation to yield the corresponding bis-carbene complex **228**. As above, spectroscopic data of the symmetrically substituted alkynediyl-bridged complexes suggests that in the ground state there is only weak π-interaction between the $(CO)_5W{=}C(NMe_2)$ fragments through the bridge, while the contrary seems to be true for the unsymmetrical alkoxycarbene–aminocarbene complex **228**, which shows a significant π-interaction between both carbene units.

Some dimetallic complexes have been also prepared by effecting a reaction on an unsaturation not-conjugated with the metal carbene bond. Thus, metathesis of the double bond of complex **229** with the mixture $WOCl_4/Ph_2SiH_2$ yielded the homodimetallic bis-carbene **230**.[82] Complex **231** was hydroborated with $HBEt_2$ to yield complex **232**. Transmetalation from boron to zinc yielded complex **233**. The reactivity of complex **233** toward D_2O and iodine was the expected, yielding complexes **234** and **235**, respectively (Scheme 47).[83]

Scheme 41



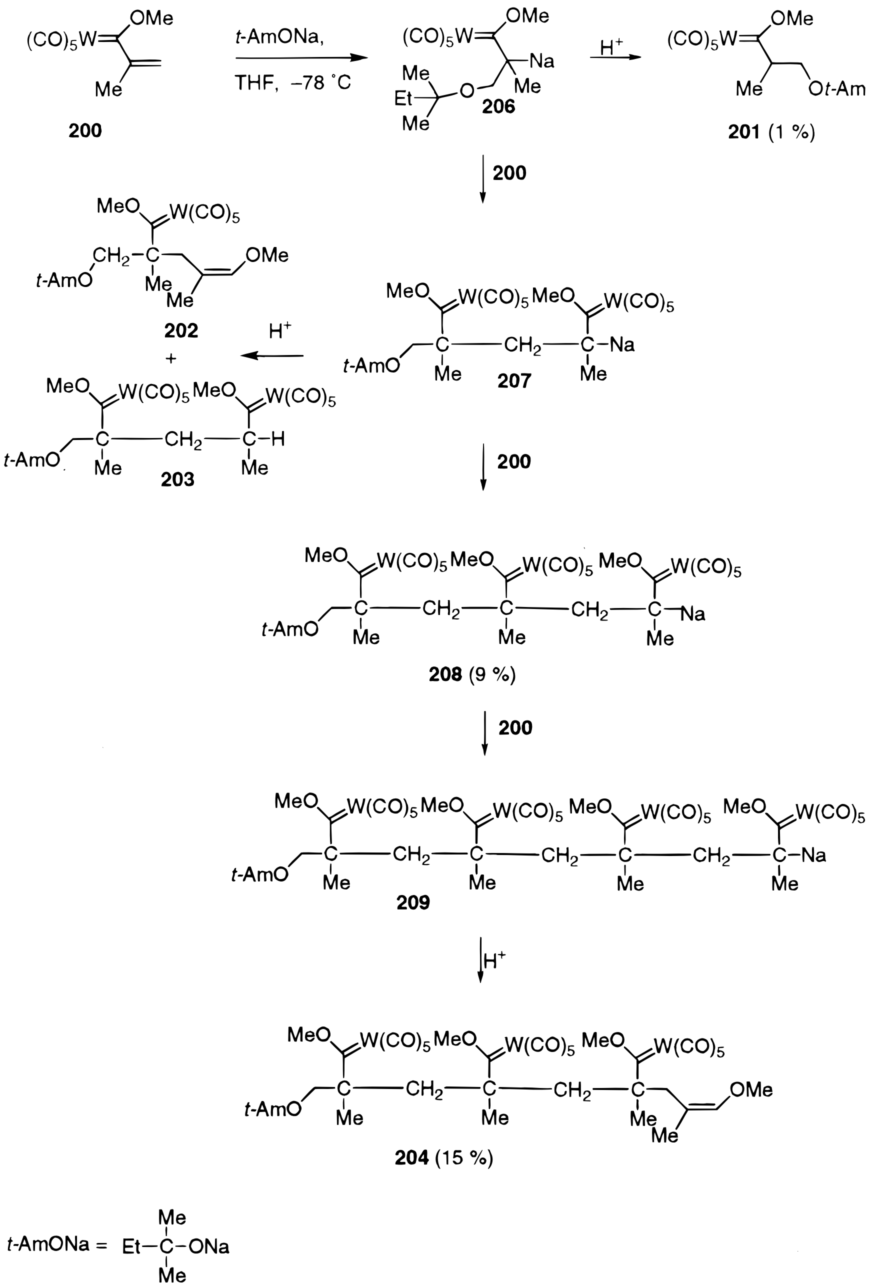
More sophisticated was the preparation of complex **236**. Dötz reaction between complexes **237** and **238** afforded the mixture of diastereomeric heterodimetallic carbene complexes **236**. The major complex of this mixture undergoes the haptotropic migration of the $Cr(CO)_3$ moiety by heating, to yield the new complex **239** (Scheme 48).[84]

D. Synthesis of Di- and Polymetallic Metal Carbenes from Allenyl Complexes

Preparation of di- or polymetallic carbene complexes by the sequence allenyl complex → carbene complex[85] has been scarcely reported. The reaction of $[(C_6Me_6)LRuCl_2]$, **240**, with [FcCCH] in the presence of MeOH yielded the heterodi- and trimetallic cationic carbene complexes **241**.[86] The reaction of $[\eta^6\text{-(arene)}Cr(CO)_3]$ having propyn-2-ol substituents **242** with $[(C_6Me_6)(PMe_3)RuCl_2]$ also occurred to yield the corresponding heterodimetallic complexes **243**. A nearly complete absence of selectivity was observed, even when an optically pure diastereomer of the alkyne **242** was used (Scheme 49).[87]

The alternative approach is to use a diyne diol to generate a dinuclear bis-ylidene complex that is then trapped in situ by the alcohol, thus generating the

Scheme 42

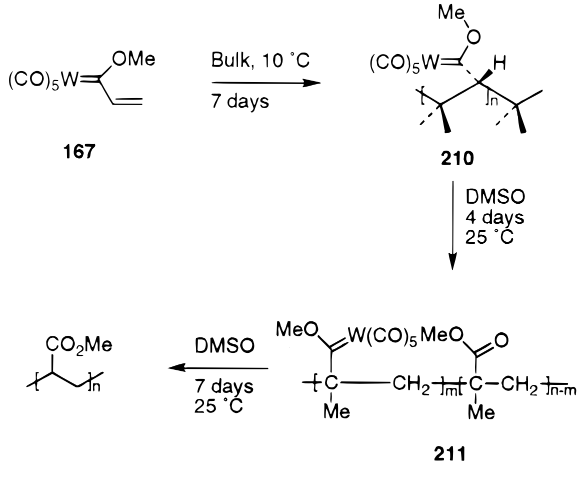


bis-carbene complex. This approach has also been described. Reaction of [W(CO)$_5$THF] with diols **244a,b** gave a mixture of mono- and bis-carbene complexes **245** and **246**. Alkoxy−amine interchange on complexes **245a,b** followed by reaction with a second mole of [W(CO)$_5$THF] gave the mixed alkoxyamino bis-carbenes **248a,b**. Unsymmetrical, diamino bis-carbene **249** was obtained by aminolysis of **248a** with piperazine (Scheme 50).[88]

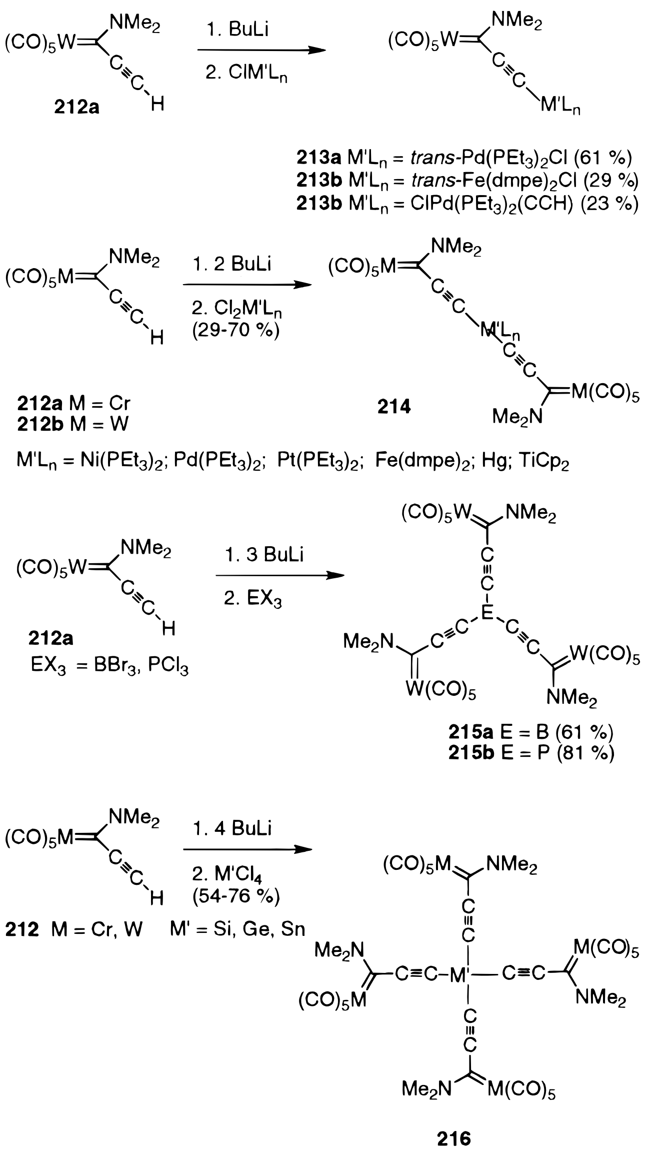
E. Synthesis of Di- and Polymetallic Metal Carbenes from Carbyne Complexes

Easily available metal carbyne complexes have been also used to introduce a second metal directly joined to the carbene carbon. The sequence usually involves the initial synthesis of a mononuclear carbene complex, its transformation to the corresponding

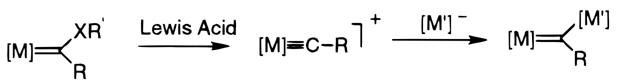
Scheme 43



Scheme 44



carbyne complex, and finally the addition of a metal nucleophile or a nucleophile having a metal nucleus to the carbyne carbon (eq 16).



$$[\mathrm{M}]{=}\mathrm{C}(\mathrm{XR'})\mathrm{R} \xrightarrow{\text{Lewis Acid}} [\mathrm{M}]{\equiv}\mathrm{C{-}R}]^{+} \xrightarrow{[\mathrm{M'}]^{-}} [\mathrm{M}]{=}\mathrm{C}([\mathrm{M'}])\mathrm{R}$$

$[M] = Cr(CO)_5$; $W(CO)_5$; η^5-$(C_5H_4Me)(CO)_2Mn$; $Cp(CO)_2Mn$ (16)
$[M'] = SnPh_3$; $AsPh_2$; $AsMe_2$; TePh; SePh

Thus, treatment of cationic carbyne complex **250** with $K[SnPh_3]$ yielded heterodimetallic monocarbene complex **251**.[89] The analogous reaction with $K[AsPh_2]$ formed the corresponding carbene complex **252**.[90] Strikingly, a totally different reaction occurred when $Li[AsMe_2]$ was used as the nucleophile. Instead of the expected addition of the As anion to the carbyne carbon to yield the complex analogous to **252**, reductive C−C coupling of two $[(CO)_5CrCNEt_2]$ fragments takes place to give the μ-bis(aminocarbene) complex **253** together with As_2Me_4. Apparently, the reductive dimerization of a cationic carbyne complex with concomitant C_α−C_α coupling can become the dominating reaction, competing with the addition of the nucleophile to the carbyne carbon atom, when strongly reducing nucleophiles are used.[91] The reaction of complex **250** with Li[TePh] afforded the expected carbene complex **254**. This complex was unstable and rearranged to a new carbyne complex **255** upon standing at room temperature or to mer-**256** if PPh_3 is present in the reaction medium (Scheme 51).[92] This approach can be also applied to dimetallic monocarbynes such as **257** that reacts with LiSePh or LiTePh to yield the corresponding carbenes **258a,b** (Scheme 51).[93]

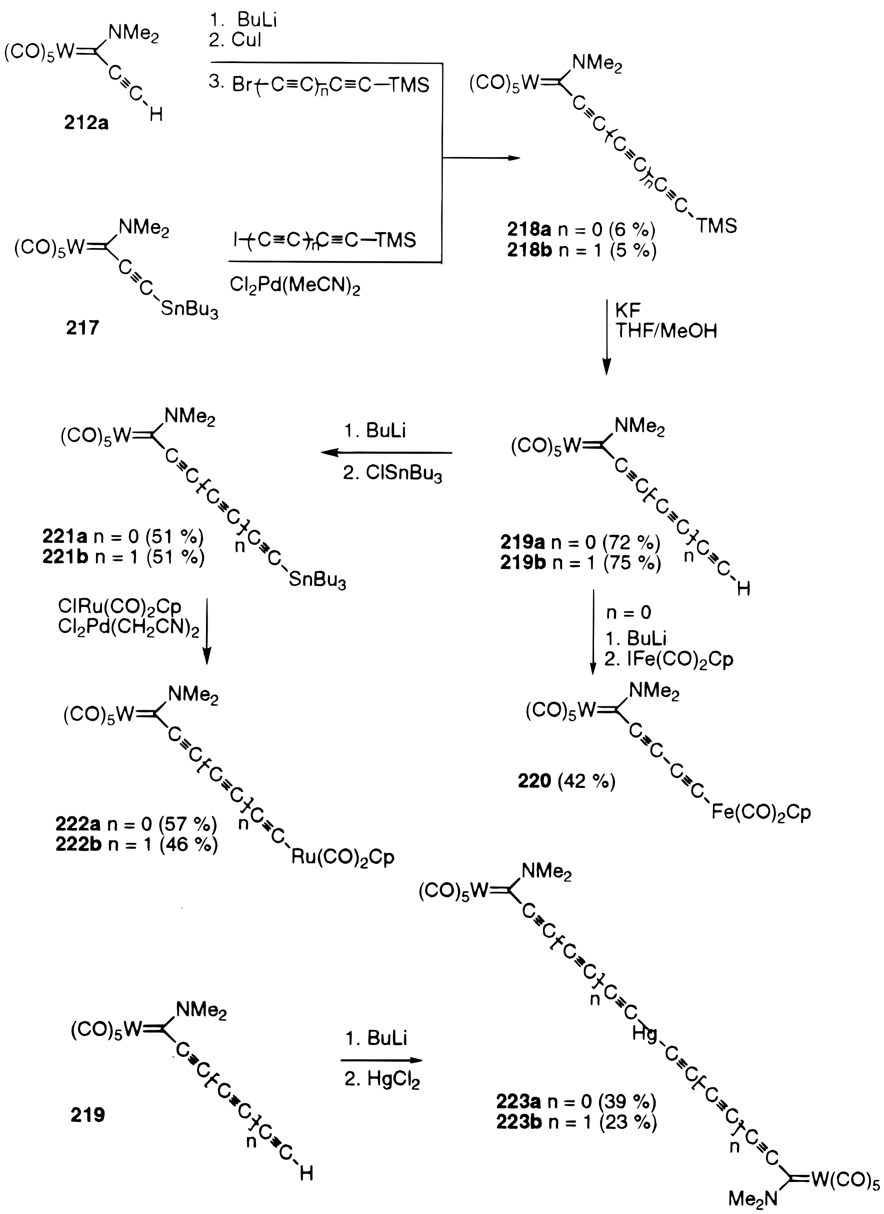
The reaction of Mn carbyne complex **259** or Re vinylidene complex **260** with benzalazine, **261**, formed the novel bicyclic bis-carbene complexes **262a,b** (Scheme 52).[94] The formation of compounds **262** is an organometallic version of the classic organic process named “criss-cross reaction”.[95] It is likely that the first step of the reaction would be the nucleophilic addition of the azine nitrogen to the electrophilic central allene carbon to form zwitterion **263**, followed by intramolecular cyclization to form **264**. This new zwitterionic intermediate **264** would add to a new equivalent of vinylidene or carbyne complex to give **265**, which will cyclize to yield the final compound **262** (Scheme 52).

III. Class II Di- and Polymetallic Metal Carbenes

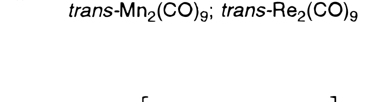
Class II di- and polymetallic carbene complexes have the metal centers joined through the heteroatom bonded to the carbene carbon (Figure 2C,D). Strictly speaking, all the lithium, sodium, or magnesium ate complexes $(CO)_5M{=}C(XM')R$ (M = Cr, W; M′ = Li, Na, Mg) obtained by standard Fischer synthesis are dimetallic carbene complexes. Nevertheless, they are not to be treated here as such due to their almost exclusive role of reaction intermediates in the preparation of other carbene complexes. One of the earliest examples describing the preparation of a complex of class II was the reaction of **266a** with $TiCpCl_2$ to yield a mixture of dimetallic monocarbene complex **267a** and trimetallic bis-carbene complex **268**.[96] The analogous reaction with complex **266b** gave exclusively dimetallic monocarbene complex **267b** (Scheme 53).[97]

Metalloxycarbenes of class II as well as the cyclic heterodimetallic carbene complexes that may be considered the link between class I and class II carbenes (they have the new metal center joined both to the heteroatom and to the carbon chain attached to the carbene ligand) derived from Ti,[98] Zr,[99] Hf,[100] Th[101] metallocenes and a group 6 metal carbene have been prepared. The synthesis, chemistry, and synthetic applications of these kind of complexes have been the subject of several reviews and will be considered only briefly here.[102] The example in Scheme 53 shows that the classical Fischer route to carbene complexes is applicable to this class of compounds. Nevertheless, metalloxycarbene complexes can be prepared without nucleophilic addition to metal

Scheme 45

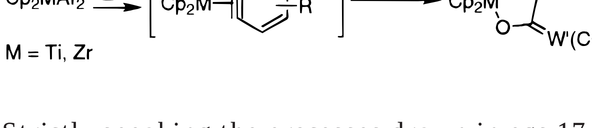


carbonyls, using very reactive η^2-olefine and aryne complexes of titanocene, zirconocene, and hafnocene and metal carbonyls (eqs 17 and 18).



(17)

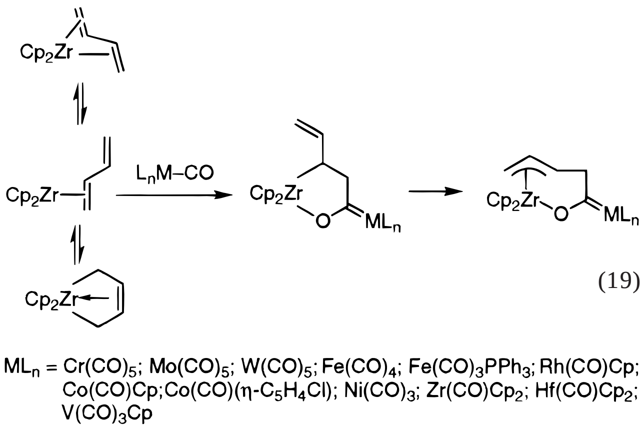
$M_xL_n = Cr(CO)_5$; $Mo(CO)_5$; $W(CO)_5$; *trans*-$Mn_2(CO)_9$; *trans*-$Re_2(CO)_9$



(18)

M = Ti, Zr

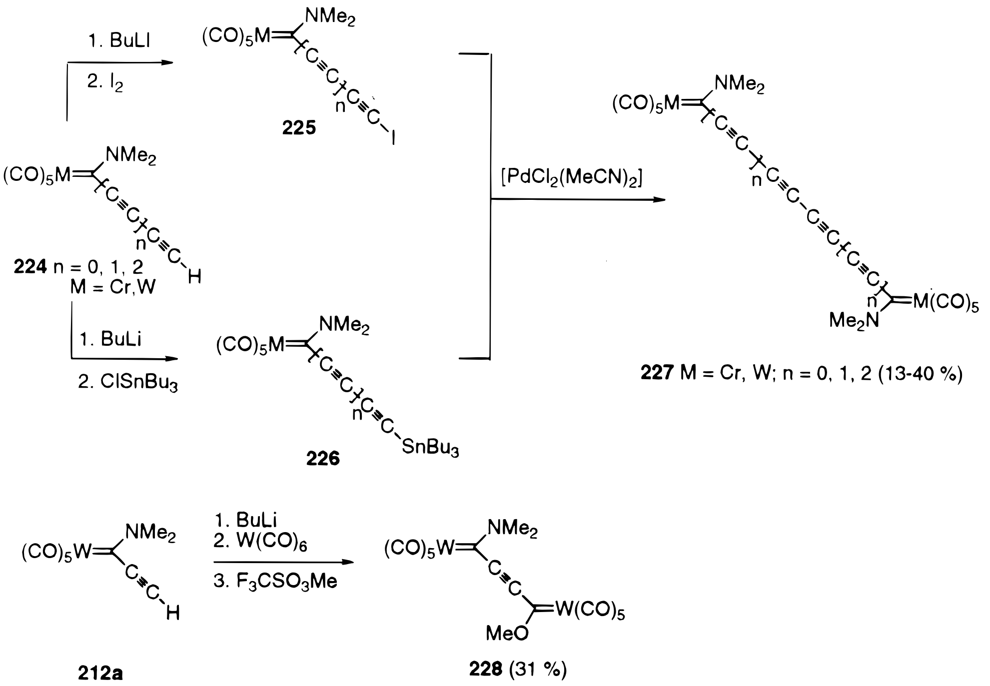
Strictly speaking the processes drawn in eqs 17 and 18 are closely related to the Fischer procedure, although the mechanism of the process may be quite different. One very general route to different metalloxycarbenes starts from (η^4-diene)metallocenes and metal carbonyls, and several dimetallic metalloxycarbenes have been prepared by this route (eq 19).[102]



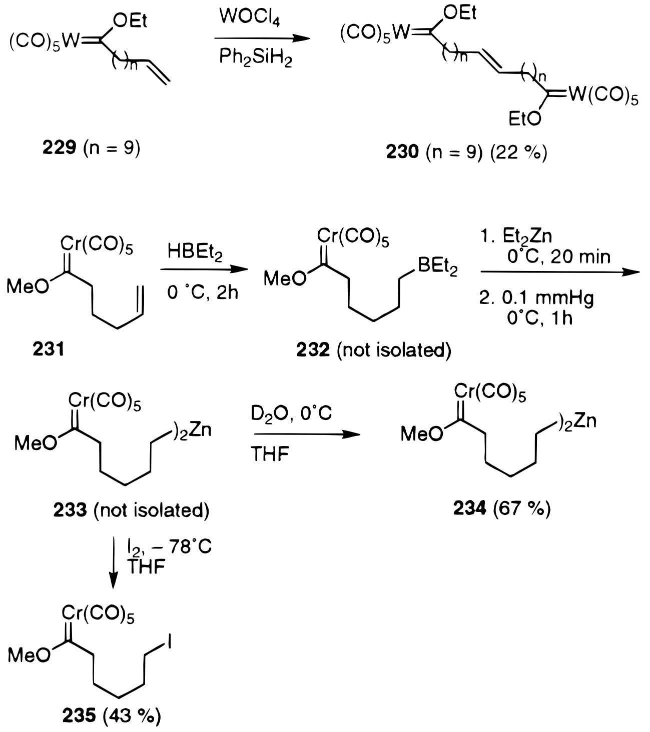
(19)

$ML_n = Cr(CO)_5$; $Mo(CO)_5$; $W(CO)_5$; $Fe(CO)_4$; $Fe(CO)_3PPh_3$; $Rh(CO)Cp$; $Co(CO)Cp$; $Co(CO)(\eta\text{-}C_5H_4Cl)$; $Ni(CO)_3$; $Zr(CO)Cp_2$; $Hf(CO)Cp_2$; $V(CO)_3Cp$

Scheme 46

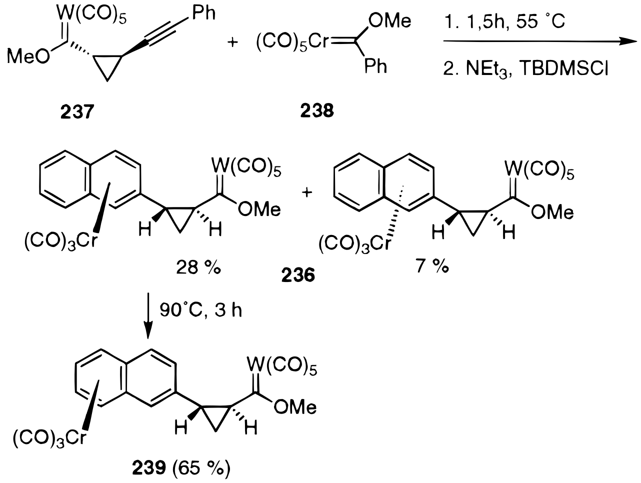


Scheme 47



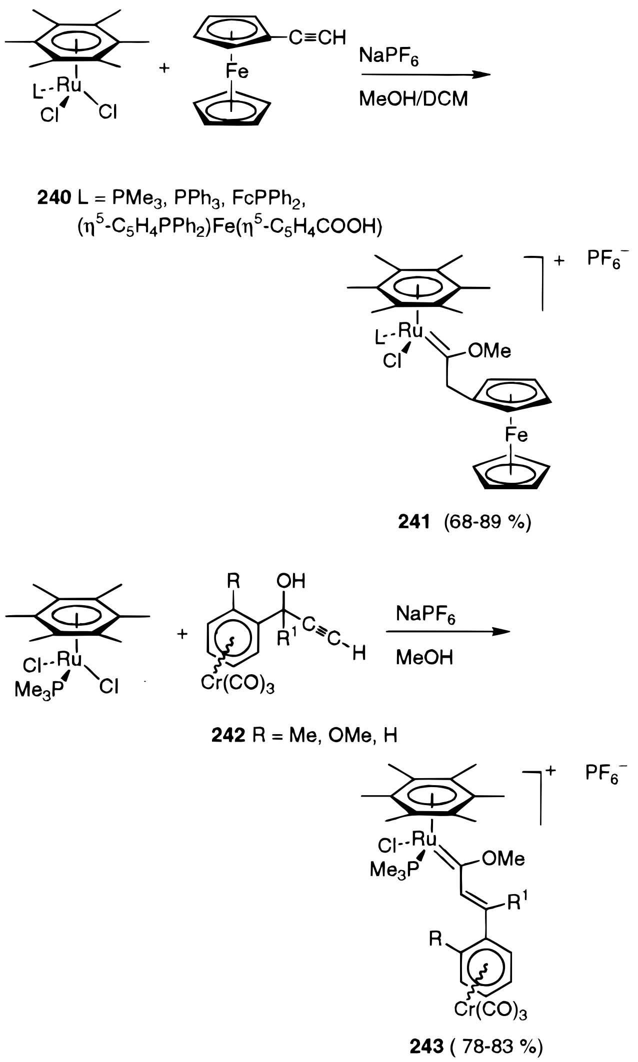
Other class II heterodimetallic boron group 6 carbene complexes have been also prepared following the standard reaction of a lithium ate complex and an electrophilic boron derivative. Thus, ate complex **269** reacted with Bu_2BCl to form the new complex **270**.[103] The reaction of complexes **271** with different dialkylchloroboranes **272** yielded the expected complexes **273** that were unstable and decomposed upon warming by loss of metal to form oxaborolane or oxazaborolydine derivatives via intramolecular C−H insertion (see below for a detailed discussion).[104] Unstable difluoroboroxymolybdenum Fischer carbene complexes **274** were obtained by trapping the ate complexes **275** with $BF_3.OEt_2$.[105] Group 6 boroxycarbene complexes **276** were prepared in a single step by addition of the dilithium amidures derived from **277** to the corresponding $M(CO)_6$, followed by quenching of the resulting ate complex with $BF_3.OEt_2$. The rich chemistry of complexes **276** will be discussed below (Scheme 54).[106]

Scheme 48



Cyclic heterodimetallic carbene complexes **278** having the structural feature M=C(R)OM′ were obtained by reacting $[Ph_3GeMn(CO)_5]$ with MeLi. Treatment of the thus formed Li salt **279** with Et_3OBF_4 yields the typical ethoxycarbene complex **280**. Acidic quenching of the ate salt **279** provokes the evolution of benzene resulting in the formation of complex **278**. Complex **281**, obtained by reaction of $[Me_3GeMn(CO)_5]$ with MeLi, loses spontaneously methane to yield **282**. The remarkable ease of cleavage can be attributed to a four center process, following the initial formation of an hydroxycarbene

Scheme 49



240 L = PMe_3, PPh_3, $FcPPh_2$, (η^5-$C_5H_4PPh_2$)Fe(η^5-C_5H_4COOH)

241 (68-89 %)

242 R = Me, OMe, H

243 (78-83 %)

complex.[107] Further evidence demonstrates that complex **282** is in equilibrium with its dimer **283a**. Complex **284**, the Re analogue of complex **282**, was prepared. It was shown to be also in equilibrium with its dimer **283b**. This last complex was characterized by X-ray difraction (Scheme 55).[108]

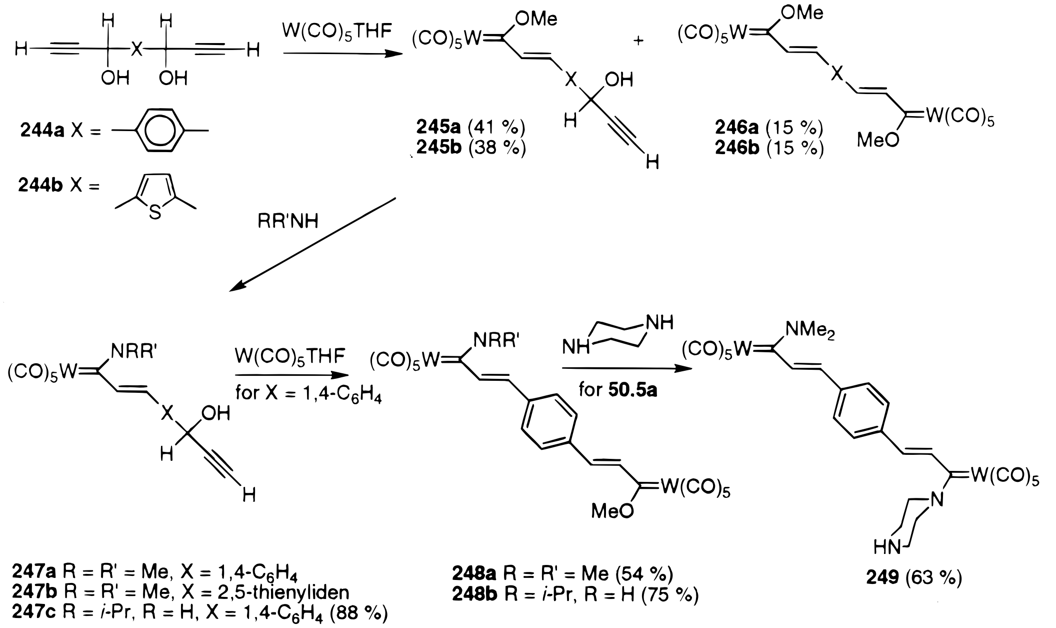
A number of complexes **285** with a selenium moiety bonded to the carbene carbon were prepared by interchange of the alkoxy group of complexes **113** with CH_3SeH. The analogous reaction with PhSeH gave complexes **286** instead of the expected derivative analogous to **285** (Scheme 56).[109]

Chromium carbenes **287a,b** having an additional Fe nucleus at the carbon side-chain attached to the heteroatom were prepared in good yields starting from ate complex **288** by sequential acylation with acetyl bromide and reaction with diene−alcohol complexes **289** (see Scheme 57).[110]

A different approach to dimetallic carbene complexes rests in joining two equal units of carbene by their heteroatom substituents, either directly or through a carbon chain (see Scheme 58). The first example uses dicyclohexylcarbodiimide (DCC) to join two molecules of hydroxycarbene complexes **290**. These reaction formed dinuclear hydroxycarbene anhydride complexes **291**.[111,112] When tungsten hydroxycarbene complex **292** was used in this chemistry, the corresponding carbene−carbyne homodimetallic complex **293** was obtained instead of the expected anhydride. This property was used to prepare the mixed chromium−tungsten carbene−carbyne complex **294** by reacting complexes **290** (R = *p*-MeC_6H_4) and **292** with DCC.[113]

Aminolysis of complex **107** with diamines **295** in a molar ratio of 2:1 formed the amino-bridged diaminocarbenes **296** when aliphatic diamines were used. Aromatic diamines such as benzidine or *o*-tolidine gave only the corresponding monocarbenes **297**. This difference in behavior was explained by the reduction in the basicity of the free amino group in the aromatic diaminomonocarbene complexes **297**, which is caused by the action of the strongly electron-

Scheme 50



244a X =

244b X =

245a (41 %)
245b (38 %)

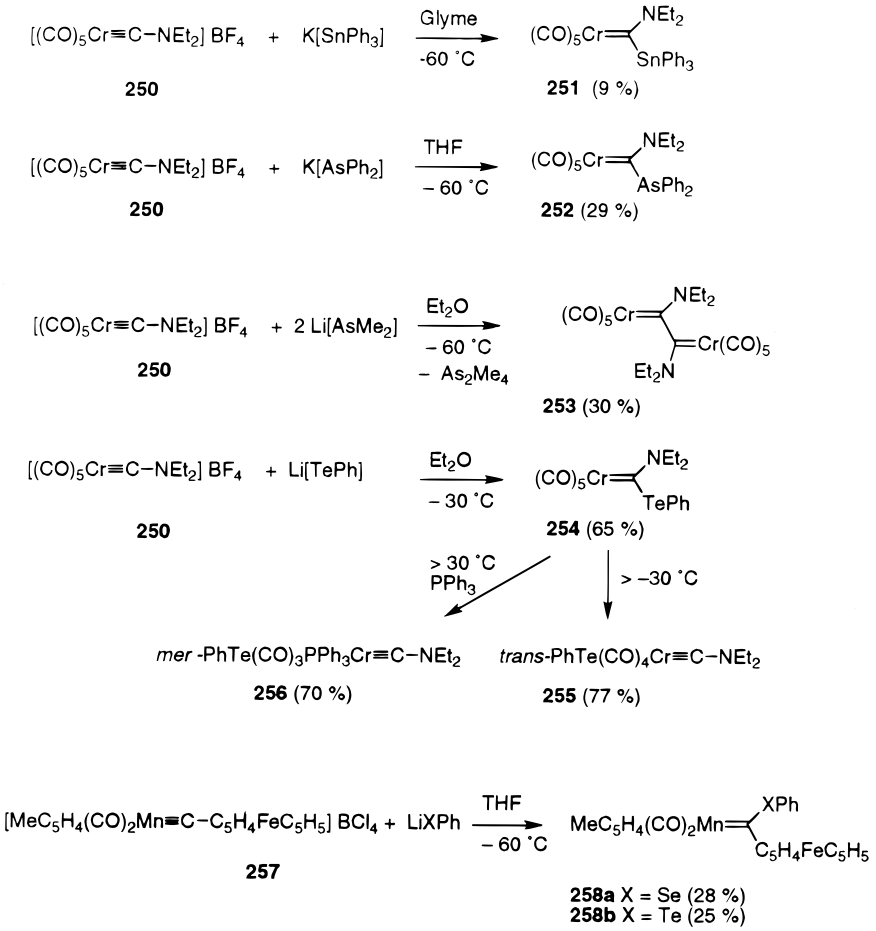
246a (15 %)
246b (15 %)

247a R = R' = Me, X = 1,4-C_6H_4
247b R = R' = Me, X = 2,5-thienyliden
247c R = *i*-Pr, R = H, X = 1,4-C_6H_4 (88 %)

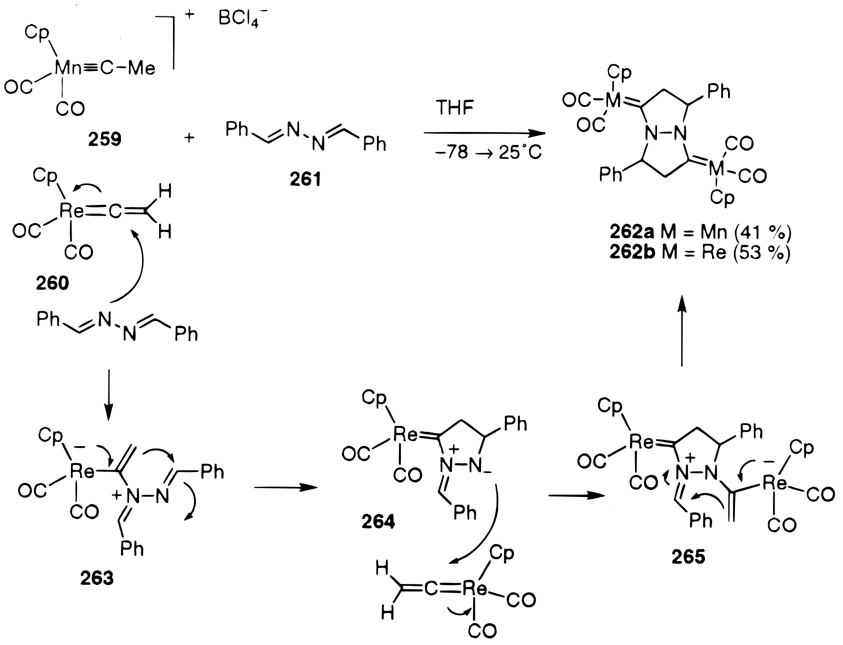
248a R = R' = Me (54 %)
248b R = *i*-Pr, R = H (75 %)

249 (63 %)

Scheme 51



Scheme 52

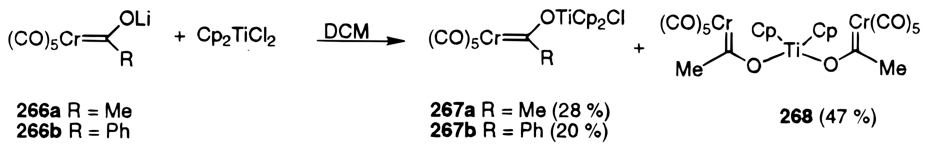


withdrawing aminocarbene group on the free amino moiety through the aromatic system.[114] The activation of the amonium salt **298** with acetyl bromide followed by quenching with different diols lead to alkoxy-bridged dialkoxycarbenes **299**. These compounds have been profusely used in the preparation of cyclam derivatives (see below) (Scheme 59).[115,116]

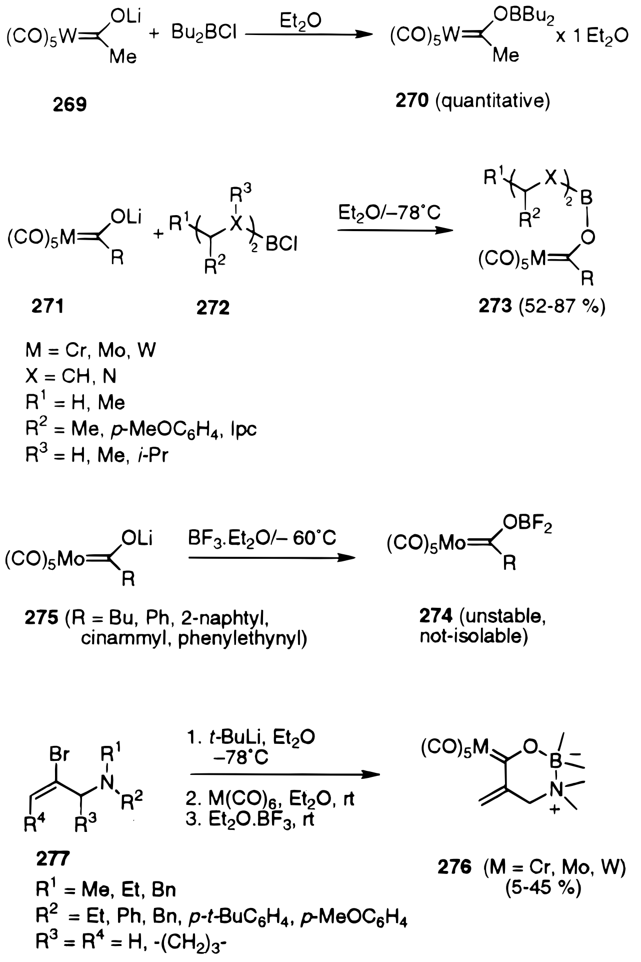
Enantiomerically pure complexes **300** and **301** have been prepared from salt **288** following a similar procedure and used in the preparation of optically active biaryl derivatives (see below) (Scheme 59).[117]

Bis-alkylation of aminocomplexes **302** also formed bis-carbene complexes **303**. These compounds were not stable and evolve to annulated mononuclear

Scheme 53



Scheme 54

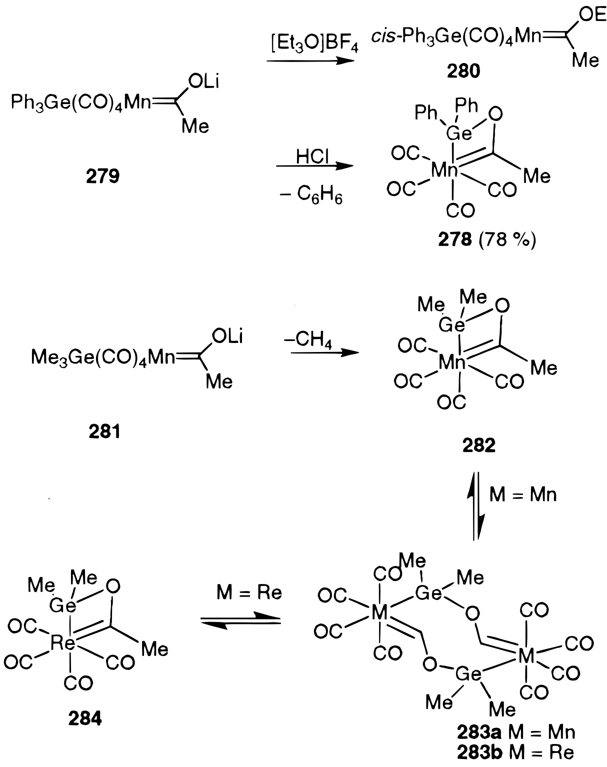


carbene complexes **304**. Thus, compounds **302** are deprotonated, and the resulting anions **305** experiments an intramolecular addition reaction to the remaining carbene carbon to form **306**. This intermediate losses the metallic moiety to form **304** after a 1,3-hydrogen shift (Scheme 60).[118]

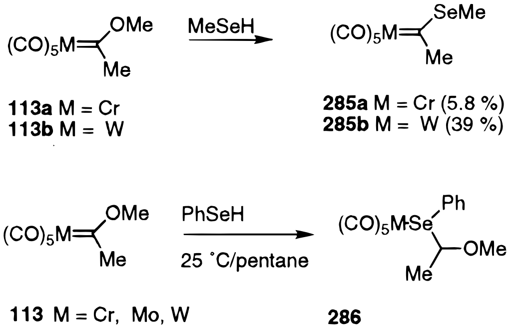
IV. Class III Di- and Polymetallic Metal Carbenes

Class III di- and polymetallic metal carbenes have the metal centers directly joined, either by a metal–metal bond or through a bidentate ligand (Figure 2E,F). As stated at the beginning of this review, the first class III dimetallic carbene **2** was prepared in 1963 by King[6] by reacting sodium pentacarbonyl manganese(–I) and either 1,3-dibromopropane or 4-butyryl chloride, although its true carbene nature was not recognized until 1970 when Casey corrected structure **3** formerly proposed by King.[7] Meanwhile, Fischer reported that the reaction of [$Mn_2(CO)_{10}$] with RLi (R = Me, Ph) followed by treatment of the lithium salts **307** with [R^2_3O]BF_4 yielded the first class III homodimetallic carbenes **308** truly characterized (Scheme 61).[119,120] Alkoxy–ammonia interchange in complex **308a** yielded amino complex **309**. However, the use of *N*,*N*-dimethylhydrazine instead of ammonia led to [$(CO)_9Mn_2NCMe$], which lacks the carbene ligand. $Re_2(CO)_{10}$ and $Tc_2(CO)_{10}$ were also used to prepare the corresponding homodimetallic monocarbenes **310a**–**d**. Heterodimetallic monocarbenes were prepared from $MnRe(CO)_{10}$ and PhLi followed by alkylation with Me_3OBF_4 and were obtained as a mixture of the two possible monocarbenes.[121]

Scheme 55

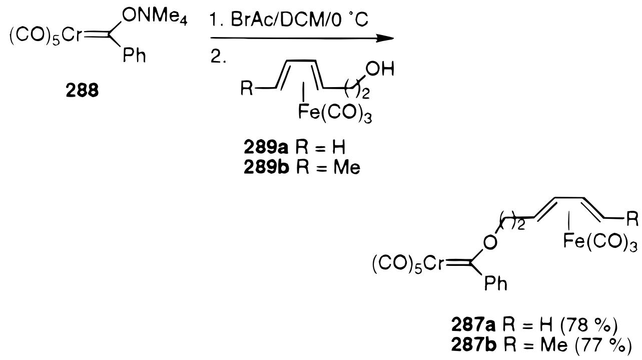


Scheme 56

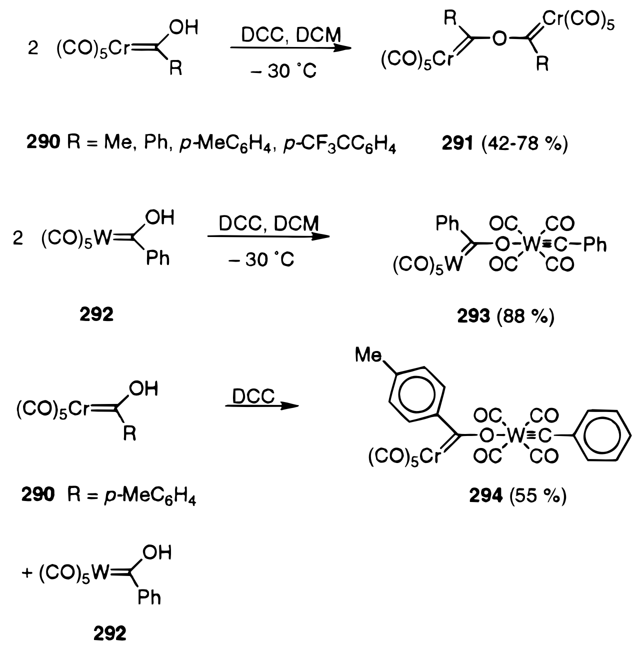


Further modifications of the basic structure of complex **2** were done by alkylation of the anions α to the carbene carbon with methyl fluorosulfonate, taking advantage of the acidity of these hydrogens.[122,123] Acylation of the anion derived from **2** with

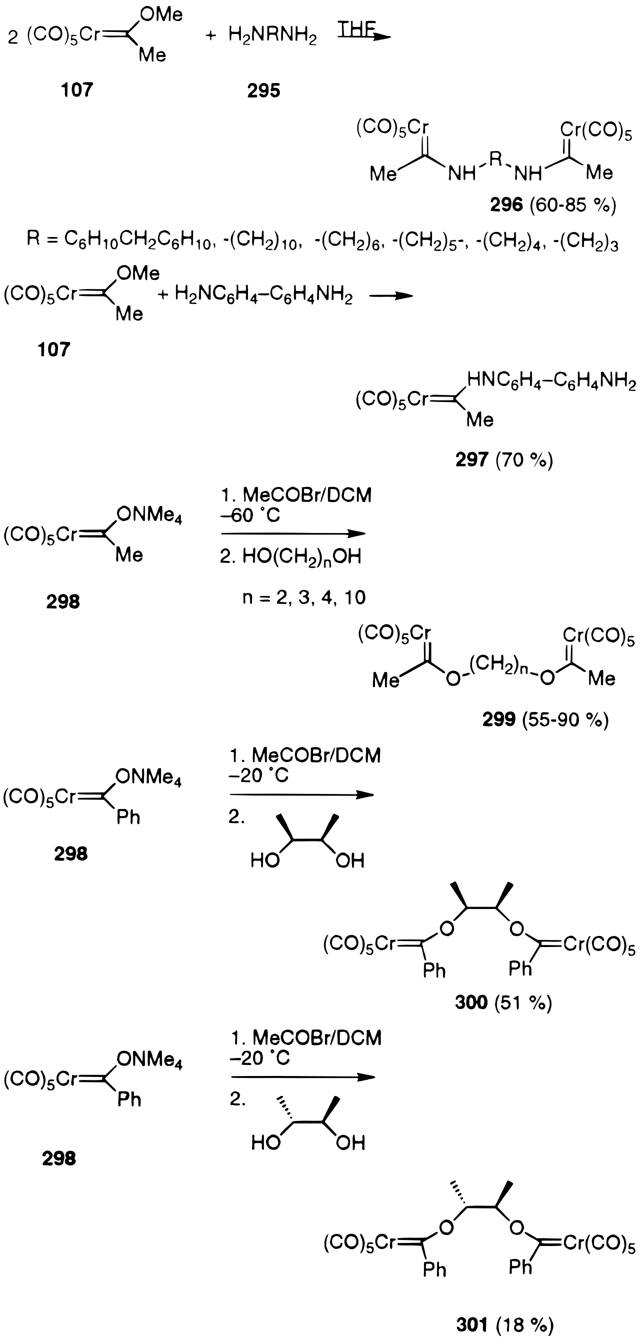
Scheme 57



Scheme 58



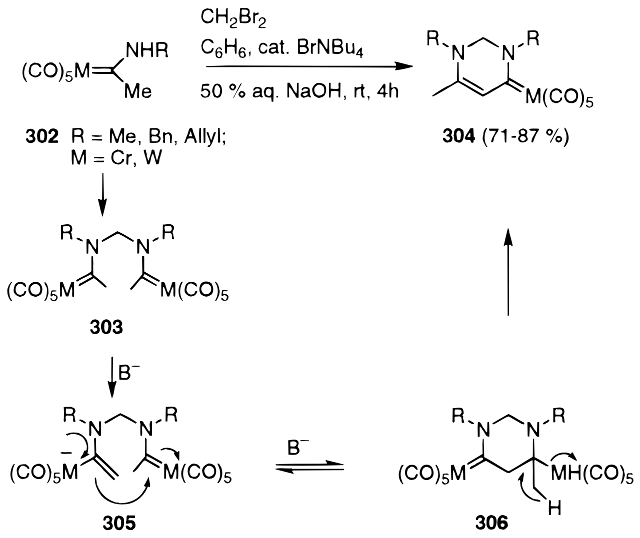
Scheme 59



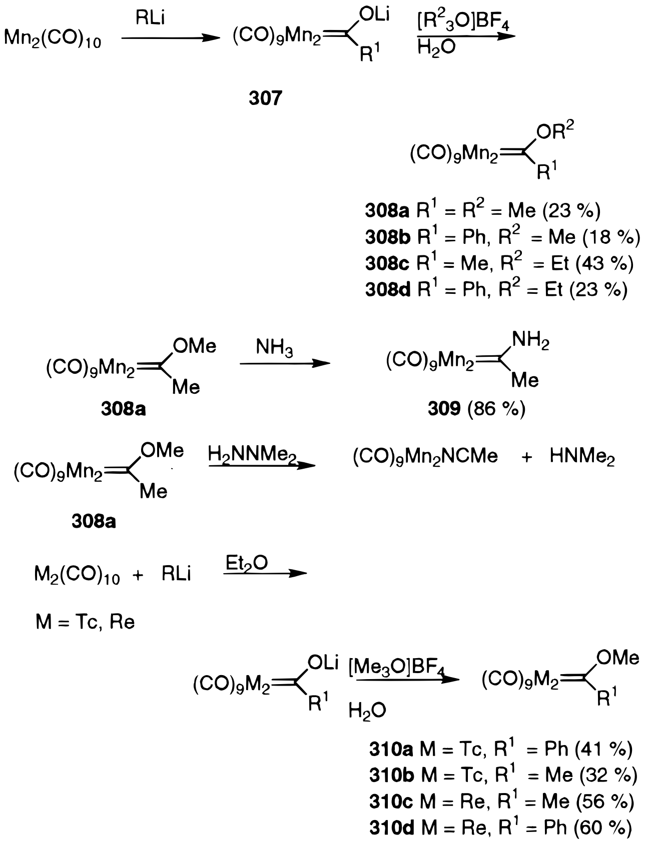
acetyl chloride lead to the unstable homodimetallic carbene **311**. This compound evolves to mononuclear carbene complex **312** by loss of the $[Mn(CO)_5]^-$ fragment (Scheme 62). Deuteration and methylation were achieved from the anion derived from **2** and DBr and $MeSO_3F$ to yield complexes **313a,b**.

The synthesis of complex **314** was developed by Casey by reacting $[Mn(CO)_5]^-$ with $[MeMn(CO)_5]$ in the presence of $[Me_3O]BF_4$. Apparently, the reagents are in equilibrium with the acylate **315**. The equilibrium is displaced to the final product **314** by action of the alkylating agent.[124] These results allow to rationalize the formation of complex **2** during the reaction of 1,3-dibromopropane and $[Mn(CO)_5]^-$. The initial attack of $[Mn(CO)_5]^-$ would form the intermediate alkylmanganese compound **316** that reacts with a new molecule of $[Mn(CO)_5]^-$ to give a dinuclear acylmanganese anion **317**. The anion is trapped by intramolecular alkylation of the acyl oxygen atom by the alkyl bromide (Scheme 63). Alternatively, the reaction of $[NaRe(CO)_5]$ with $[RMn(CO)_5]$ (R = Me, Ph), followed by alkylation with $MeOSO_2F$ yielded the heterodimetallic monocarbenes **318**.[125,126] Nevertheless, the reaction of metal carbonyl anions with methyl metal carbonyl compounds is not a general route to prepare homo- and heterodimetallic monocarbene complexes.[126] It was determined that the formation of acyl anions such as **315** or **317** and their further trapping with an alkylating agent was only feasible for the reactions of $[RMn(CO)_5]$ (R = Me, Ph) with $[Mn(CO)_5]^-$ or $[Re(CO)_5]^-$. These reactions produced complexes **318a,b** while highly nucleophilic complexes such as $[CpFe(CO)_2]^-$ reacted with $[MeMn(CO)_5]$ by methyl transfer. Other methyl metal carbonyls including $[CpMo(CO)_3Me]$, $[CpFe(CO)_2Me]$, and $[CpW(CO)_3Me]$ were not reactive. It should be noted that compounds **318a,b** have the carbene ligand attached to the Re center rather than to Mn. According to the mechanism proposed, the reaction would produce a dinuclear carbon complex with the carbene ligand bonded to Mn, **319**. Formation of the observed product may be due to a rearrangement of

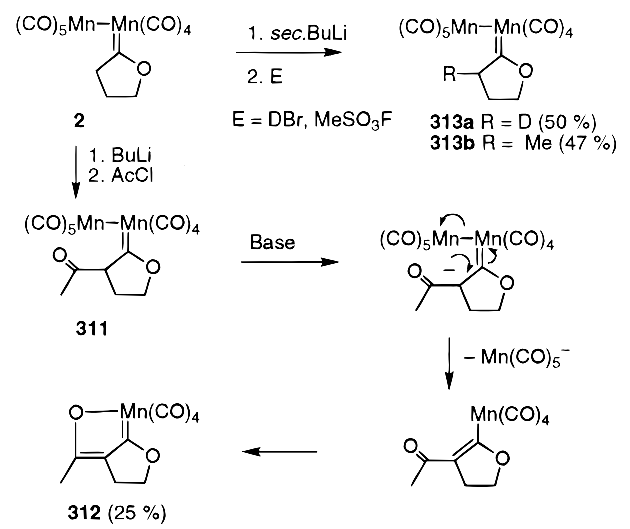
Scheme 60



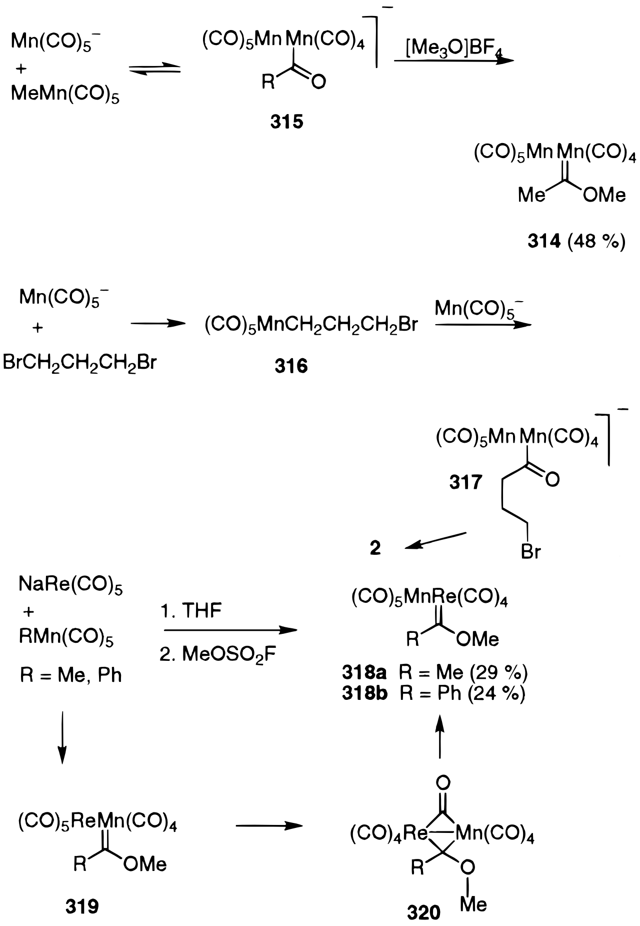
Scheme 61



Scheme 62



Scheme 63

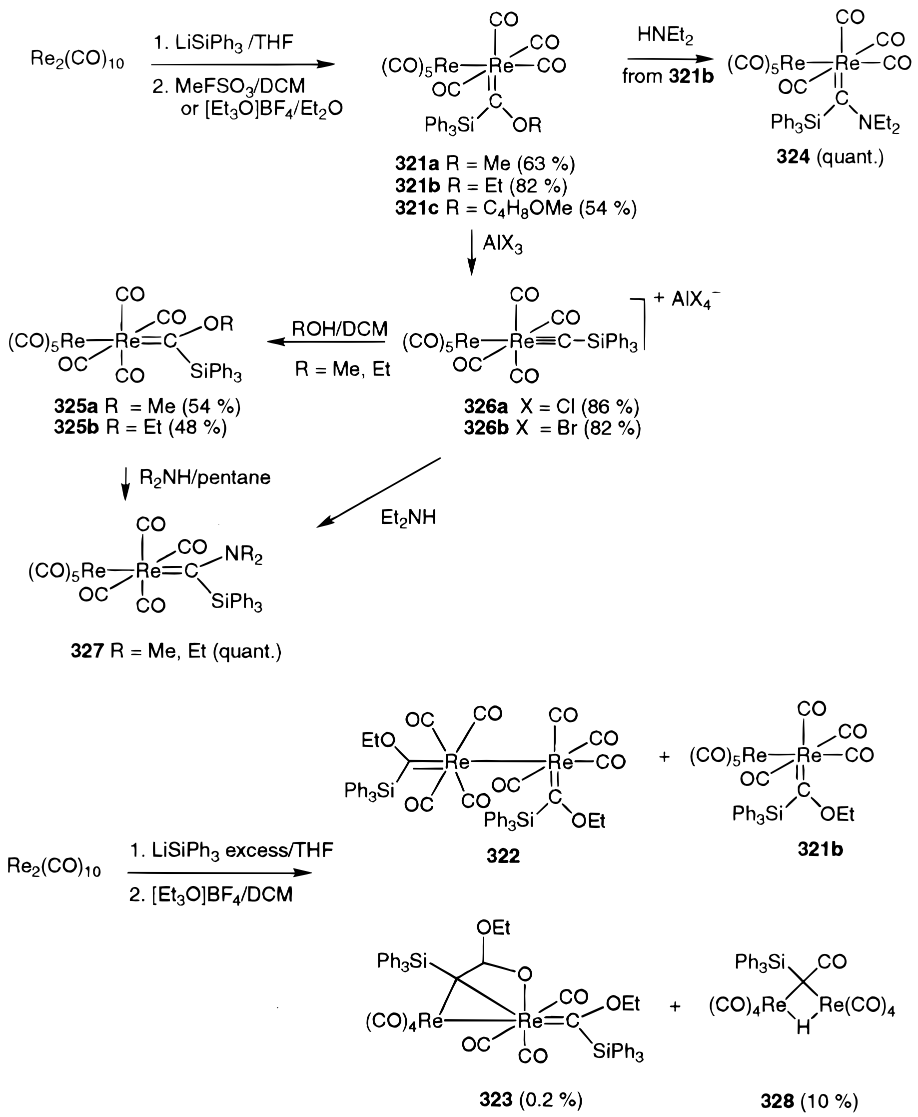


compound **319** to **318** probably through the intermediate **320**.

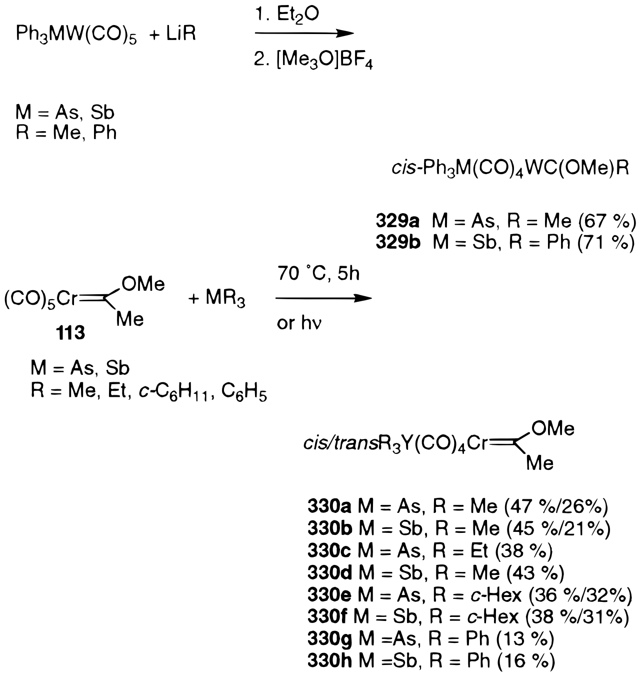
Complexes **321**–**323** having a silicon moiety attached to the carbene carbon have been prepared following the standard Fischer procedure. Thus, reaction of $Re_2(CO)_{10}$ with $LiSiPh_3$ yields after alkylation complexes **321a**–**c**. Complex **321b** gives compound **324** upon aminolysis. Interestingly, attempts to prepare compounds **321a**–**c** by the addition of alcohols to the corresponding carbyne complexes **326a,b** produced the axial complexes **325a,b**.[127] An analogous result was obtained when Et_2NH was used instead of alcohols. Aminocarbenes **327** having an axial configuration were formed by aminolysis of **325**. The reaction of $Re_2(CO)_{10}$ with an excess of $LiSiPh_3$ and subsequent alkylation by Et_3OBF_4 yields not only complex **321b** and the expected bis-carbene **322** but also a dinuclear carbene complex **323**, in which both Re atoms are bridged by a μ-carboethoxy(silyl)alkylidene ligand and the octacarbonyl[μ-(triphenylsilylacyl)ketenyl](μ-hydrido)dirhenium **328** (Scheme 64).[128,129]

Heterodimetallic monocarbenes **329** with the second metal center being a main group metalloid

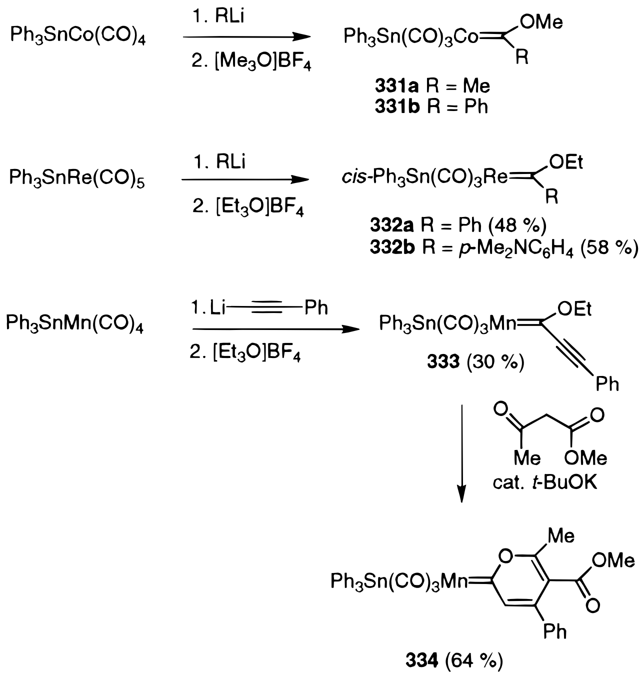
Scheme 64



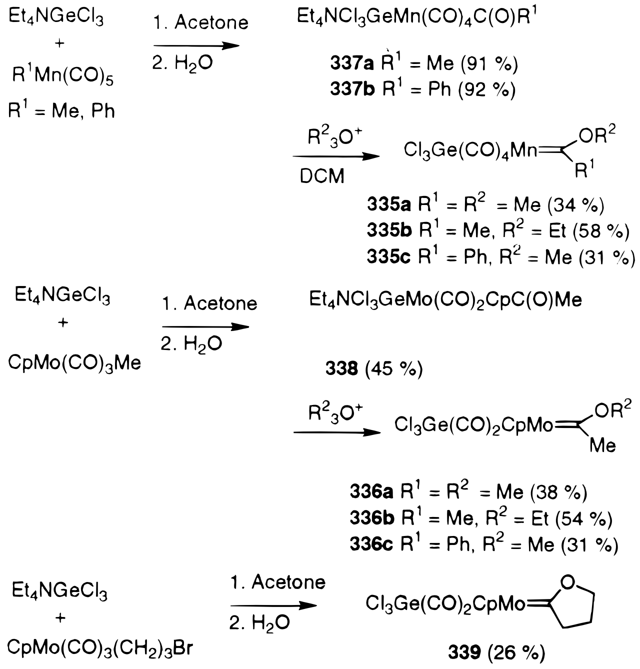
Scheme 65



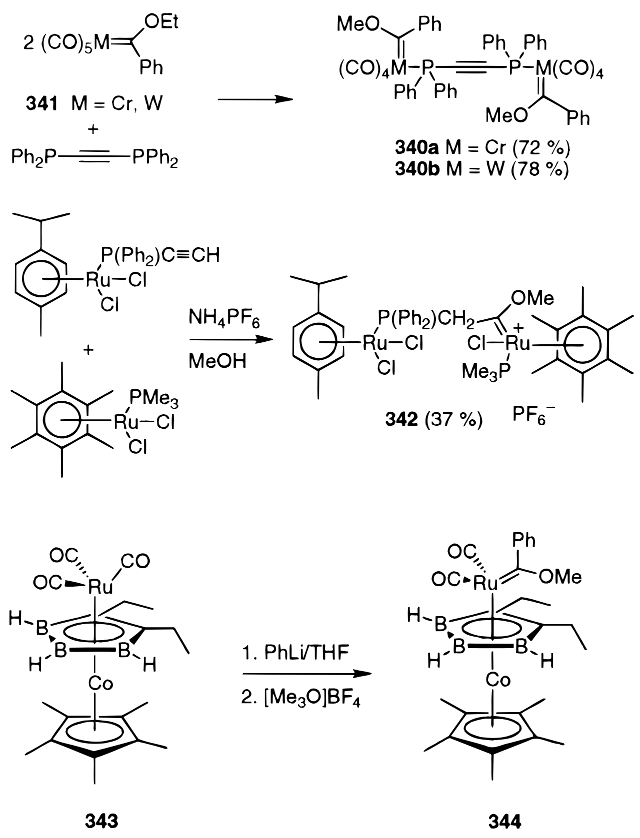
Scheme 66



Scheme 67

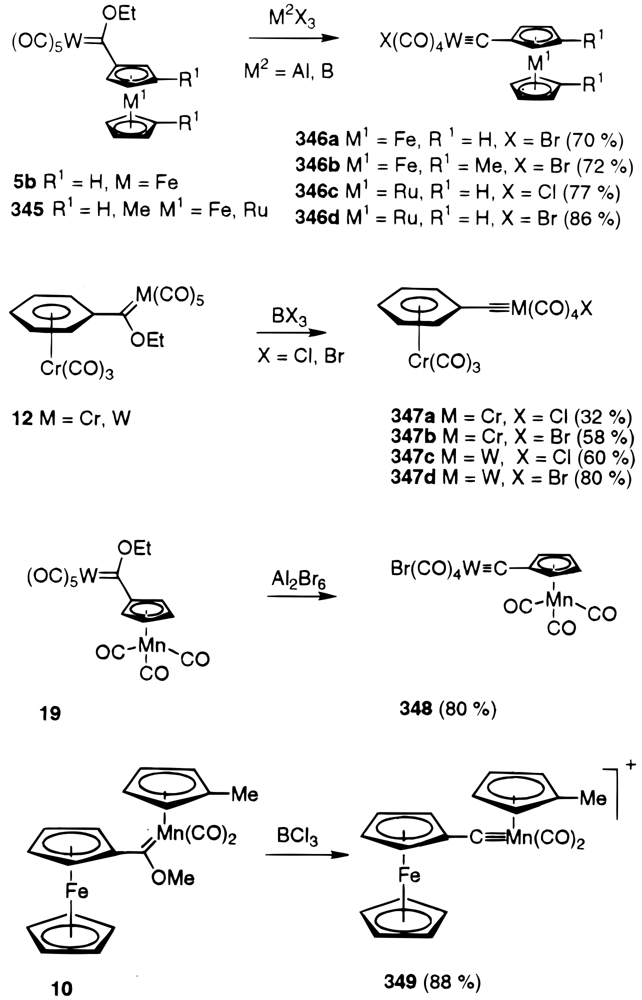


Scheme 68



element were prepared as early as 1969 from [$Ph_3AsW(CO)_5$] or [$Ph_3SbW(CO)_5$] following the standard Fischer procedure (see Scheme 65). Both complexes were the cis-isomers.[130] An alternative synthesis of this kind of complexes was the ligand substitution on preformed monocarbene complexes. This process is highly efficient with YR_3 (Y = As, Sb), but it is not applicable to BiR_3 (R = Me, Et, *c*-Hex). In fact, the reaction of complex **130** with trialkylbismute derivatives lead to $(CO)_5CrBiR_3$ instead of the corresponding dimetallic monocarbene.[131]

Scheme 69

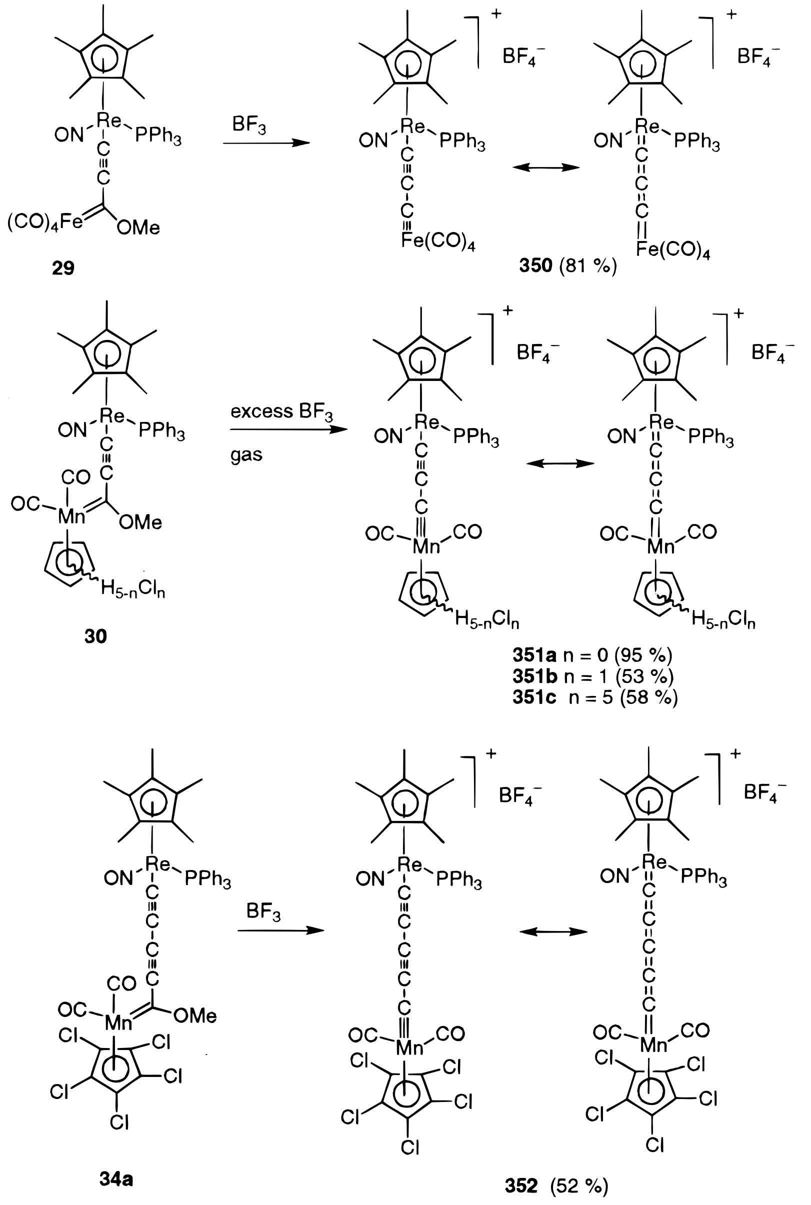


Heterodimetallic SnCo **331**, SnRe **332,** and SnMn **333** monocarbene complexes have also received wide attention. Thus, complexes **331a,b** have been prepared by reaction of [$(CO)_4CoSnPPh_3$] and the corresponding lithium reagents followed by alkylation.[132] *cis*-SnRe complexes **332a,b** have been prepared following an analogue procedure from [$(CO)_5ReSnPPh_3$].[133] The SnMn complex **333** was prepared from lithium phenylacetylide and [$(CO)_5MnSnPPh_3$]. This complex was elaborated to pyranylidene complex **334** by reaction with methyl 4-oxobutanoate in the presence of a catalytic amount of base.[134] Complexes **331**–**333** were obtained always as cis-isomers (Scheme 66).

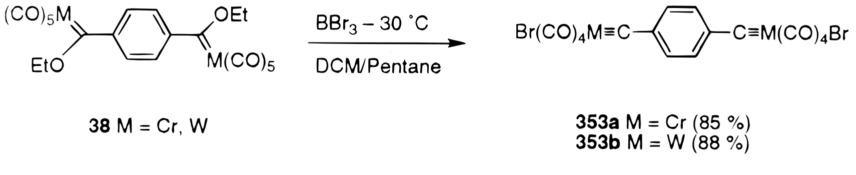
Preparation of complexes **335** and **336** by reaction of Et_4NGeCl_3 with [$MeMn(CO)_5$], [$PhMn(CO)_5$], or [$CpMo(CO)_3Me$] followed by alkylation of the resulting trichlorogermylacyl carbonyl metallate ions **337** and **338** has been also reported.[135] The cyclic heterodimetallic monocarbene complex **339** was obtained directly by reaction of Et_4NGeCl_3 with $CpMo(CO)_3(CH_2)_2Br$ (Scheme 67).

Dinuclear carbenes having both metal nuclei joined by a bidentate ligand are the scarcest and have been prepared following the different methods above. Dötz reported the formation of complexes **340** by reaction between complexes **341** and bis(diphenylphosphino)-

Scheme 70



Scheme 71



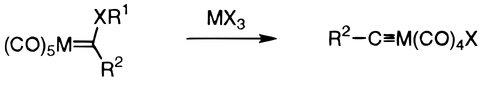
acetylene under controlled conditions.[136] The reaction of [(η^6-arene)$RuCl_2(PPh_2CCH)$] with [$(C_6Me_6)(PMe_3)RuCl_2$] in the presence of methanol yielded the dimetallic cationic complex **342**.[137] Application of Fischer synthesis to dimetallic carborane **343** allowed us to obtain the expected trimetallic carbene complex **344** (Scheme 68).[138]

V. Reactivity

Compared to the myriad of reactions that have been reported for carbene complexes with a single metal center, the reactivity as well as the applications to organic synthesis of carbenes having more than one metal nucleus have been scarcely investigated. Nevertheless, as will be discussed below, some general trends may be extracted from the available data.

A. Synthesis of Di- and Polymetallic Carbyne Complexes

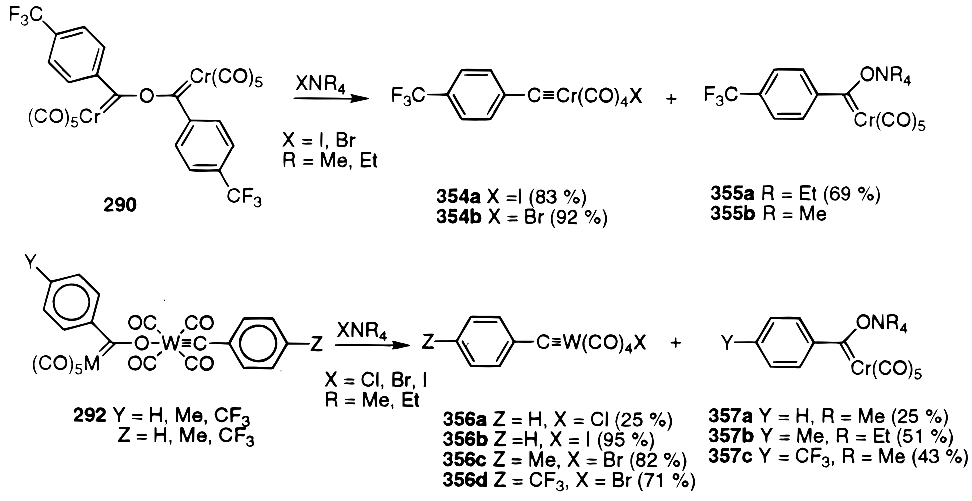
The rearrangement carbene–carbyne (eq 20) is a



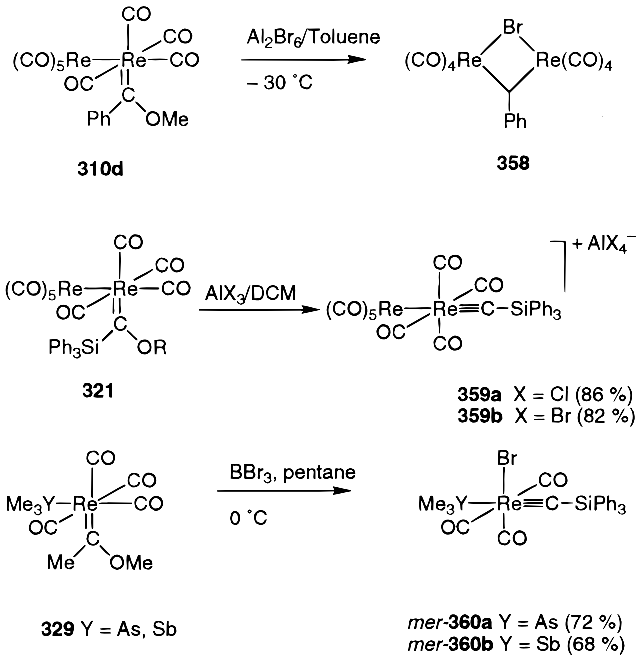
$$(CO)_5M{=}C(XR^1)(R^2) \xrightarrow{MX_3} R^2{-}C{\equiv}M(CO)_4X \qquad (20)$$

well-known process[139] taking place in the presence

Scheme 72



Scheme 73

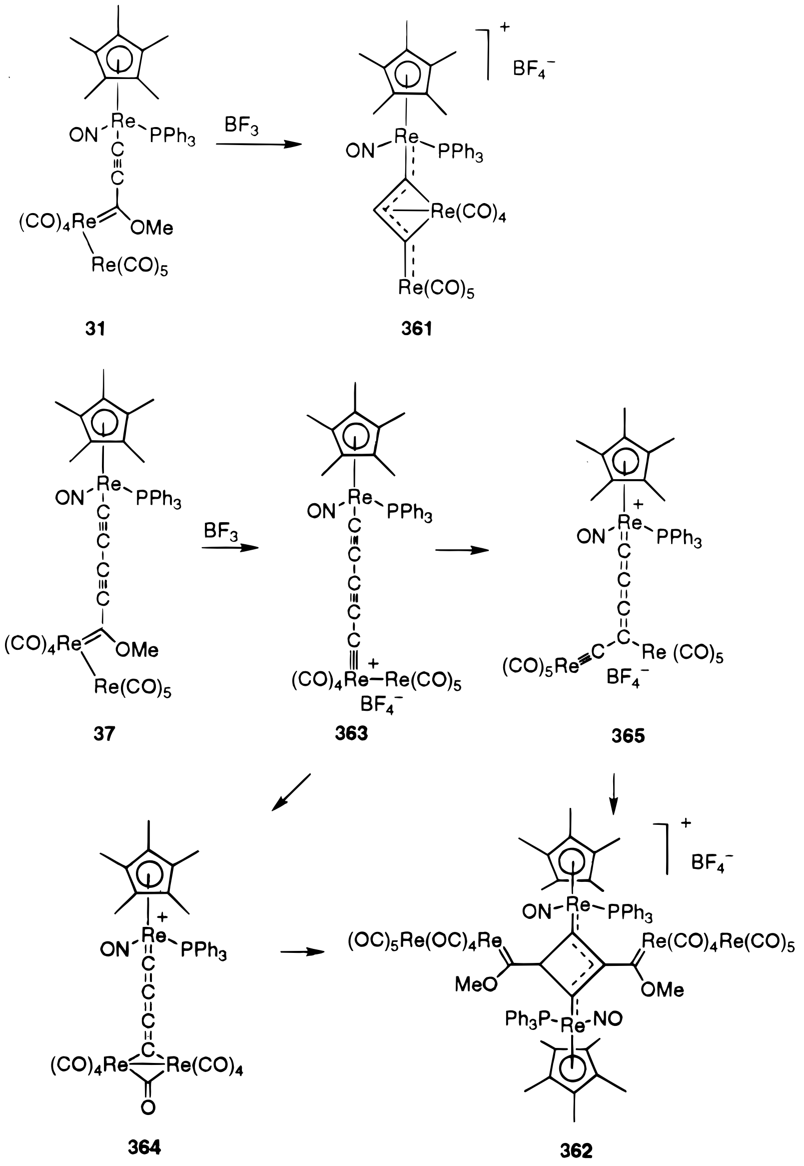


of a Lewis acid and acid chloride or, in general, a reagent capable to inhibit the stabilizing donation of the lone electron pair of the heteroatom bonded to the carbene carbon. This rearrangement has been applied to monocarbene complexes having more than one metal nucleus, and in most cases, the reaction occurs uneventfully, despite the presence of the additional metal centers. This fact was first demonstrated in the reaction of complex **5b** with Al_2Br_6 to yield the raspberry-red *trans*-bromo(tetracarbonyl)ferrocenylcarbyne tungsten complex **346a**.[140] Following this early example, other metallocene–carbene complexes **345** were also converted to the corresponding *trans*-carbyne complexes **346** by treatment with boron and aluminum halides.[10] Complexes **12** having an arenetricarbonyl group[11] as well as complexes **19** with a Mn nucleus[14] also formed the corresponding carbyne complexes **347** and **348**, by an analogous treatment. Heterodimetallic Mn carbene complex **10** formed the expected cationic carbyne complex **349** upon treatment with BCl_3 (Scheme 69).[93]

This chemistry has been used in the preparation of different conjugated carbyne complexes in the search of new forms of coordinated carbon. Complexes of class I lacking additional M–M bonds at the carbene moiety are converted to the corresponding carbyne dimetallic complexes as in the case of Fe or Mn heterodimetallic monocarbenes **29**, **30**, and **34a** by the action of an excess of BF_3 gas. Bond distances obtained from **351a** by X-ray diffraction analysis confirm that these complexes are best represented by a cumulene structure than for a conjugated carbyne (Scheme 70).[19,23,24]

Homodimetallic bis-carbynes have been obtained from the corresponding bis-carbenes. Thus, bis (*trans*-halogenotetracarbonyl)metallocarbynes **353** have been prepared by reaction of bis-carbenes **38** with BBr_3 (Scheme 71).[25,141] From the IR and Raman spectra of complexes, it was deduced that the carbyne frag-

Scheme 74



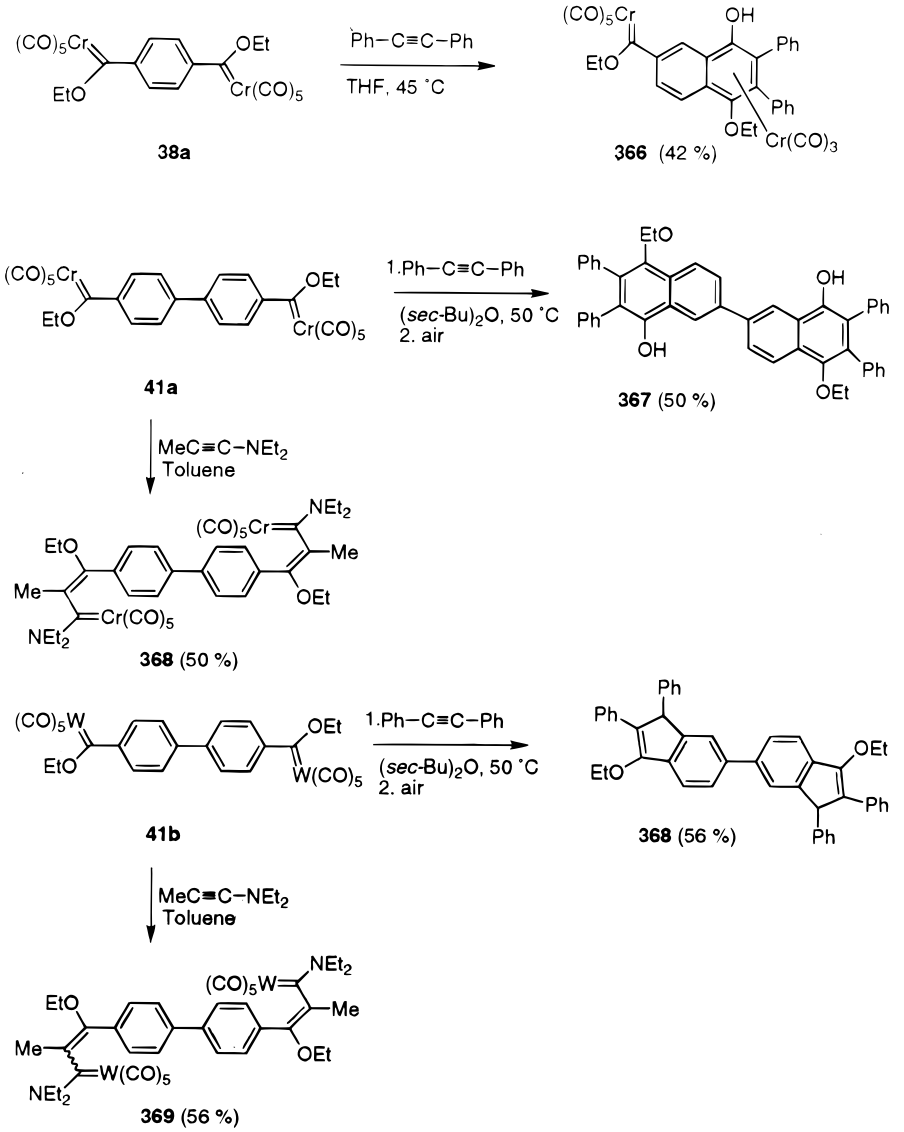
ment influences the π-electronic distribution of the ring by placing the π-electrons on the bonds parallel to the axis of the complex molecule.[141]

Data about the behavior of carbene complexes of type II toward Lewis acids are not available when the metal nuclei are separated by a carbon chain. However, bis-carbene complex **290** ($R = CF_3$) formed monocarbyne complexes **354** together with the ammonium salt **355** by treatment with ammonium halides.[111] Treatment of complexes **292** with ammonium halides also lead to the same mixture of complexes: the mononuclear carbynes **356a**−**d** and the ammonium salts **357a**−**c** (Scheme 72).[112,113]

The behavior of carbenes of class III in the carbene → carbyne rearrangement appears to be more metal-dependent. Thus, reaction of dirhenium monocarbene complex **310d** with Al_2Br_6 resulted in the expulsion of the MeO group, elimination of a CO molecule, and entry of a Br atom into the complex to yield μ-bromo-μ-phenylmethylidyne-bis(tetracarbonyl)rhenium, **358**, instead of the corresponding carbyne complex (Scheme 73).[142] The reaction of other dimetallic monocarbene rhenium complexes **321** with AlX_3 resulted in the formation of heterodimetallic carbyne complexes **359** with retention of the silicon moiety.[127] Series of heterodimetallic chromium carbyne complexes **360** have been also prepared by reaction of the corresponding heterodimetallic monocarbene complexes *cis*-**329** and boron trihalides.[143]

Complex **31** behaves like its analogue **310d**. Instead of the corresponding carbyne complex, the rearranged product **361** was obtained.[20,21] A similar rearrangement was proposed for the reaction of complex **37** and BF_3 to yield a new, air stable, orange-red powder for which structure **362** was proposed.[19] The proposed mechanism for the rearrangement of **37** to **362** involved the initial abstraction of the MeO group by the BF_3 to yield the desired carbyne complex **363**. Two alternative pathways may be written from **363** to explain the rearrangement of the $Re(CO)_5$ moiety. One possibility would be isomerization to a species in which the C_3 terminus bridges the Re−Re bond, such as **364**. Another would be a 1,3-sigma-

Scheme 75



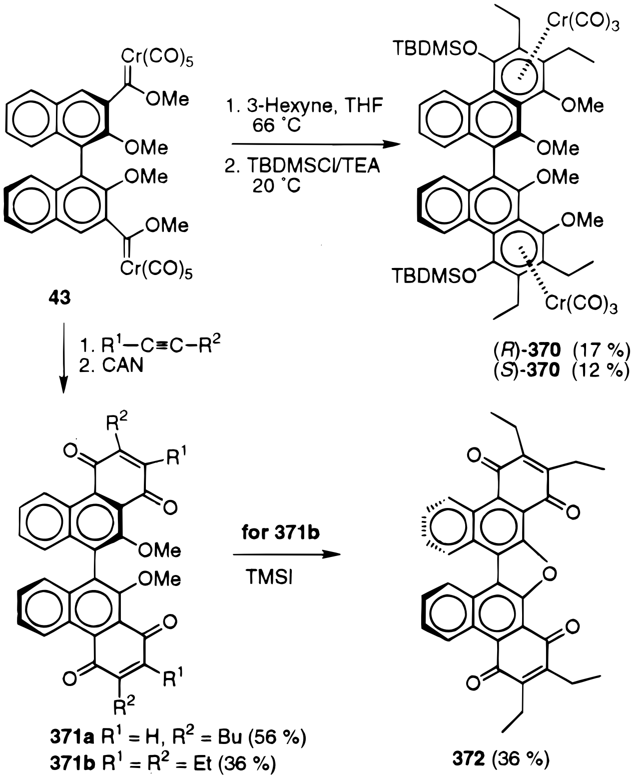
tropic shift of the Re(CO)$_5$ group in **363** to yield **365** (Scheme 74).

B. Benzannulation and Related Processes

The reaction of an α,*β*-unsaturated carbene complex with an alkyne to yield a hydroquinone derivative, known as the Dötz reaction, is perhaps one of the best studied reactions of chromium carbene complexes.[3,5] The nature of the reaction products is heavily dependent on different factors, like the nature of the substituents, the solvent, etc. The outcome of the reaction of homo- and heterodimetallic carbene complexes with alkynes is more influenced by the presence of the second metal center than any other reaction of these compounds. One of the first examples using a homodimetallic chromium biscarbene to obtain a monohydroquinone derivative was the reaction of complex **38a** with an excess of tolan (Scheme 75). Compound **366**, which retains a carbene moiety, was obtained. Formation of the expected double benzannulation products was not observed. The analogous tungsten bis-carbene complex did not yield any identifiable product under analogous reaction conditions. In contrast, biphenyl-derived bis-carbene complex **41a** yielded the expected double benzannulation product **367** upon reaction with diphenylacetylene.[144] When 1-diethylamino-1-propyne was employed, complex **368** derived from the insertion of the alkyne into the M=C bond was obtained in good yields.[24] Tungsten bis-carbene **41b** reacted also with tolan, but bis-indene **368** was obtained instead of the bis-hydroquinone compound related to **367**.[144] Data about the stereochemistry of **368** were not given. The reaction of **41b** with 1-diethylamino-1-propyne yielded a mixture of amino biscarbenes **369** arising from the insertion of the alkyne into the Cr=C bond.

1,1′-Binaphthol axial chiral bis-carbene complexes of chromium **43** were also used in double benzannulation reactions to produce biphenanthrenol **370** after reaction with 3-hexyne. Since the primary reaction products were monoprotected hydroquinone Cr(CO)$_3$ complexes that are notorously sensitive to oxidation, they were in situ protected by TBDMSCl forming compounds **370**. On the basis of the C_2 symmetry of

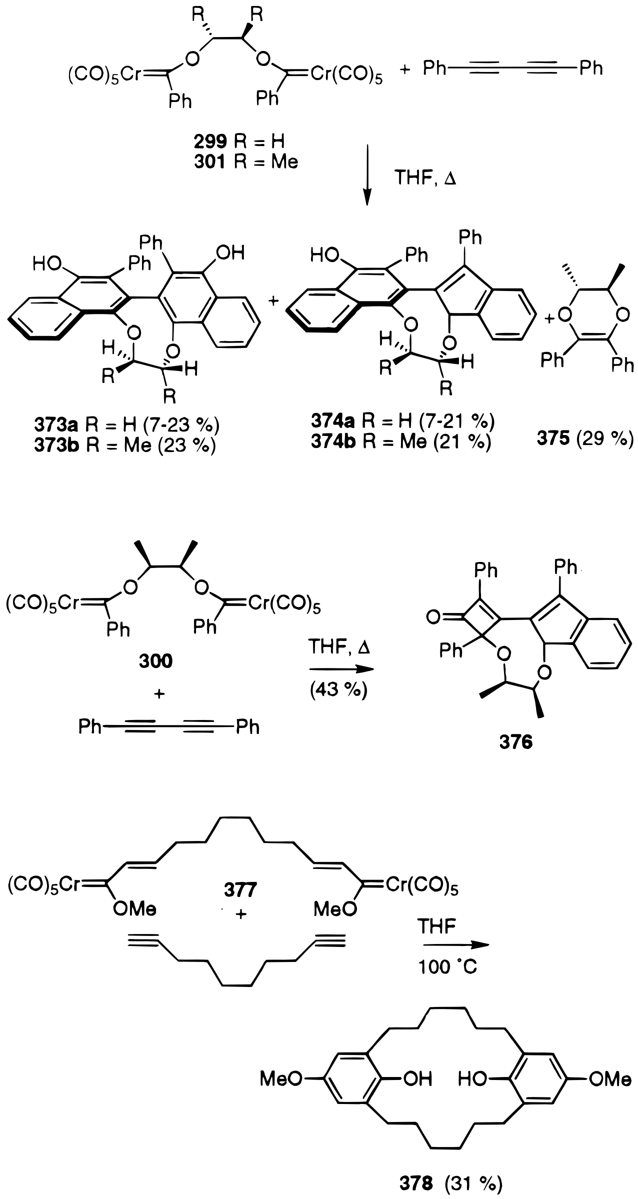
Scheme 76



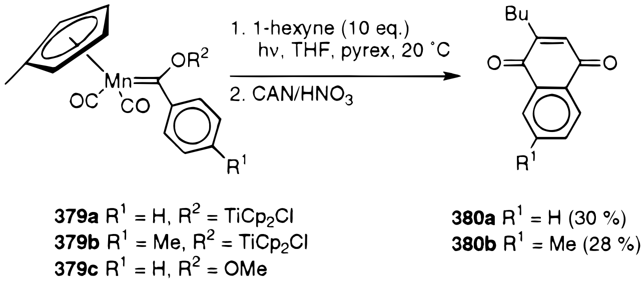
the enantiomerically pure starting complex **43**, two new elements of planar chirality arose from the annulation reaction, and four diastereomers of **370** may be, in principle, possible. Two of each were isolated in diastereomerically pure form. Both diastereomers differ in their number of ^{1}H and ^{13}C NMR signals. One isomer produces only half set of signals, indicating a C_2 symmetry, whereas the other isomer gives rise to the expected set of signals indicating a C_1 symmetry. Alternatively, in situ oxidation of the annulation products of complex **43** and 1- and 3-hexyne by $(NH_4)_2Ce(NO_3)_6$ (CAN) afforded the expected dimethoxy bi(phenantrenequinones) **371**. Compound **371b** was converted into helicene **372** by treatment with TMSI (Scheme 76).[145]

Complex **299** ($n = 2$) was reacted with diphenylbutadiyne to form a mixture of the double annulation product, 2,2′-binaphthol **373a**, and the indenylnaphthalene **374a**. The latter product resulted from the failure of CO to insert in one of the annulation steps, and it was obtained as a single diastereomer. The **373a/374a** ratio was strongly dependent on the reaction conditions (solvent and temperature). Optically pure complex **301** also reacted with diphenylbutadiyne to produce a mixture of compounds **373b** and **374b**, both in optically pure form. Together with these compounds, dihydrodioxane **375** arising from the thermal decomposition of the starting carbene complex **301** was obtained. Strikingly, *meso*-biscarbene **300** gave compound **376** as a single diastereomer.[117] On the other hand, the reaction of 1,9-decadiyne with bis-carbene **377** has been reported to produce macrocyclic cyclophane **378**. This reaction opens the possibility to prepare unsymmetrical [*n*,*m*]-cyclophanes from the macrocyclization of bis-carbene complexes with diynes (Scheme 77).[146]

Scheme 77

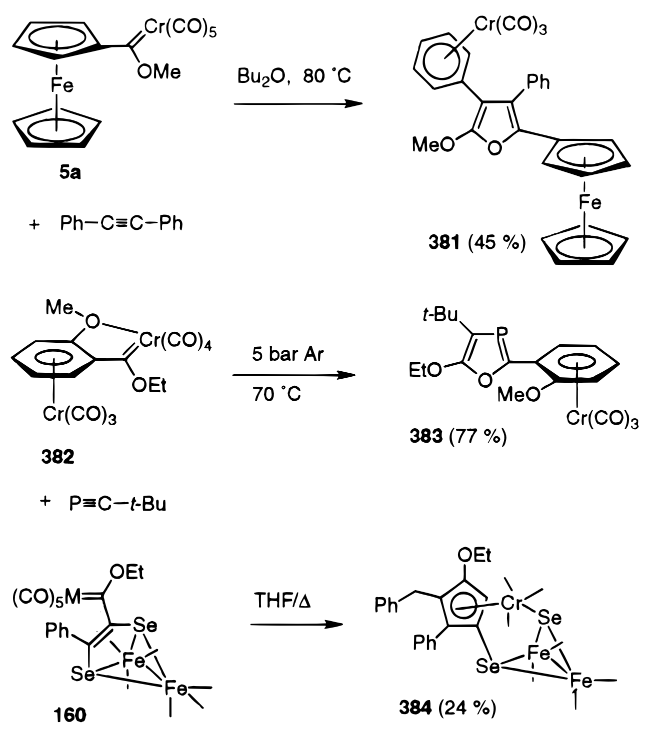


Scheme 78

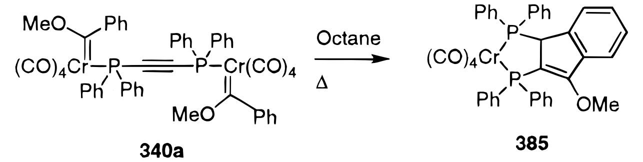


The reaction of titanoxymanganese carbene complexes **379a,b** yielded the corresponding quinone products **380a,b** when heated in the presence of 10 equiv of 1-hexyne, albeit in low yields. Better results were obtained when the same reactions were carried out photochemically, although yields of quinone **380** were still low. The presence of the titanium moiety was indispensable for the reaction to occur, since alkoxy manganese complex **379c** was unreactive toward alkynes. A comparison of bond distances

Scheme 79



Scheme 80

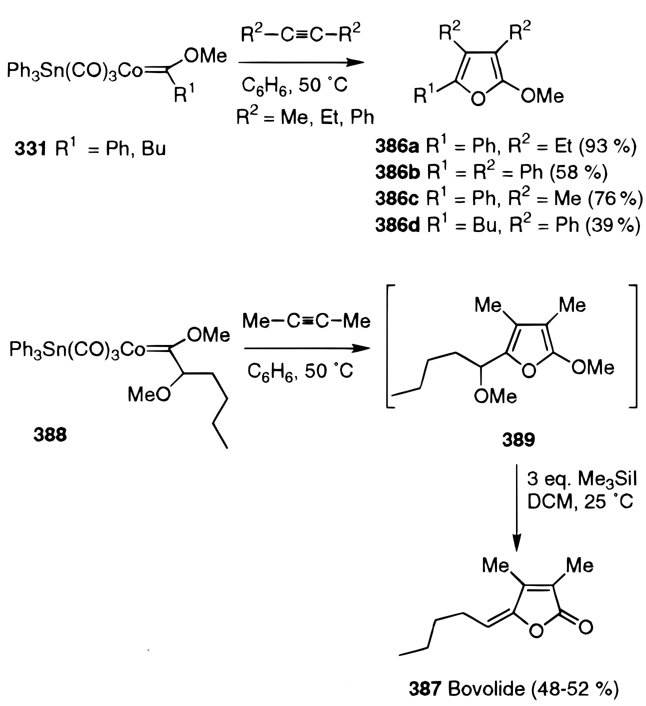


between complexes **379a** and **379c** shows that Mn engages in increased π-donation to the CO ligands upon Ti(IV) substitution and, therefore, perhaps less π-donation to the carbene center. Data suggest that the enhanced reactivity of the dimetallic structure may be due to an increase in electrophilicity at the carbene carbon or to changes in the nature of the MLCT excited state (Scheme 78).[98d]

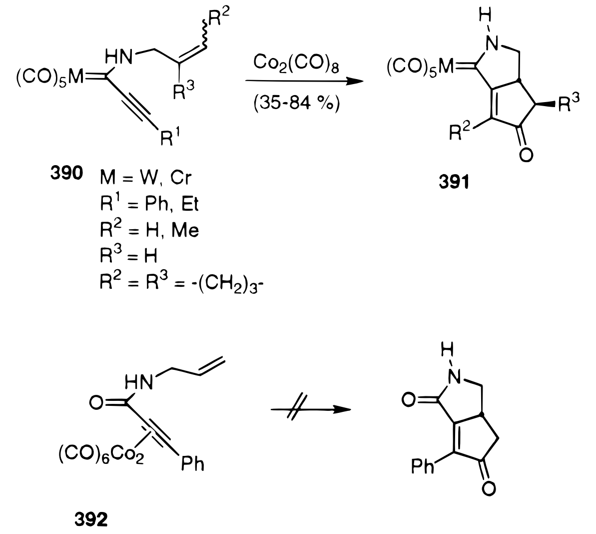
The effect of the second metal center on the nature of the reaction between heterodimetallic monocarbene complexes and alkynes is more patent in ferrocenyl-substituted chromium carbene **5a** that reacts with tolan in boiling Bu_2O to form tricarbonyl[(5-ferrocenyl-2methoxy-3-η^6-phenyl-4-phenyl)furan]chromium(0), **381**.[147] Analogously, the reaction of complex **382** and *t*-Bu-phosphalkyne formed oxaphosphole **383**. The product of phosphannulation, the linear phosphaanthracene, was not formed.[148] The influence of the additional metal centers is also clearly shown in the α,β-unsaturated Fischer carbene complex anchored on an $Fe_2(CO)_6(\mu\text{-Se})_2$ core **160** that resulted in the formation of a new complex **384** by heating. Compound **384** is clearly derived from 2 molecules of the starting compound from which one unit of $Fe_2(CO)_6\text{-}(\eta\text{-Se})_2$ should be formally expelled. No reaction mechanism was proposed for this unusual transformation (Scheme 79).[68]

Complex **340a** yielded tetracarbonyl[1,2-bis(phosphino)indene]chromium **385** by heating (Scheme 80).[136a]

Scheme 81



Scheme 82

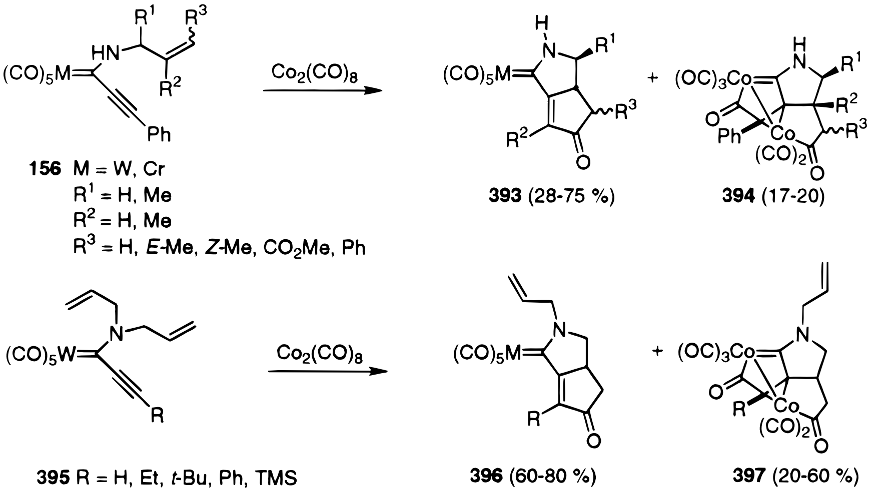


Other heterodimetallic complexes gave also products different from hydroquinones in their reactions with alkynes. Thus, cobalt complexes **331** gave furane derivatives **386** by reaction with internal alkynes. These reactions have been exploited to develop an expedite entry to bovolide **387**. Reaction of heterodimetallic complex **388** with 2-butyne formed furan **389**, which was transformed without isolation into bovolide by treatment with an excess of TMSI (Scheme 81).[132c]

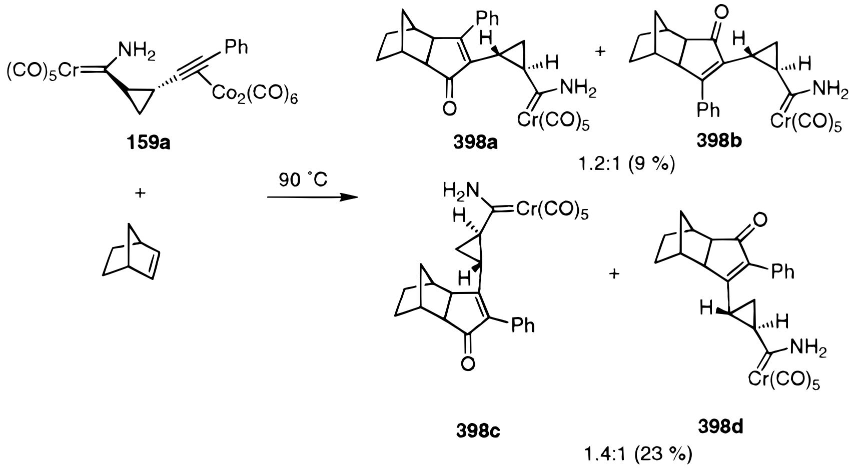
C. Pauson–Khand and Related Processes

The cocyclization of an alkyne$-Co_2(CO)_6$, an alkene, and a ligand CO to yield a cyclopentenone derivative is known as the Pauson−Khand reaction (P−K reaction), and it is a powerful method to raise molecular complexity in a single synthetic step. This reaction has been extensively applied in organic

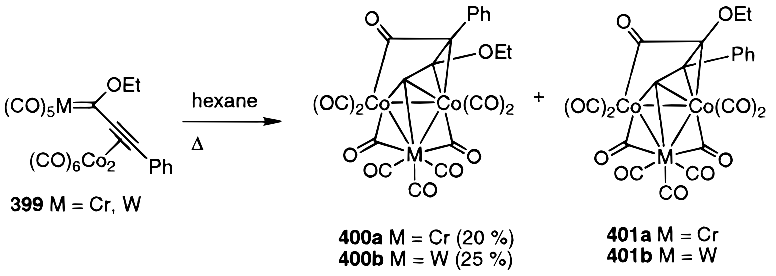
Scheme 83



Scheme 84



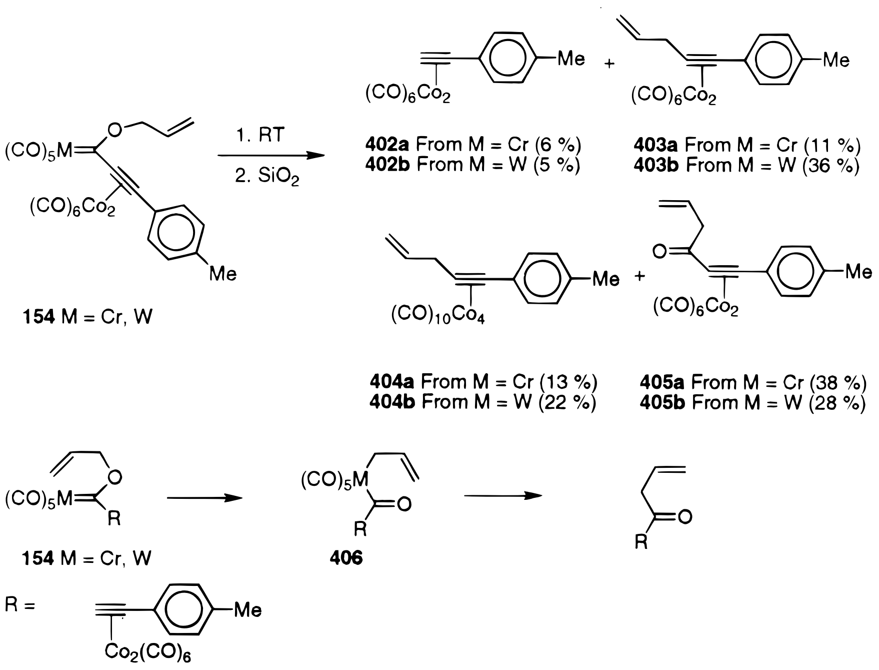
Scheme 85



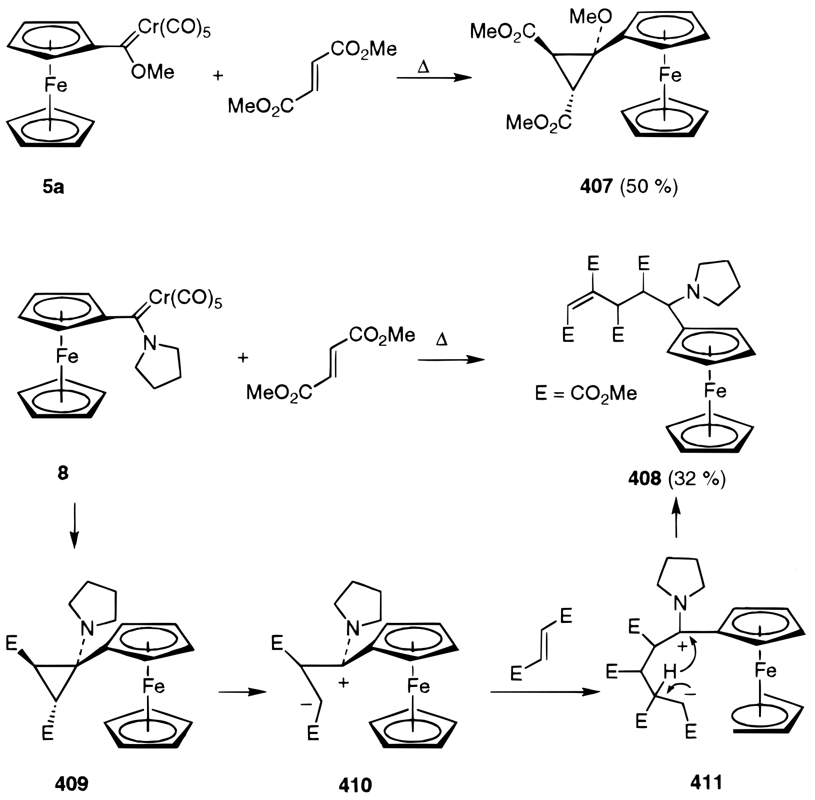
synthesis.[56] As stated earlier in this paper, the $(CO)_5M$ carbene moiety of group 6 metal carbene complexes effects an activating role toward this reaction. Thus, complexes such as **390** easily give bicyclic cyclopentenones **391**, while the analogous amide complex **392** forms the corresponding alkyne–$Co_2(CO)_6$ complex that is unreactive (Scheme 82).[57]

The reaction represented in Scheme 82 is usually carried out without isolation of the heterotrimetallic monocarbenes. A general study on the effect of the substituion at the allyl moiety was carried out on complexes **156** and resulted compatible with the formation of cyclopentenone metal carbene complexes **393**, except when carbomethoxy or phenyl groups are placed at the end of the double bond or a furyl group is attached to the double bond internal carbon. These compounds only formed the expected alkyne–$Co_2(CO)_6$ complexes.[62] Substitution of the double bond hydrogens by methyl groups promotes formation of dinuclear cobalt monocarbene complexes **394** together with the expected complexes **393**. The reaction was more sensitive to the substitution at the alkyne carbon. Replacement of the Ph group by a Me group resulted in an acceleration, while the bulkiest substituents such as Me_3Si or *t*-Bu led to alkyne–$Co_2(CO)_6$ complexes but not to cyclopentenone complexes. The effect of placing a second allyl group at the nitrogen was an increase on reactivity. Complexes **395** having Me_3Si or *t*-Bu groups attached to the triple bond were now reactive leading to bicyclic cyclopentenone monocarbenes. This effect was attributed to the availability of one allyl group to react,

Scheme 86



Scheme 87



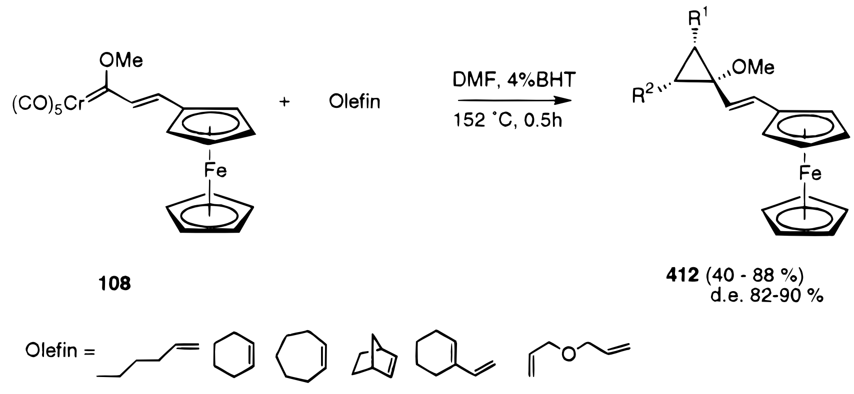
once the coordination of the alkyne by the $Co_2(CO)_8$ has forced the second allyl group to coordinate the chromium center (an effect that may render the monoallyl complexes unreactive). Again bulky substituents on complexes **395** promote the formation of dinuclear cobalt carbenes **397** (Scheme 83).[57,60,62,63]

The intermolecular P−K reaction between alkyne−$Co_2(CO)_6$ complex **159a** and norbornene led to the corresponding P−K products **398** as a mixture of regio- and diasteromers with almost no selectivity. The diastereomeric ratio was analogous to that found in the reaction of ester analogous to **159a** and norbornene (Scheme 84).[64]

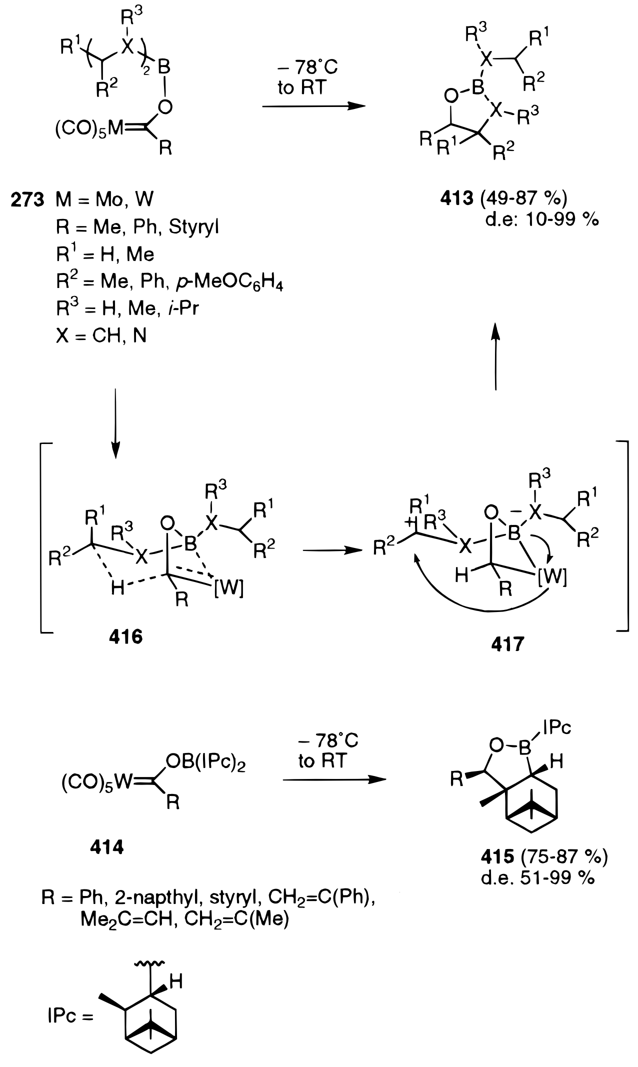
Thermolysis of complexes **399** lacking the olefin component of the P−K reaction resulted in formation of isomeric heterotrimetallic clusters **400** and **401** having a bridging carbyne ligand. Compounds **400** and **401** were isolated and characterized as mixtures. No mechanism for this rearrangement was proposed (Scheme 85).[149]

The attempted intramolecular P−K reaction of (allyloxy)(alkynyl)carbene−$Co_2(CO)_6$ complexes **154**

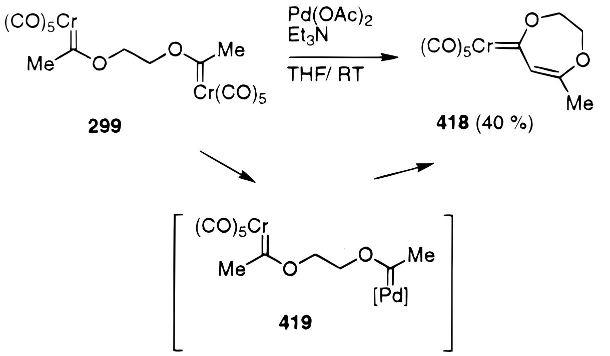
Scheme 88



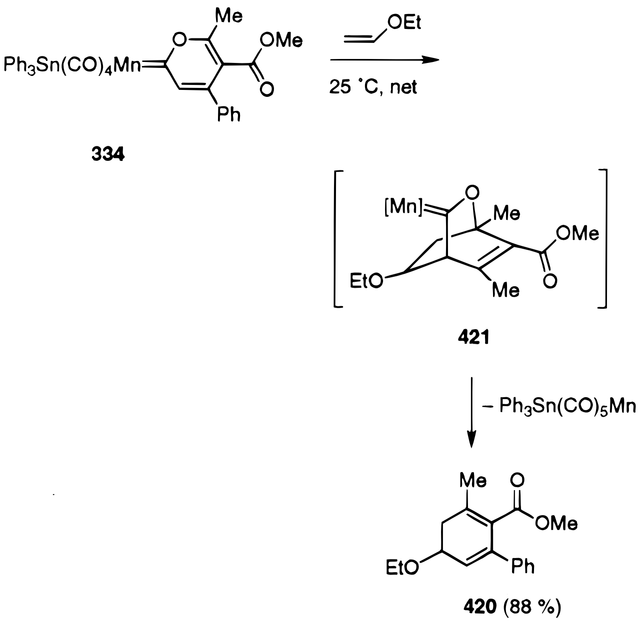
Scheme 89



Scheme 90



Scheme 91



gave no P−K product but a novel retro-Fischer reaction.[61] Thus, these complexes evolved to a mixture of products **402**−**405** upon standing several days at room temperature in a petroleum ether solution. The enyne complex **402** can be regarded as the result of a formal retro-Fischer reaction of **154** in the presence of the $Co_2(CO)_6$ fragment. The formation of enynone **405** may be explained through a [3,3]-sigmatropic rearrangement of the allyloxy fragment, followed by the reductive elimination of the pentacarbonyl moiety on intermediate **406** (Scheme 86).

D. Cyclopropanation and C−H Insertion Reactions

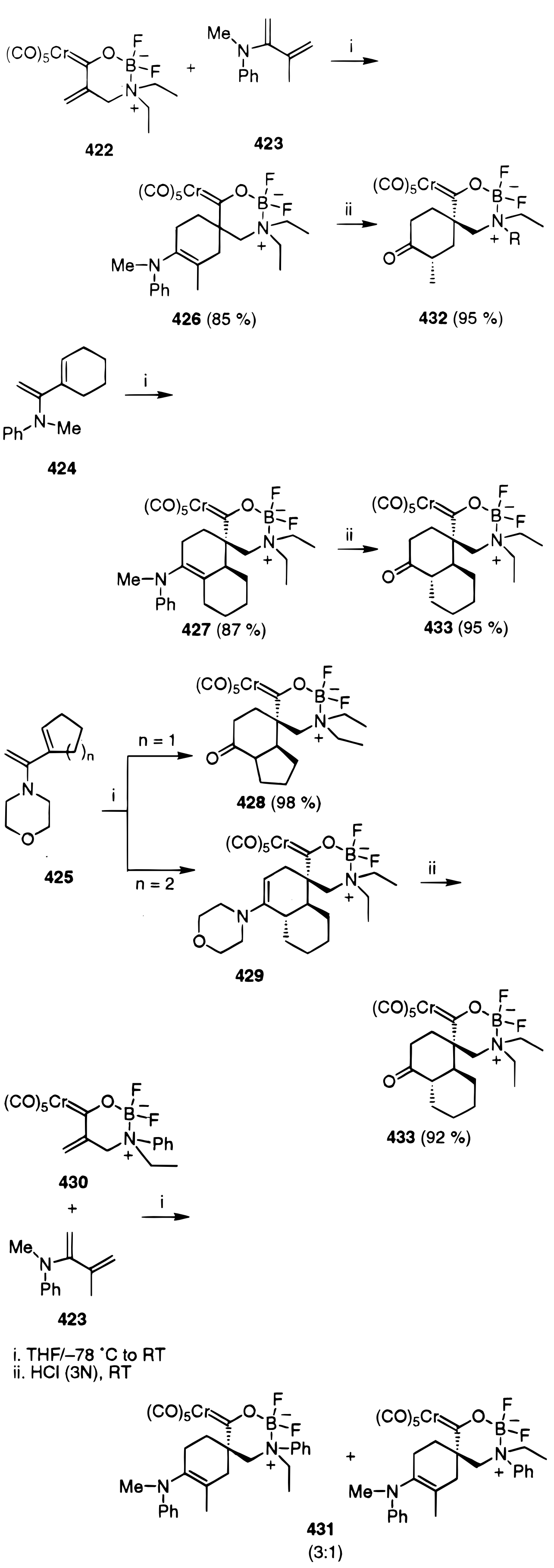
The cyclopropanation of alkenes by group 6 metal carbenes is one of the earliest reaction tested on these complexes.[2] The use of dimetallic carbene complexes for this kind of processes is scarce to date. Ferrocenyl alkoxychromium complex **5a** was heated with a large excesses of dimethyl fumarate to give the corresponding mixture of diastereomeric cyclopropanes **407** in low yields.[150] The analogous reaction with aminocarbene complex **8** (R_2 = pyrrolydinyl) gave, however, the pentene derivative **408**. Use of 1,1-diphenylethene instead of dimethyl fumarate resulted exclusively in recovering of starting material when complex **5a** was used, while aminocarbene **8** (R_2 = pyrrolydinyl) gave 3,3-diphenylpropyonylferrocene as a minor product. Formation of the observed products in the reactions of aminocarbene **8** was explained by the initial formation of cyclopropanes **409**, which were unstable and reacted with a further molecule of olefin through zwitterion **410** to give **411**. This last intermediate evolves finally to the pentene derivative **408** (Scheme 87).

Complex **108** reacted with electronically neutral alkenes to yield the cyclopropanes **412** with high diastereoselectivity.[47a] These results are significant due to the fact that the cyclopropanation of electronically neutral alkenes is not an easy process when effected intermolecularly, while it becomes very efficient in an intramolecular fashion.[151] Thus, for example, alkyl, alkynyl, and aryl chromium carbenes led to unidentified polymeric materials when heated in the presence of 1-hexene, while complex **108** gives the corresponding cyclopropane in 88% yield (Scheme 88).

Unstable boroxy Fischer carbene complexes **273** evolve to oxaborolane or oxazaborolidine derivatives **413** via C−H insertion processes.[104] Compounds **413** are produced in moderate yield when both R^1 and R^2 are alkyl groups or H and a donor group. Conversely, the reaction did not work when R^1 was H and R^2 was an alkyl or electron-withdrawing group. The nature of the metal plays an important role in the reaction rate, while the product distribution remained mainly unaltered by switching from Cr to Mo or W. Thus, longer reaction times were required for W and Cr carbenes than for Mo carbenes to complete this reaction. The use of chiral carbene complexes **414** derived from (−)-chlorodiisopinocamphenylborane resulted in C−H insertion processes to form compounds **415** with diastereoselectivities in some cases higher than 99%. A mechanism to account for the formation of oxaborolanes **413** involves intramolecular hydride transfer to the carbene carbon in the complex **273**. This transfer is favored, presumably, by an interaction between the boron and the metal of carbene complex, as depicted in Scheme 88, to give the formal carbocation intermediate **417**, which readily affords the oxaborolane derivatives **413** by simultaneous formation of a C−C bond and loss of the metal fragment (Scheme 89).

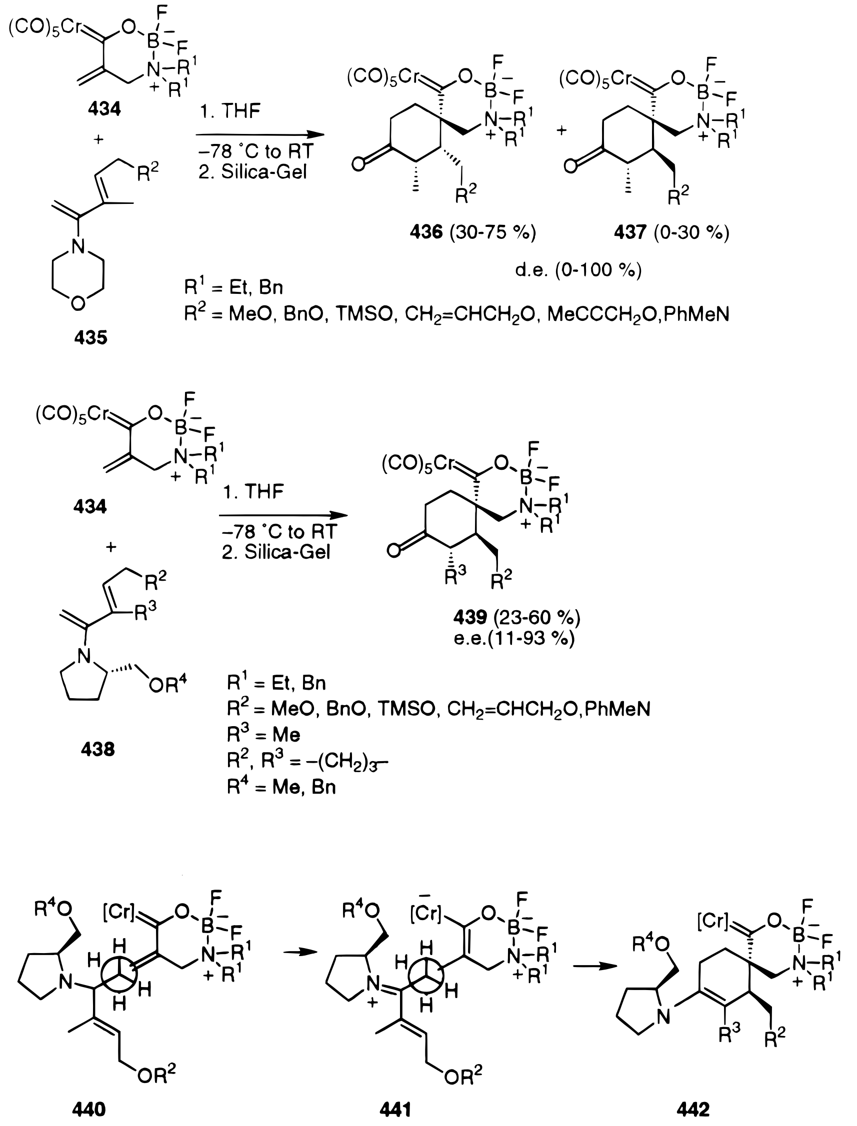
Complex **299** ($n = 2$) experiments an intramolecular C−H insertion by reaction with $Pd(OAc)_2$ to yield the mononuclear cyclic carbene complex **418**.[152] Tansmetalation of one of the carbene moieties from chromium to Pd leads to a heterodimetallic intermediate **419**. Insertion of the Pd center in a methyl C−H bond of the remaining Cr carbene moiety followed by β-hydrogen elimination would lead to the observed carbene product **418** (Scheme 90).

Scheme 92



i. THF/–78 °C to RT
ii. HCl (3N), RT

Scheme 93



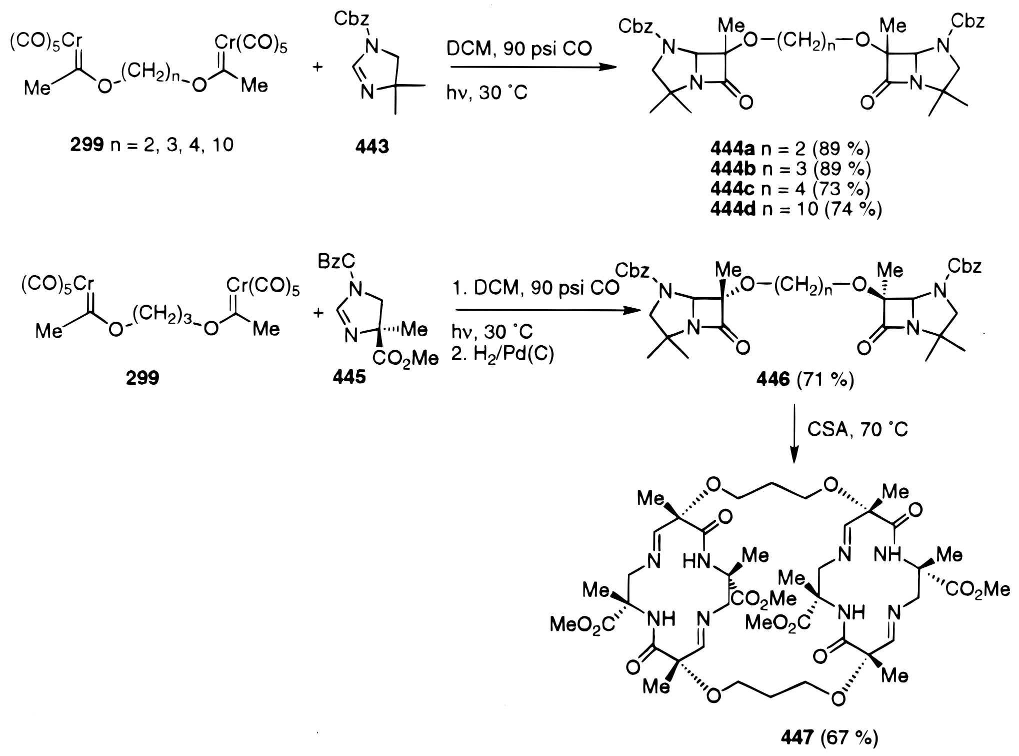
E. Cycloaddition Processes

The strong electron-withdrawing ability of the pentacarbonyl group makes alkenylcarbene complexes highly active dienophiles in Diels−Alder reactions.[153] In fact, [4+2] cycloadditions on group 6 alkoxyalkenylcarbene mononuclear complexes are exceptionally regioselective and, in general, endo-selective, while the corresponding amino derivatives gave the corresponding exo-adducts, which are less reactive. Cycloaddition chemistry of dimetallic carbene complexes has been, in comparison, less studied. That is rare since these complexes offer an unique opportunity to study the influence of the second metal in the cycloaddition process. The use of tin-substituted manganese carbene complex **334** in an inverse electron-demand Diels−Alder reaction with ethylvinyl ether formed dihydrobenzene **420** as the reaction product.[134] The initial chromium Diels−Alder adduct **421** could not be isolated as it experiments a retro Diels−Alder process with the extrusion of the metal nucleus, a reaction that is very fast even at room temperature (Scheme 91).

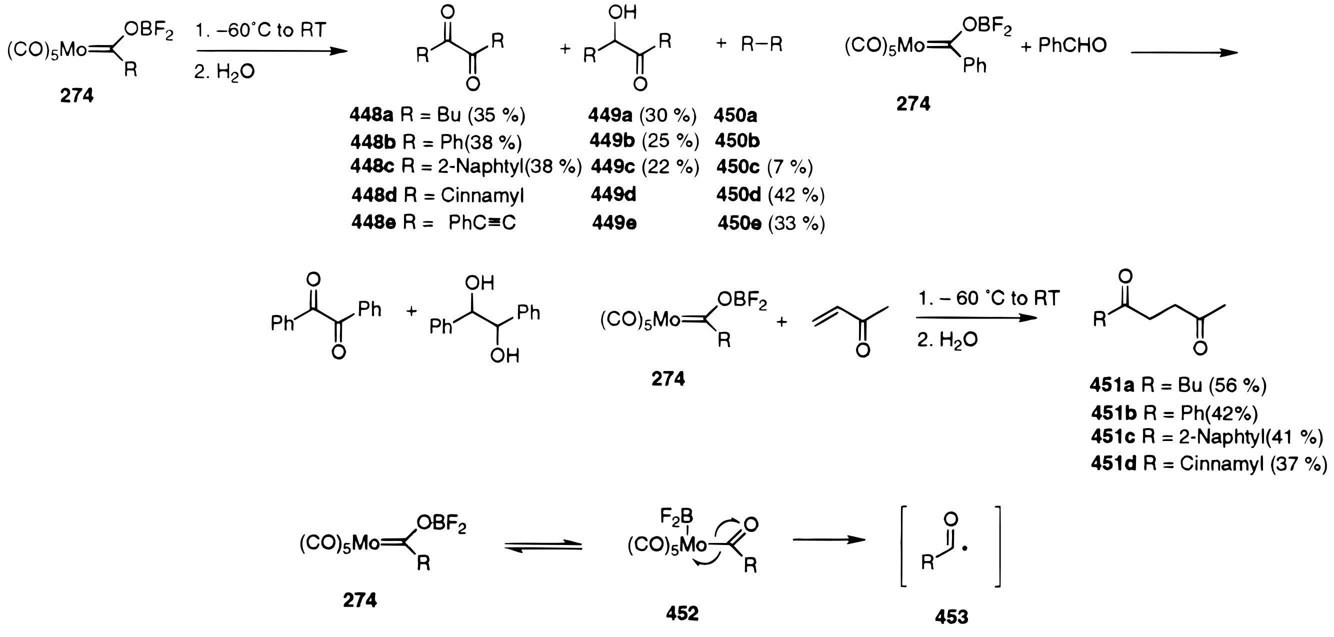
The exo-selectivity of a Diels−Alder process is recognized to be a property of conformationally restricted *s*-cis-dienophiles. The cyclic chelate structure of boroxyvinyl carbene complexes such as **422** temporally fixes the *s*-cis conformation of the exocyclic C−C and C−Cr double bonds. This fact makes these complexes excellent reagents to participate in highly selective exo-Diels−Alder processes with 2-amino-1,3-dienes. Thus, complex **422** reacts with achiral aminodienes **423**−**425** to give cycloadducts **426**−**429** with complete selectivity. The introduction of a stereogenic racemic nitrogen like in carbene **430** decreases the selectivity to 3:1 on its reaction with enamine **423** to give cycloadducts **431**. The enamine moiety in cycloadducts **426, 427,** and **429** could be hydrolyzed to form the corresponding ketone complexes **432** and **433** with complete selectivity (Scheme 92).[106]

The reaction of carbene complexes **434** with heteroatom-substituted 2-aminodienes **435** led, in turn, to mixtures of endo/exo-adducts **436/437** with the endo-adduct **436** being the major or even the exclusive isomer. The high selectivity of these reactions was used to develop a highly enantioselective [4+2] cycloaddition using (*S*)-prolinol-derived dienes **438** as the chiral components. Very high ee were obtained

Scheme 94



Scheme 95

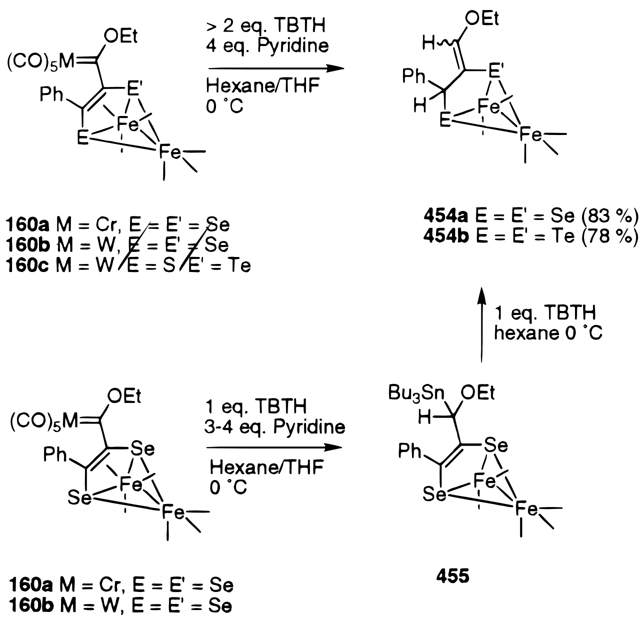


in most cases, and most strikingly, adducts **439** were always exo-isomers. Should the observed results be explained by invoking a concerted mechanism, the dienophile had to be added to the more hindered face of the diene. Therefore, zwitterionic species **441** formed by an initial anti-attack to the β-carbon of the complex by the enamine moiety of the diene through its less hindered face were proposed as the reaction intermediates. Ring closure on these species would yield the observed cycloadducts. The diene–dienophile approach topology represented in **440** would explain the observed stereochemistry and would be favored by a greater number of close contacts between the metal center and the prolinol unit. Zwitterion **441** would undergo the final ring closure by Michael addition of the carbene enolate-like moiety to the α,β-unsaturated iminium salt. This closure would occur with the CH_2OR^2 unit positioned anti to the metal fragment. Finally, conversion of enamine **442** to the reaction product **439** creates the third contiguous stereocenter (Scheme 93).[106]

F. Photochemistry

Irradiation (visible light) of a chromium carbene complex is believed to produce a metal bounded

Scheme 96



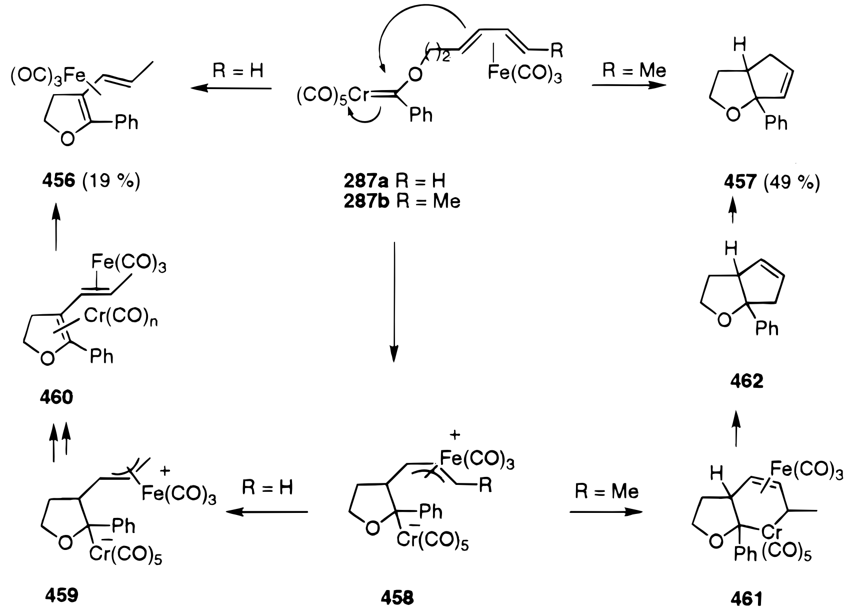
ketene through the reversible insertion of a CO ligand into the metal carbene bond (eq 2). Although this reaction has been extensively applied in organic synthesis, very few examples of the use of homo- or heterodimetallic carbene complexes in photocarbonylation reactions have been reported. Bis-carbene complexes **299** were reacted with protected imidazoline **443** to yield bis-azapenams **444** in fair yields and as 1:1 mixtures of diastereomers.[115] Irradiation of optically active imidazoline **445** in the presence of bis-carbene **299** ($n = 3$) followed by deprotection of the Cbz group gave optically active bis-azapenam **446** as a single diastereomer.[116] Bis-azapenams experiment an interesting acid-catalyzed dimerization ring-opening reaction to produce bis-dioxocyclams. An example is the conversion of optically pure **446** to bis-dioxocyclam **447** by treatment with CSA (Scheme 94).[116]

G. Other Reactions

Difluoroboroxymolybdenum Fischer carbenes **274** are precursors of acyl radicals.[105] These complexes are stable only at low temperature and underwent loss of the metal fragment upon heating affording, after hydrolysis, mixtures of 1,2-diketones **448**, 1,2-hydroxyketones **449**, and in some cases dimers **450**. Decomposition of complexes **274** in the presence of radical aceptors such as benzaldehyde or methyl vinyl ketone resulted in the trapping of the acyl radicals generated from these complexes. Thus, reaction of **274** (R = Ph) in the presence of benzaldehyde gave a mixture of benzyl and 1,2-diphenyl-1,2-ethanediol. The reaction with methyl vinyl ketone resulted in the formation of the Michael adducts **451** and variable amounts of compounds **448**–**450**. Formation of the observed products is explained by the equilibrium between complexes **274** and an acyl-molybdenum complex **452**, presumably favored by the interaction between boron and molybdenum. The homolytic scission of the C–Mo bond leads to the acyl radicals **453**. 1,2-Diketones **448a**–**e** would be formed by dimerization of **453**, while hydroxyketones **449a**–**e** would be formed by further reaction of **448** and **452** by a double electron transfer with the subsequent release of a $Mo(CO)_5$ moiety. Benzaldehyde inhibits the electron transfer, generating a radical anion that dimerizes to form 1,2-diphenyl-1,2-ethanediol. Conjugated addition of **453** to methyl vinyl ketone would yield the corresponding Michael adduct **451** (Scheme 95)

Complexes **160a**–**c** experiment displacement of the carbene ligand by reaction with an excess of Bu_3SnH in the presence of pyridine to afford vinyl ethers **454** as *E*/*Z* mixtures.[67] When the reaction was carried out in the presence of 1 equiv of Bu_3SnH, complex **455** could be obtained as a minor product together with the above mixture of vinyl ethers. This complex could be transformed to the corresponding enol ether

Scheme 97



mixture by treatment with one additional equiv of stannane (Scheme 96).

Heating complexes **287a,b** formed furane derivatives **456** and **457** by the nucleophilic addition of the diene ligand to the carbene carbon center to give the allylic dimetallic derivative **458**. The evolution of these intermediates is strongly dependent on the substitution of the diene terminal carbon. Thus, complex **287** having an unsubstituted terminal double bond evolves by syn/anti π-allyl isomerization to produce **459** followed by β-H-elimination/H-addition to form **460** and final loss of the chromium moiety to yield the observed product. Substitution at the diene terminal carbon inhibites the π-allyl isomerization and favors the attack of the anionic chromium onto the allyl system to form **461**, which evolves to the final product via reductive elimination, iron decomplexation, and, finally, double bond isomerization on **462** (Scheme 97).[110]

VI. Conclusions

From the diverse di- and polymetallic carbene complexes listed through this review, it seems clear that the compounds that have been of use in organic synthesis (meaning they have been sucessfully involved in the building of C−C bonds with or without retention of the metallic moiety) are a minority. Even if one considers those that have been used to prepare other organometallic compounds, there are still an overhelming amount of di- and polymetallic carbene complexes whose reactivity has not been tested. The attraction for searching new classes of reactions involving the multimetal system to study the interaction between the diverse metallic centers as well as the possibility of achieving the modulation of the reactivity caused on a basic metal carbene structure by the change on the additional metal centers confer to this class of compounds both the attraction for the unknown and the elegance and charm of the well-known. In any case, much chemistry remains to be done in di- and polymetallic (Fischer) carbene complexes to achieve its full potential as reagents for organic synthesis.

VI. Acknowledgment

Support for this work under Grants PB97-0323 and 2FD97-0314-CO2-02 from the Dirección General de Enseñanza Superior e Investigación Científica y Técnica (MEC−Spain) and the European Commission is acknowledged. I thank Prof. Mar Gómez-Gallego (UCM) for her encouragment, valuable suggestions, and patience in correcting the manuscript.

VII. References and Notes

(1) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.
(2) (a) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1970**, *103*, 1273. (b) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356. (c) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 3966.
(3) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644. (b) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177.
(4) (a) McGuire, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 5538. (b) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, Ch.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680. (c) Hegedus, L. S.; de Weck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.
(5) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Wulff, W. D. in *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1065. (d) Schwindt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143. (e) Rudler, H.; Audouin, M.; Chelain, E.; Denise, B.; Goumont, R.; Massoud, A.; Parlier, A.; Pacreau, A.; Rudler, M.; Yefsah, R.; Alvarez, C.; Delgado-Reyes, F. *Chem. Soc. Rev.* **1991**, *20*, 503. (f) Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381. (g) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 470. (h) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G.; Eds.; Pergamon: Oxford, 1995; Vol. 12, p 549. (i) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271. (j) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105. (k) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163. (l) Alcaide, B.; Casarrubios, L.; Domínguez, G.; Sierra, M. A. *Curr. Org. Chem.* **1998**, *2*, 551.
(6) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1922.
(7) Casey, C. P. *J. Chem. Soc., Chem. Commun.* **1970**, 1220.
(8) (a) van den Beuken, E. K.; Feringa, B. L. *Tetrahedron* **1998**, *54*, 12985. (b) Vogl, E. M.; Gröger, H.; Shibasaki, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1570. (c) Shibasaki, M.; Sasai, H.; Arai, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1237. (d) Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1049.
(9) Connor, J. A.; Lloyd, J. P. *J. Chem. Soc., Dalton Trans.* **1972**, 1470.
(10) Fischer, E. O.; Gammel, F. J.; Besenhard, J. O.; Frank, A.; Neugebauer, D. *J. Organomet. Chem.* **1980**, *191*, 261.
(11) Fischer, E. O.; Gammel, F. J.; Neugebauer, D. *Chem. Ber.* **1980**, *113*, 1010.
(12) Terblans, Y. M.; Lotz, S. *J. Chem. Soc., Dalton Trans.* **1997**, 2177.
(13) Waldbach, T. A.; van Eldik, R.; van Rooyen, P. H.; Lotz, S. *Organometallics* **1997**, *16*, 4056.
(14) Fischer, E. O.; Postnov, V. N.; Kreissl, F. R. *J. Organomet. Chem.* **1977**, *127*, C19.
(15) Behrendt, U.; Pfeifer, R.-M.; Wartchow, R.; Butenschön, H. *New J. Chem.* **1999**, *23*, 891.
(16) Pyshnograeva, N. I.; Setkina, V. N.; Andrianov, V. G.; Struchkov, Y. T.; Kursanov, D. N. *J. Organomet. Chem.* **1981**, *206*, 169.
(17) Lee, Y.-J.; Kim, S.-J.; Kang, Ch.-H.; Ko, J.; Kang, S. O., Carroll, P. J. *Organometallics* **1998**, *17*, 1109.
(18) (a) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969. (b) Beck, W.; Niemer, M.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923. (c) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547.
(19) Weng, W.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3824.
(20) Weng, W.; Arif, A. M.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 891.
(21) Fallon, S. B.; Weng, W.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1997**, *16*, 2008.
(22) Fallon, S. B.; Szafert, S.; Arif, A. M.; Gladysz, J. A. *Chem. Eur. J.* **1998**, *4*, 1033.
(23) Weng, W.; Bartik, T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2199.
(24) Bartik, T.; Weng, W.; Ramsden, J. A.; Szafert, S.; Fallon, S. B.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 11071.
(25) Fischer, E. O.; Röll, W.; Huy, N. H. T.; Ackermann, K. *Chem. Ber.* **1982**, *115*, 2951.
(26) Huy, N. H. T.; Lefloch, P.; Robert, F.; Jeannin, Y. *J. Organomet. Chem.* **1987**, *327*, 211.
(27) Dötz, K. H.; Tomuschat, P.; Nieger, M. *Chem. Ber.* **1997**, *130*, 1605.
(28) Albrecht, T.; Sauer, J.; Nöth, H. *Tetrahedron Lett.* **1994**, *35*, 561.
(29) Neidlein, R.; Gürtler, S.; Krieger, C. *Helv. Chim. Acta* **1994**, *77*, 2303.
(30) Anderson, D. M.; Bristow, G. S.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Skelton, B. W. *J. Chem. Soc., Dalton Trans.* **1987**, 2843.
(31) Berke, H.; Härter, P.; Huttner, G.; v. Seyerl, J. *J. Organomet. Chem.* **1981**, *219*, 317.
(32) (a) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702. (b) Schwindt, M. A., Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.
(33) Havránek, M.; Husak, M.; Dvorak, D. *Organometallics* **1995**, *14*, 5024.
(34) Semmelhack, M. F.; Lee, G. R. *Organometallics* **1987**, *6*, 1839.
(35) Dötz, K. H.; Ehlenz, R.; Straub, W.; Weber, J. C.; Airola, K.; Nieger, M. *J. Organomet. Chem.* **1997**, *548*, 91.
(36) (a) Bernasconi, C. F. *Chem. Soc. Rev.* **1997**, *26*, 299. (b) Bernasconi, C. F.; Leyes, A. E.; García-Río, L. *Organometallics* **1998**, *17*, 4940.

(37) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1975**, *102*, 175.
(38) (a) Macomber, D. W.; Hung, M.-H.; Verma, A. G.; Rogers, R. D. *Organometallics* **1988**, *7*, 2072. (b) Macomber, D. W.; Hung, M.-H.; Madhukar, P.; Liang, M.; Rogers, R. D. *Organometallics* **1991**, *10*, 737.
(39) Macomber, D. W.; Madhukar, P.; Rogers, R. D. *Organometallics* **1991**, *10*, 2121.
(40) Breimair, J.; Weidmann, T.; Wagner, B.; Beck, W. *Chem. Ber.* **1991**, *124*, 4, 2431.
(41) Kelley, C.; Terry, M. R.; Kaplan, A. W.; Geoffroy, G. L.; Lugan, N.; Mathieu, R.; Haggerty, B. S.; Rheingold, A. L. *Inorg. Chim. Acta* **1992**, *198*−*200*, 601.
(42) Aumann, R.; Läge, M.; Krebs, B. *Chem. Ber.* **1994**, *127*, 731.
(43) Rose-Munch, F.; Susanne, C.; Balssa, F.; Rose, E. *J. Organomet. Chem.* **1994**, *476*, C25.
(44) Rose-Munch, F.; Le Corre-Susanne, C.; Balssa, F.; Rose, E.; Vaisserman, J.; Licandro, E.; Papagni, A.; Maiorana, S.; Meng, W.-d.; Stephenson, G. R. *J. Organomet. Chem.* **1997**, *545*−*546*, 9.
(45) Weidmann, T.; Sünkel, K.; Beck, W. *J. Organomet. Chem.* **1993**, *459*, 219.
(46) Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.
(47) (a) Barluenga, J.; Fernández-Acebes, A.; Trabanco, A. A.; Flórez, J. *J. Am. Chem. Soc.* **1997**, *119*, 7591. (b) del Amo, J. C.; Sierra, M. A.; Mancheño, M. J.; Gómez-Gallego, M. Unpublished results. (c) Mongin, C.; Ortin, Y.; Lugan, N.; Mathieu, R. *Eur. J. Inorg. Chem.* **1999**, 739.
(48) Briel, O.; Fehn, A.; Beck, W. *J. Organomet. Chem.* **1999**, *578*, 247.
(49) Macomber, D. W.; Madhukar, P. *J. Organomet. Chem.* **1992**, *433*, 279.
(50) Geisbauer, A.; Polborn, K.; Beck, W. *J. Organomet. Chem.* **1997**, *542*, 205.
(51) Aumann, R.; Jasper, B.; Fröhlich, R.; Kotila, S. *J. Organomet. Chem.* **1995**, *502*, 137−141.
(52) Lattuada, L.; Licandro, E.; Maiorana, S.; Molinari, H.; Papagni, A. *Organometallics* **1991**, *10*, 807.
(53) Geisbauer, A.; Mihan, S.; Beck, W. *J. Organomet. Chem.* **1995**, *501*, 61.
(54) (a) Cron, S.; Morvan, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 1611. (b) Mahias, V.; Cron, S.; Toupet, L.; Lapinte, C. *Organometallics* **1996**, *15*, 5399.
(55) Rabier, A.; Lugan, N.; Mathieu, R.; Geoffroy, G. L. *Organometallics* **1994**, *13*, 4676.
(56) For reviews on the P−K reaction, see: (a) Schore, N. E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G. Eds.; Pergamon: Oxford, 1995; Vol. 12, p 703. (b) Schore, N. E. *Org. React.* **1991**, *40*, 1. (c) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855.
(57) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1470.
(58) Wienand, A.; Reissig, H.-U.; Fischer, H.; Pflumm, D.; Troll, C. *J. Organomet. Chem.* **1992**, *427*, C9.
(59) Dötz, K. H.; Christoffers, J. *J. Organomet. Chem.* **1992**, *426*, C58.
(60) Jordi, L.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Mejias, M.; Molins, E. *Organometallics* **1992**, *11*, 3507.
(61) Christoffers, J.; Dötz, K. H. *Organometallics* **1994**, *13*, 4189.
(62) Jordi, L.; Ricart, S.; Viñas, J. M.; Moretó, J. M. *Organometallics* **1997**, *16*, 2808.
(63) Schick, U.; Jordi, L.; Ricart, S.; Veciana, J.; Dötz, K. H.; Moretó, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 2283.
(64) Kretschik, O.; Nieger, M.; Dötz, K. H. *Chem. Ber.* **1997**, *130*, 507.
(65) Mathur, P.; Ghosh, S.; Sarkar, A.; Satyanarayana, C. V. V.; Rheingold, A.; Liable-Sands, L. M. *Organometallics* **1997**, *16*, 3536.
(66) Mathur, P.; Ghosh, S.; Sarkar, A.; Satyanarayana, C. V. V.; Puranik, V. G. *Organometallics* **1997**, *16*, 4392.
(67) Mathur, P.; Ghosh, S.; Sarkar, A.; Satyanarayana, C. V. V.; Drake, J. E.; Yang, J. *Organometallics* **1997**, *16*, 6028.
(68) Mathur, P.; Ghosh, S.; Sarkar, A.; Rheingold, A. L.; Guzei, I. A. *Organometallics* **1998**, *17*, 770.
(69) Parlier, A.; Rose, F.; Rudler, M.; Rudler, H. *J. Organomet. Chem.* **1982**, *235*, C13.
(70) Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Organometallics* **1994**, *13*, 3502.
(71) Aumann, R.; Fröhlich, R.; Kotila, S. *Organometallics* **1996**, *15*, 4842.
(72) Aumann, R.; Hinterding, P.; Krüger, C.; Goddard, R. *J. Organomet. Chem.* **1993**, *459*, 145.
(73) Jordi, L.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *J. Organomet. Chem.* **1993**, *444*, C28.
(74) Aumann, R.; Hildmann, B.; Fröhlich, R. *Organometallics* **1998**, *17*, 1197.
(75) Aumann, R.; Yu, Z.; Fröhlich, R. *Organometallics* **1998**, *17*, 2897.
(76) Macomber, D. W.; Hung, M.-H. *J. Organomet. Chem.* **1989**, *366*, 147.
(77) Macomber, D. W.: Hung, M.-H.; Liang, M.; Verma, A. G.; Madhukar, P. *Macromolecules* **1988**, *21*, 1187.
(78) Hartbaum, C.; Roth, G.; Fischer, H. *Eur. J. Inorg. Chem.* **1998**, 191.
(79) Hartbaum, C.; Fischer, H. *Chem. Ber.* **1997**, *130*, 1063.
(80) Hartbaum, C.; Fischer, H. *J. Organomet. Chem.* **1999**, *578*, 186.
(81) Hartbaum, C.; Mauz, E.; Roth, G.; Weissenbach, K.; Fischer, H. *Organometallics* **1999**, *18*, 2619.
(82) Alvarez-Toledano, C.; Parlier, A.; Rudler, H.; Daran, J.-C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 576.
(83) Stadtmüller, H.; Knochel, P. *Organometallics* **1995**, *14*, 3163.
(84) Kretschik, O.; Nieger, M.; Dötz, K. H. *Organometallics* **1996**, *15*, 3625.
(85) For a compilation of methods of preparation of heteroatom-substituted metal carbene complexes using this approach, see: Zaragoza-Dörwald, F. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 1999; pp 25−27.
(86) Stepnicka, P.; Gyepes, R.; Lavastre, O.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 5089.
(87) Ruíz, N.; Péron, D.; Sinbandith, S.; Dixneuf, P.; Baldoli, C.; Maiorana, S. *J. Organomet. Chem.* **1997**, *533*, 213.
(88) Péron, V.; Porhiel, E.; Ferrand, V.; Le Bozec, H. *J. Organomet. Chem.* **1997**, *539*, 201.
(89) Fischer, E. O.; Pardy, R. B. A.; Schubert, U. *J. Organomet. Chem.* **1979**, *181*, 37.
(90) (a) Schubert, U.; Fischer, E. O.; Wittmann, D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 643. (b) Fischer, E. O.; Wittmann, D.; Himmelreich, D.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1982**, *115*, 3141.
(91) Fischer, E. O.; Wittmann, D.; Himmelreich, D.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 444.
(92) Fischer, H.; Fischer, E. O.; Cai, R.; Himmelreich, D. *Chem. Ber.* **1983**, *116*, 1009.
(93) Fischer, E. O.; Wanner, J. K. R. *Chem. Ber.* **1985**, *118*, 2489.
(94) Terry, M. R.; Mercando, L.; Kelley, C.; Geoffroy, G. L.; Nombel, P.; Lugan, N.; Mathieu, R.; Ostrander, R. L.; Owens-Waltermire, B. E.; Rheingold, A. L. *Organometallics* **1994**, *13*, 843.
(95) Grashey, R. *Azomethine Imines.* In *1,3-Dipolar Cycloaddition Chemistry*; Taylor, D. C., Weissberger, A. Eds.; General Heterocyclic Chemistry Series; John Wiley: New York, 1984; Vol. 1, p 733.
(96) Fischer, E. O.; Fontana, S. *J. Organomet. Chem.* **1972**, *40*, 159.
(97) Raubenheimer, H.-G.; Fischer, E. O. *J. Organomet. Chem.* **1975**, *91*, C23.
(98) (a) Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1145. (b) Sabat, M.; Gross, M. F.; Finn, M. G. *Organometallics* **1992**, *11*, 745. (c) Sabat, M.; Reynolds, K. A.; Finn, M. G. *Organometallics* **1994**, *13*, 2084. (d) Balzer, B. L.; Cazanoue, M.; Sabat, M.; Finn, M. G. *Organometallics* **1992**, *11*, 1759. (e) Beckhaus, R.; Oster, J.; Kempe, R.; Spannenberg, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1565. (f) Anslyn, E. V.; Santarsiero, B. D.; Grubbs, R. H. *Organometallics* **1988**, *7*, 2137.
(99) (a) Schneider, A.; Gade, L. H.; Breuning, M.; Bringmann, G.; Scowen; I. J.; McPartlin, M. C. *Organometallics* **1998**, *17*, 1643. (b) Erker, G.; Berlekamp, M.; López, L.; Grehl, M.; Schönecker, B.; Krieg, R. *Synthesis* **1994**, 212. (c) Erker, G.; Mena, M.; Hoffmann, U.; Menjón, B.; Petersen, J. L. *Organometallics* **1991**, *10*, 291. (d) Erker, G.; Sosna, F. *Organometallics* **1990**, *9*, 1949. (e) Erker, G.; Sosna, F.; Betz, P.; Werner, S.; Krüger, C. *J. Am. Chem. Soc.* **1991**, *113*, 564. (f) Erker, G.; Pfaff, R.; Krüger, V.; Werner, S. *Organometallics* **1991**, *10*, 3559. (g) Erker, G.; Sosna, F.; Zwettler, R.; Krüger, C. *Organometallics* **1989**, *8*, 450. (h) Erker, G.; Sosna, F.; Hoffmann, U. *J. Organomet. Chem.* **1989**, *372*, 41. (i) Beckhaus, R.; Thiele, K.-H. *J. Organomet. Chem.* **1989**, *368*, 315. (j) Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R.-D. *J. Am. Chem. Soc.* **1984**, *106*, 7649. (k) Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 584. (l) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218.
(100) (a) Erker, G.; Lecht, R. *J. Organomet. Chem.* **1986**, *311*, 45. (b) Erker, G.; Lecht, R.; Schlund, K. A.; Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 666.
(101) Erker, G.; Mühlenbernd, T.; Benn, R.; Rufiñska, A. *Organometallics* **1986**, *5*, 402.
(102) Reviews: (a) Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397. (b) Erker, G. *Polyhedron* **1988**, *7*, 2451. (c) Erker, G.; Sosna, F.; Hoffmann, U. *J. Organomet. Chem.* **1989**, *372*, 41. (d) Beckhaus, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 686.
(103) Fischer, E. O.; Gibbins, S. G.; Kellerer, W. *J. Organomet. Chem.* **1981**, *218*, C51.
(104) Barluenga, J.; Rodríguez, F.; Vadecard, J.; Bendix, M.; Fañanás, F.; López-Ortiz, F. *J. Am. Chem. Soc.* **1996**, *118*, 6090.
(105) Barluenga, J.; Rodríguez, F.; Fañanás, F. *Organometallics* **1997**, *16*, 5384.
(106) (a) Barluenga, J.; Canteli, R.-M.; Flórez, J.; García-Granda, S.; Gutiérrez-Rodríguez, A. *J. Am. Chem. Soc.* **1994**, *116*, 6949. (b)

Barluenga, J.; Canteli, R.-M.; Flórez, J.; García-Granda, S.; Gutiérrez-Rodríguez, A.; Martín, E. *J. Am. Chem. Soc.* **1998**, *120*, 2514.

(107) Webb, M. J.; Stewartz, R. P.; Graham, W. A. G. *J. Organomet. Chem.* **1973**, *59*, C21.

(108) Webb, M. J.; Bennett, M. J.; Chan, L. Y. Y.; Graham, W. A. G. *J. Am. Chem. Soc.* **1974**, *96*, 5931.

(109) Fischer, E. O.; Kreis, G.; Kreissl, F. R.; Kreiter, C. G.; Müller, J. *Chem. Ber.* **1973**, *106*, 3910.

(110) Yeh, M.-Ch. P.; Chuang, L.-W.; Chang, S.-C.; Lai, M.-L.; Chou, C.-C. *Organometallics* **1997**, *16*, 4435.

(111) Fischer, E. O.; Weiss, K.; Kreiter, C. G. *Chem. Ber.* **1974**, *107*, 3554.

(112) Weiss, K.; Fischer, E. O. *Chem. Ber.* **1976**, *109*, 1120.

(113) Fischer, E. O.; Weiss, K. *Chem. Ber.* **1976**, *109*, 1128.

(114) Fischer, E. O.; Fontana, S. *J. Organomet. Chem.* **1972**, *40*, 367.

(115) Dumas, S.; Lastra, E.; Hegedus, L. S. *J. Am. Chem. Soc.* **1995**, *117*, 3368.

(116) Hsiao, Y.; Hegedus, L. S. *J. Org. Chem.* **1997**, *62*, 3586.

(117) Bao, J.; Wulff, W.; Fumo, M. J.; Grant, E. B.; Heller, D. P.; Whitcomb, M. C.; Yeung, S.-M. *J. Am. Chem. Soc.* **1996**, *118*, 2166.

(118) Amin, S. R.; Sawant, S. S.; Puranik, V. G.; Sarkar, A. *Organometallics* **1995**, *14*, 3617.

(119) Fischer, E. O.; Offhaus, E. *Chem. Ber.* **1969**, *102*, 2549.

(120) Huttner, G.; Regler, D. *Chem. Ber.* **1972**, *105*, 1230.

(121) Fischer, E. O.; Offhaus, E.; Müller, J.; Nöthe, D. *Chem. Ber.* **1972**, *105*, 3027.

(122) Casey, C. P.; Boggs, R. A.; Anderson, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8947.

(123) Casey, C. P.; Boggs, R. A.; Marten, D. F.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1973**, 243.

(124) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 3554.

(125) Casey, C. P.; Cyr, C. R. *J. Organomet. Chem.* **1973**, *57*, C69.

(126) Casey, C. P.; Cyr, C. R.; Anderson, R. L. Marten, D. F. *J. Am. Chem. Soc.* **1975**, *97*, 3053.

(127) Fischer, E. O.; Rustemeyer, P. *J. Organomet. Chem.* **1982**, *225*, 265.

(128) Schubert, U.; Ackermann, K.; Rustemeyer, P. *J. Organomet. Chem.* **1982**, *231*, 323.

(129) Fischer, E. O.; Rustemeyer, P.; Orama, O.; Neugebauer, D.; Schubert, U. *J. Organomet. Chem.* **1983**, *247*, 7.

(130) Fischer, E. O.; Aumann, R. *Chem. Ber.* **1969**, *102*, 1495.

(131) Fischer, E. O.; Richter, K. *Chem. Ber.* **1976**, *109*, 1140.

(132) (a) Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691. (b) Carre, F.; Cerveau, G.; Colomer, E.; Corriu, R. J. P.; Young, J. C. *J. Organomet. Chem.* **1979**, *179*, 215. (c) Wulff, W.; Gilberston, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520.

(133) Filippou, A. C.; Fischer, E. O.; Müller, G. *J. Organomet. Chem.* **1987**, *329*, 223.

(134) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550.

(135) Dean, W. K.; Graham, W. A. G. *J. Organomet. Chem.* **1976**, *120*, 73.

(136) (a) Dötz, K. H.; Pruskil, I.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1983**, *116*, 2337. (b) Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689.

(137) Gaye, M.; Demerseman, B.; Dixneuf, P. H. *J. Organomet. Chem.* **1992**, *424*, 65.

(138) Stockman, K. E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *J. Am. Chem. Soc.* **1992**, *114*, 8733.

(139) (a) Mayr, A.; Hoffmeisteir, H. *Adv. Organomet. Chem.* **1991**, *32*, 227. (b) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281.

(140) Fischer, E. O.; Schluge, M.; Besenhard, J. O. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 683.

(141) Dao, N. Q.; Fevrier, H.; Jouan, M.; Fischer, E. O.; Röll, W. *J. Organomet. Chem.* **1984**, *275*, 191.

(142) Fischer, E. O.; Huttner, G.; Lothar, T.; Lindner, A. F.; Kreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 231.

(143) Fischer, E. O.; Richter, K. *Chem. Ber.* **1976**, *109*, 2547.

(144) Huy, N. H. T.; Lefloch, P. *J. Organomet. Chem.* **1988**, *344*, 303–311.

(145) Tomuschat, P.; Kröner, L.; Steckhan, E.; Nieger, M.; Dötz, K. H. *Chem. Eur. J.* **1999**, *5*, 700.

(146) Wang, H.; Wulff, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 10573.

(147) Dötz, K. H.; Dietz, R.; Neugebauer, D. *Chem. Ber.* **1979**, *112*, 1486.

(148) Dötz, K. H.; Tiriliomis, A.; Harms, K. *Tetrahedron* **1993**, *49*, 5577.

(149) Moldes, I.; Ros, J.; Torres, M. R.; Perales, A.; Mathieu, R. *J. Organomet. Chem.* **1994**, *464*, 219.

(150) Connor, J. A.; Lloyd, J. P. *J. Chem. Soc., Perkin Trans. 1* **1973**, 17.

(151) (a) Söderberg, B. C.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113. (b) Barluenga, J.; Montserrat, J. M.; Flórez, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1068. (c) Toledano, C. A.; Rudler, H.; Daran, J.-C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 574. (d) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908.

(152) Sierra, M. A.; Mancheño, M. J.; Sáez, E.; del Amo, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 6812.

(153) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726. (b) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642.

CR9804137