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Metalloxy Fischer Carbene Complexes: An Efficient Strategy to Modulate Their Reactivity

José Barluenga* and Francisco J. Fañanás

Instituto Universitario de Química Organometálica 'Enrique Moles', Unidad Asociada al C.S.I.C. Julián Clavería 8, Universidad de Oviedo, 33071 Oviedo, Spain

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1. Introduction

Metal carbene complexes are among the most important organometallic compounds and since the discovery by Fischer[1] of stable carbene complexes for chromium, molybdenum, and tungsten, organic chemists have developed widespread applications of these complexes in synthetic organic chemistry.[2] The majority of the work in this field has been focused on the reactions of alkoxy and aminocarbene complexes, both thermal[2d,e] and photochemical.[2f] Replacing the heteroatom substituent with aryl groups increases the reactivity of the metal carbene while decreasing the carbene stability.[3] Substitution of the alkoxy or amino moiety by hydrogen provides a further increase in electrophilic reactivity linked with a considerable decrease in carbene stability.[4] On the other hand, the presence of a second, electron deficient, metal bound through oxygen to

* Corresponding author. Tel.: +34-98-5103450, fax: +34-98-5103450; e-mail: barluenga@sauron.quimica.uniovi.es

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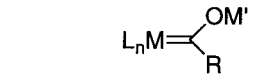


L_nM = [V], [Nb], [Cr], [Mo], [W], [Mn], [Re], [Fe], [Ru], [Co], [Rh], [Pt]
M' = [Sc], [Ti], [Zr], [Hf], [Th], [U], [Si], [Sn], [B], [Al], [P]

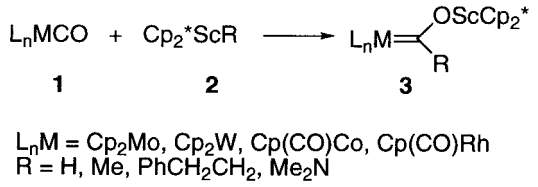
Figure 1.

the carbene heteroatom offers the opportunity to control the carbene reactivity by steric and electronic variation of the Lewis acidic component. In this report the preparation and synthetic applications of the bimetallic systems represented in Fig. 1 are discussed.

2. Scandoxycarbene Complexes

Reaction of metal carbonyls **1** with substituted permethylscandocene **2** at 25°C leads to the corresponding scandoxycarbene complexes **3** in 50–60% yield (Scheme 1).[5] This reaction is strongly dependent on the size of the R group, and bulky groups are not added to the metal carbonyls **1** even at elevated temperatures, probably due to steric interactions with the cyclopentadienyl ligands. Only much less encumbered monocyclopentadienyl systems **1** [L_nM=Cp(CO)Co, Cp(CO)Rh] do not so severely constrain the type of R group which may be added. Presumably, the reaction of **1** and **2** involves an initial adduct formation, by interaction between the highly electrophilic scandium centre and the carbonyl oxygen,[6] followed by intramolecular nucleophilic attack of the scandium substituent to the polarized CO bond (Scheme 1).

The scandoxycarbene complexes **3** are relatively stable and on heating in benzene for days at 80°C they slowly decompose to unidentified products. When heated to 80°C under hydrogen, however, **3** (L_nM=Cp_2W, R=Me) is cleanly converted to **3** (L_nM=Cp_2W, R=H) and methane. This reaction is thought to proceed by considering an equilibrium between **1**, **2** and **3** and the reaction of **2** (R=Me) with hydrogen generates methane and **2** (R=H),[7] which reacts rapidly to form **3** (L_nM=Cp_2W, R=H). On the other hand, no reaction is observed between **3** and dimethylamine and treatment of **3** with methanol leads instead to cleavage of the Sc–Cp^* bond and subsequent decomposition.



L_nM = Cp_2Mo, Cp_2W, Cp(CO)Co, Cp(CO)Rh
R = H, Me, $PhCH_2CH_2$, Me_2N

Scheme 1.

L_nM = $(CO)_5Mo$, $(CO)_5W$, $(CO)_4Fe$, $(CO)_3Ni$

Scheme 2.

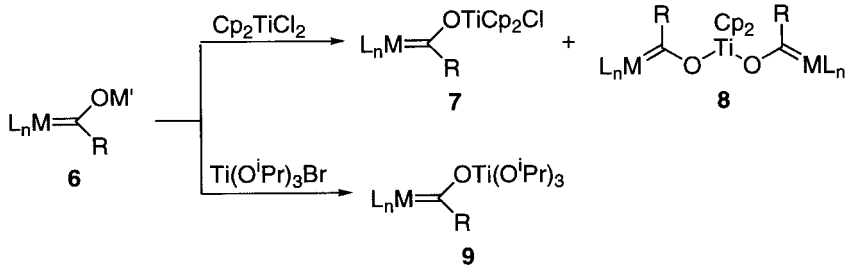
3. Titanoxycarbene Complexes

3.1. Nucleophilic addition to metal carbonyls

There are a number of different routes to prepare titanoxycarbene complexes. The simplest method is the Fischer route in which the reaction of tetrakis(dimethylamino)-titanium **4** with metal carbonyls **1** affords the titanoxy Fischer carbene complexes **5** in 70–75% yield (Scheme 2).[8]

The reaction of acylmetallate complexes **6**, generated by the Fischer method,[1] with titanocene dichloride furnishes an equimolecular mixture of the titanoxycarbene **7** and the biscarbene complexes **8**.[9] The compounds **7** are exclusively formed by keeping the temperature at −40°C.[10] Likewise, addition of tri-*i*-propoxytitanium bromide to the corresponding acylmetallate complex **6** at room temperature gives rise to the bimetallic complexes **9** (Scheme 3).[11]

Complexes **7**, **8** and **9** are very stable in the solid state but in solution they are generally less stable than their methoxycarbene analogues and decompose in a few hours. On the other hand, X-ray crystallographic determinations of these complexes[11] suggest a higher contribution of the resonance structures **7′** and **9′** to the bonding than in the alkoxycarbene complexes (Fig. 2).[12] The metal–carbene carbon bond distances of titanoxycarbene complexes **7** and **9** are, however, very close to those of the alkoxycarbene derivatives.



M' = Li, NMe_4
L_nM = $(CO)_5Cr$, $(CO)_5Mo$, $(CO)_5W$, Cp'$(CO)_2Mn$ (Cp' = MeC_5H_4)
R = NMe_2, Me, Bu, C(Me)=CH_2, Ph, 4-MeC_6H_4, 2-Furyl

Scheme 3.

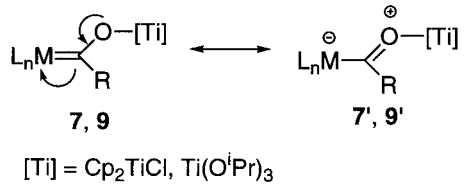


Figure 2.

Significant carbenoid character, therefore, apparently remains in these systems and this may be modified by using suitable ligands on the Lewis acidic centre.

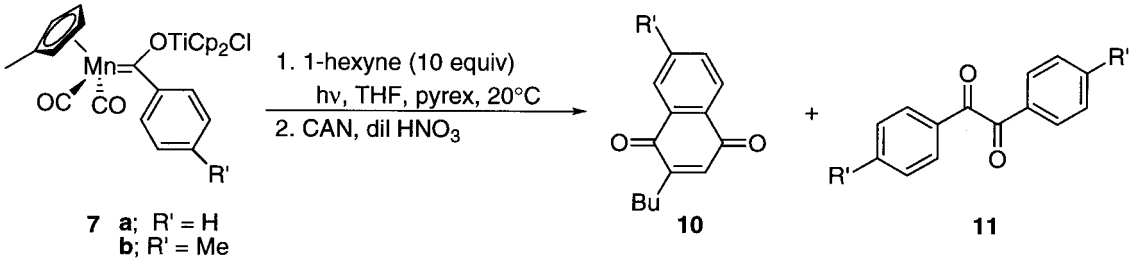
With regard to the reactivity of these systems, the carbene complexes **7a**,**b** [$L_nM{=}Cp'(CO)_2Mn$, R=C_6H_4R', **a**, R′=H, **b**, R′=Me] are active in benzannulation reactions under photochemical conditions, or in refluxing of toluene, affording the naphthoquinone derivatives **10** in 28–30% yield, in the presence of 10 equiv. of 1-hexyne followed by oxidative work-up, as shown in Scheme 4.[13] In addition, small amounts (5–10%) of 1,2-diketones **11**, derived from the coupling of two aryl carbene fragments are produced, probably as a consequence of the acyl character of these complexes. These results are in marked contrast to those obtained starting from methoxymanganesecarbene analogues, which under the same reaction conditions do not react, thus demonstrating that Fischer carbene complexes can be activated by electron-deficient metals.

3.2. Non-nucleophilic addition to metal carbonyls

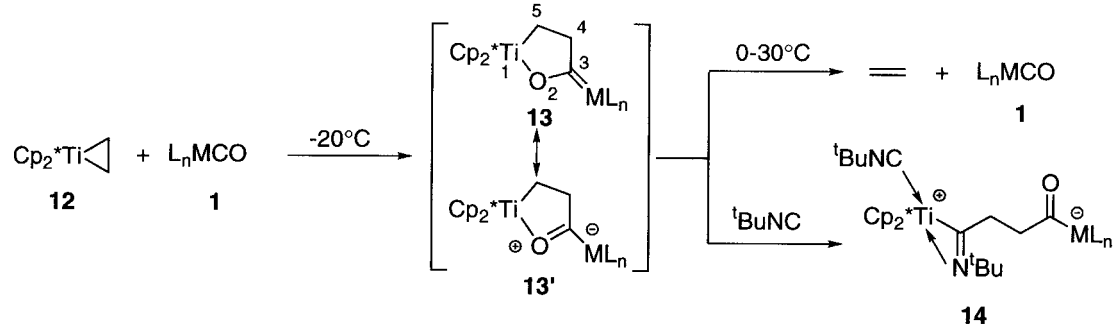
3.2.1. η^2-Alkene and alkyne titanium complexes. Titanoxycarbene complexes can also be prepared by routes avoiding nucleophilic addition to metal carbonyls. The reaction of (ethylene)bis(η^5-pentamethylcyclopentadienyl)-titanium **12**[14] with various metal carbonyls **1** at −20°C affords titanoxycarbene–metal complexes **13** in 30–57% yield (Scheme 5).[15] The complexes **13** are thermally unstable in solution even at −20°C, while in the solid state they are relatively stable. The molecular structure of **13** [$L_nM{=}(CO)_9Re_2$] reveals an important contribution from the dipolar resonance structure **13′**, as previously indicated for complexes **7** and **9** in Fig. 2.

Since compound **12** can be viewed as a titanacyclopropane complex,[16] formation of **13** can be considered to proceed by a [2+2]-pericyclic type reaction.[16] This can also be envisaged as a migratory insertion of the carbonyl ligand into a strained titanium–carbon σ bond, favoured by the remarkable oxophilic nature of titanium.

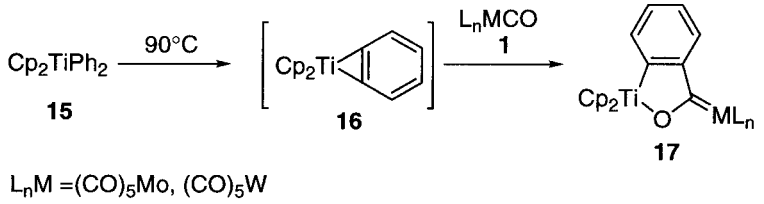
When the complexes **13** are heated from 0 to 30°C in toluene, quantitative formation of ethylene and the corresponding metal carbonyl **1** is observed, which indicates that the C3–C4 bond of **13** is selectively cleaved during thermolysis. Such fission of the carbene carbon–carbon bond is unusual for Fischer type carbene complexes.[17] Otherwise, the reaction of **13** and *t*-butylisocyanide at −35°C results in the formation of complexes **14** in 80% yield (Scheme 5).[15b,18] The complexes **14** can be generated by migratory insertion of the *t*-butylisocyanide into the titanium–carbon bond of the acyl resonance structure **13′** and further complexation of a second molecule of *t*-butylisocyanide. These results suggest that the complexes **13** have chemical properties characteristic of metallacyclopentanes[14,19] and oxametallacyclopentanes[20] of group 4 transition metals.



Scheme 4.



Scheme 5.



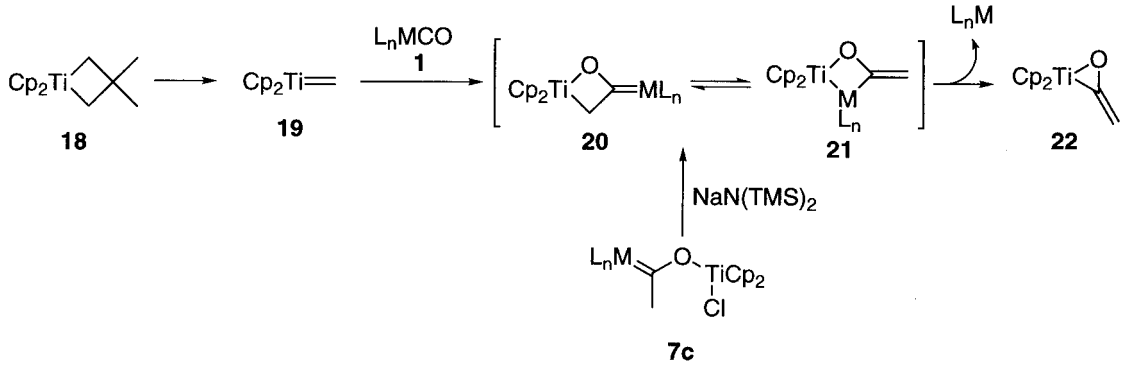
Scheme 6.

Erker et al. have used (η^2-benzyne)titanocene **16** as a reagent for carbene complex synthesis. The titanoxycarbene complexes **17** are formed by the reaction of **16**, easily generated in situ at 90°C from diphenyltitanocene **15**, with the carbonyl complexes **1** (Scheme 6).[21]

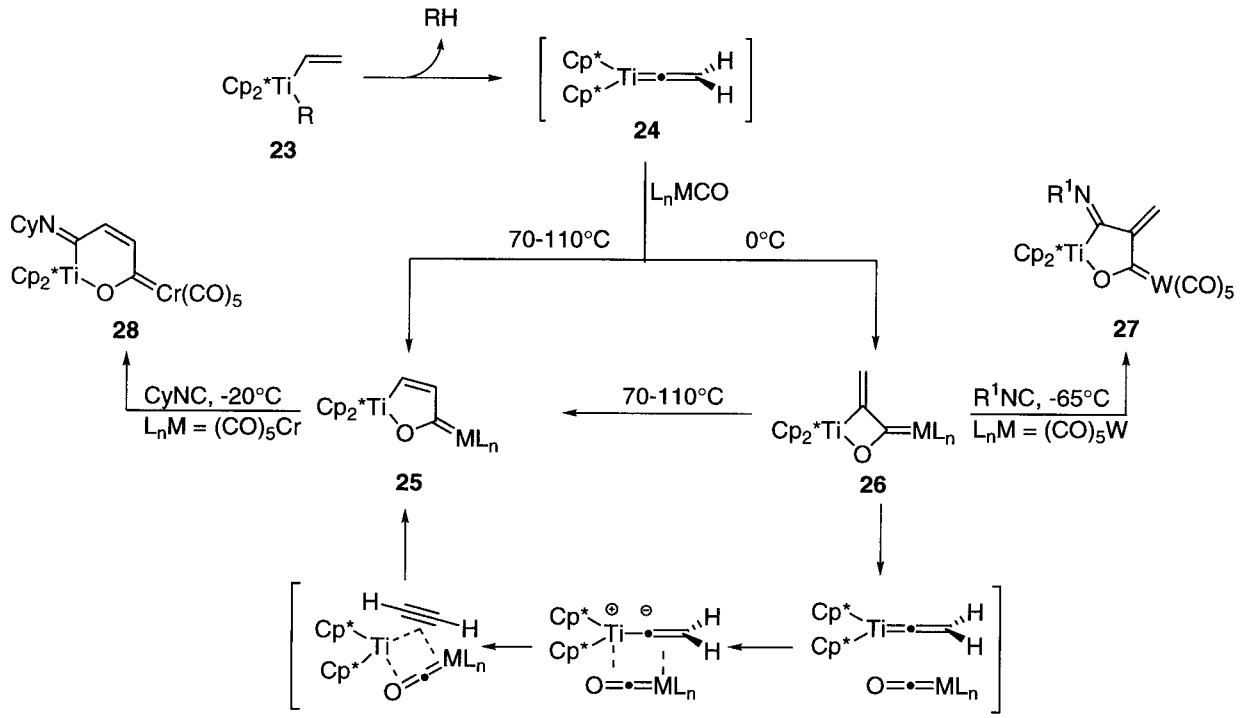
3.2.2. Alkylidene titanium complexes. Alkylidene titanium complexes may be used as starting materials to prepare titanoxycarbene complexes by reaction with metal carbonyls. β,β-Dimethyltitanocene metallacyclobutane **18**, for example, reacts with metal carbonyls **1** at 5°C to yield a titanocene adduct **22** through the intermediate formation of a cyclic titanoxycarbene complex.[22] According to the ^{1}H NMR-monitored reaction, **18** initially cleaves to form methylenetitanocene **19** and *i*-butylene. Insertion of the carbonyl group of **1** into **19**, presumably by initial coordination of the carbonyl oxygen to the titanium, followed by nucleophilic attack of the methylene carbon on the electrophilic carbonyl carbon,[23] leads to a 1:1 equilibrium mixture of the four-membered metallacyclic titanoxycarbene complexes **20** and the titanocene–metal-bridged ketene adduct **21**. Finally, **20** and **21** rearrange to **22** releasing the metal fragment L_nM (Scheme 7). Independent synthesis of the proposed intermediates **20** and **21** provides additional structural evidence. Deprotonation of **7c** [L_nM=$(CO)_5$Cr] at −50°C with sodium hexamethyldisilazide yields the same intermediates formed in the reaction of **18** and hexacarbonylchromium. At temperatures below −10°C, the intermediates **20** and **21** do not rearrange to the titanocene ketene **22** at a perceptible rate (Scheme 7).[22]

Similarly, vinylidenetitanocene **24** is readily generated by thermolysis of the (alkyl)(vinyl)titanocene complexes **23**.[24] If **23a** (R=CH=CH_2) is heated at 70–100°C in the presence of the metal carbonyls **1**, ethylene is liberated and the binuclear Fischer carbene complexes containing a five-membered titanacycle **25** are formed (Scheme 8).[25] On the other hand, the compound **23b** (R=Me) undergoes loss of methane at lower temperatures (5–20°C) than that required for elimination of ethylene from **23a**.[24b] Thus, treatment of **23b** with the metal carbonyls **1** in equimolecular amounts at 0°C affords the Fischer carbene complexes with the oxatitanacyclobutane structure **26** in 30–55% yield (Scheme 8).[26,27] The formation of compound **26** can be considered as a formal [2+2] cycloaddition reaction of the Schrock carbene fragment of **24** and the carbonyl group of **1**. The complexes **26** are relatively stable in the solid state but in solution they decompose at low temperatures (−78 to −20°C) generating the starting materials **1** and **24**. On heating at temperatures from 70 to 110°C, however, the complexes **26** undergo an isomerization reaction leading to the titanoxycarbene complexes **25**. The isomerization course of **26** to **25** can be explained as depicted in Scheme 8. Firstly, an inverse cycloreversion from the bimetallic oxetane **26** to the vinylidenetitanocene **24** and metal carbonyls **1** in a non-classical behaviour[27a] followed by coordination of the metal carbonyl to the carbon–carbon double bond of the vinylidene takes place. This leads to a vinylidene–acetylene transformation by a metal-mediated 1,2-proton shift. Subsequently, the coordinated acetylene undergoes cycloaddition with the metal carbonyl forming the complexes **25**.[28] The generation of the vinylidene fragment **24** as an intermediate is confirmed by trapping with ethylene, isocyanate, or by protonation. No cycloreversion is observed for the titanaoxolene carbene complexes **25.**

Although the complexes **25** and **26** contain vinylcarbene units, they do not react with alkynes as in a Dötz reaction. They react with isonitriles however, undergoing an insertion reaction in the titanium–carbon σ-bond instead of the cycloaddition reaction observed for the alkoxyvinyl carbene complexes.[29] Thus, when complex **26a** [L_nM=$(CO)_5$W] is treated with 2,6-dimethylphenylisonitrile at −65°C, the



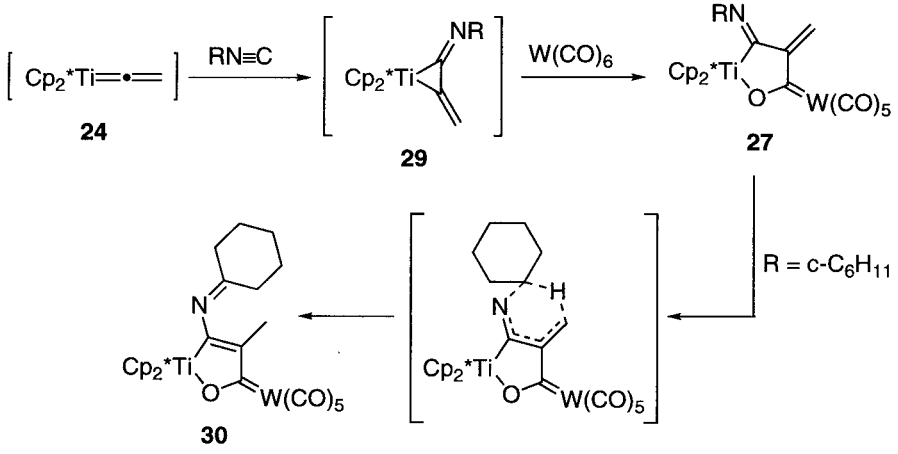
Scheme 7.



R = $CH{=}CH_2$, Me
R^1 = 2,6-$Me_2C_6H_3$, Cy (c-C_6H_{11})
L_nM = $(CO)_5Cr$, $(CO)_5Mo$, $(CO)_5W$, $Cp(CO)_2Mn$, $Cp'(CO)_2Mn$
$Cp(CO)_2Re$, $(CO)_9Mn_2$, $(CO)_9Re_2$, $(CO)_4Fe$, (CO)acacRh

Scheme 8.

oxatitanacyclopentylidenecarbene complex **27** is formed in 70% yield. In contrast, when **25b** [$L_nM{=}(CO)_5Cr$], which does not react with 2,6-dimethylphenylisonitrile, is treated with cyclohexylisonitrile, a reversible insertion reaction into the titanium–carbon bond takes place at −20°C and the six-membered metallacycle **28** is generated in 77% yield (Scheme 8).[28] The different reactivity of **25** and **26** towards isonitriles is believed to be due to the ease with which **26** undergoes a cycloreversion reaction generating **24**, which would react with isonitriles to give 1-azabutatrienetitanocene complexes **29**. Subsequent cycloaddition with **1** would give **27**. In fact, vinylidenetitanocene **24** reacts with isonitriles to afford the highly reactive azabutatriene titanocene complexes **29**, in a [2+1] addition reaction,



R = 2,6-$Me_2C_6H_3$, c-C_6H_{11}

Scheme 9.

which are trapped with tungsten hexacarbonyl **1** [$L_nM{=}(CO)_5W$] giving the oxatitanacyclopentylidene metal complexes **27**.[27b] For **27b** (R=*c*-C_6H_{11}) a rearrangement through a 1,5-proton shift to the oxatitanacyclopentene complex **30** takes place, probably caused by the formation of a conjugated triene system (Scheme 9).[27b]

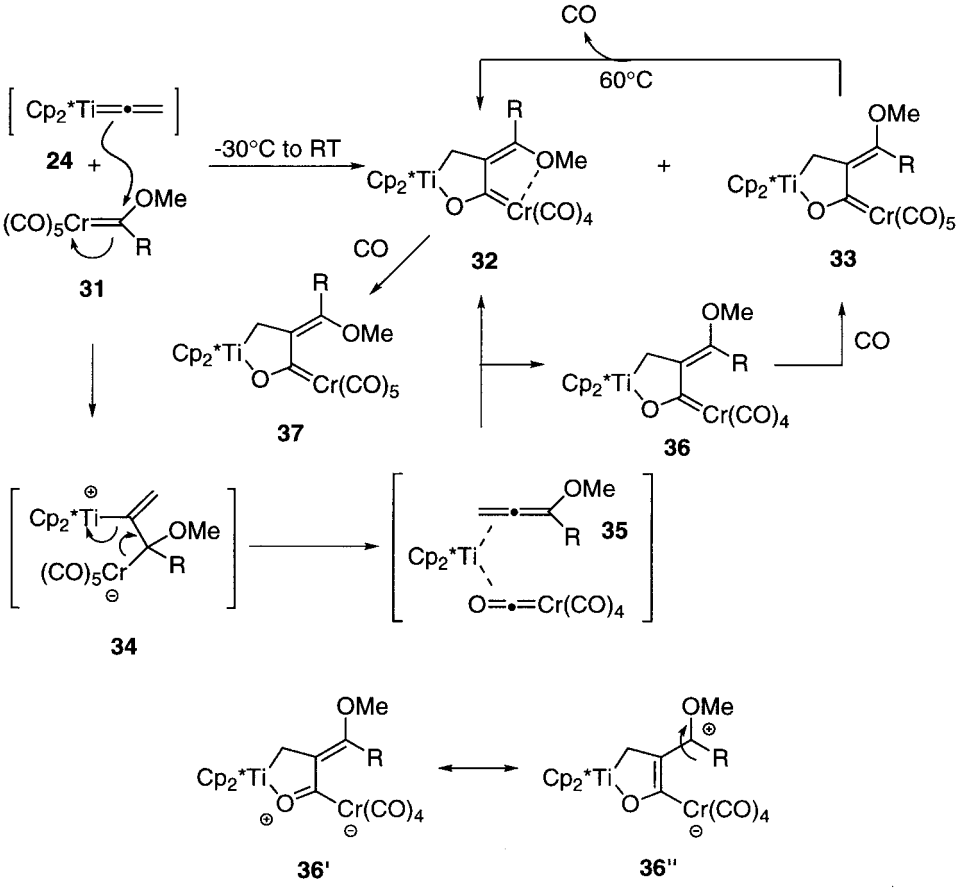
3.3. From titanium Schrock- and Fischer-type carbene complexes

Vinylidenetitanocene **24** can also be trapped with classical Fischer-type carbene complexes. Treatment of the chromium methoxycarbene complex **31** with the in situ-generated **24** at temperatures between −30 and 25°C gives the heterobimetallic complexes **32** and **33** by an unusual coupling of the Fischer carbene complexes **31** with the intermediate Schrock carbene complex **24** (Scheme 10).[30] This reaction represents the first example of an intermolecular coupling of inversely polarised carbene ligands. The formation of **32** and **33** can be accounted for by initial attack of the nucleophilic carbene carbon of **24** on the electrophilic carbene carbon of **31** to afford the intermediate **34**. A metathesis favoured by coordination of CO to the oxophilic titanium centre leads to the allene derivative **35**. Titanium-centred cycloaddition of the allene molecule **35** with the remaining $Cr(CO)_5$ fragment gives rise directly to **32** and **36**, depending on the mode of approach of the allene molecule. Fast carbon monoxide addition converts the unsaturated complexes **36** into **33**. Under a CO atmosphere the methoxy coordination to the chromium centre in **32** is reverted and the pentacarbonyl complexes **37** are formed. Otherwise, **33** can be thermally (60°C) converted into **32** by elimination of one carbon monoxide ligand. This very unusual isomerization can be explained by considering the ionic acyl resonance structure **36′** of the intermediate tetracarbonyl complex **36**. Rotation across the carbon–carbon bond of the resonance structure **36″** and further methoxy complexation to chromium leads to **32** (Scheme 10)[31]

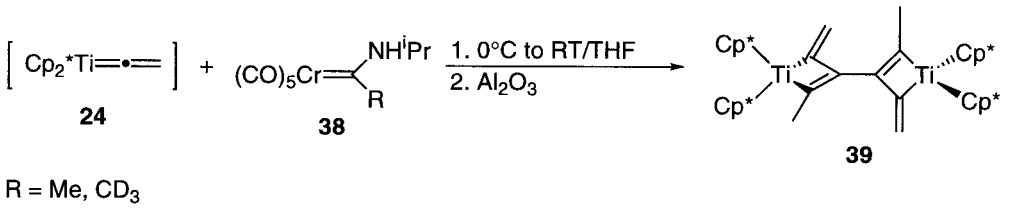
A different type of reaction is found starting from aminocarbene complexes. When the aminocarbene complexes **38** are used to trap **24**, formation of the homodinuclear titanium complex **39** only is observed, independent of the starting carbene **38** used.[31] These results indicate that the carbene fragment of **38** does not participate in the construction of the complex **39** (Scheme 11). The different reaction paths starting from alkoxy or aminocarbene complexes **31** and **38**, respectively, can be attributed to a reduced carbene carbon electrophilicity and a higher stability of the latter due to a stronger π-donor ability of the nitrogen atom.

4. Zirconoxycarbene Complexes

The synthesis of zirconoxycarbene complexes is very similar to that described for their titanium analogues. Two



Scheme 10.

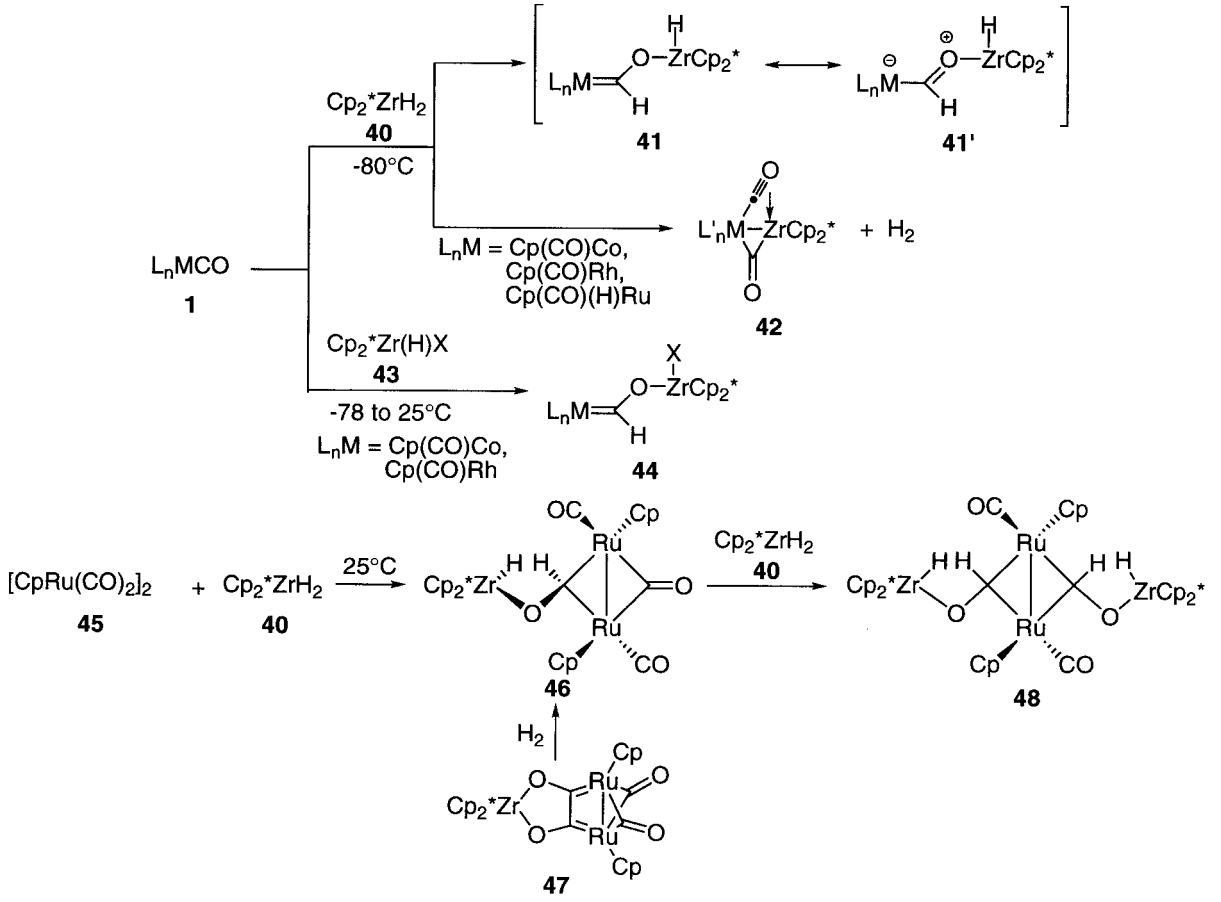


Scheme 11.

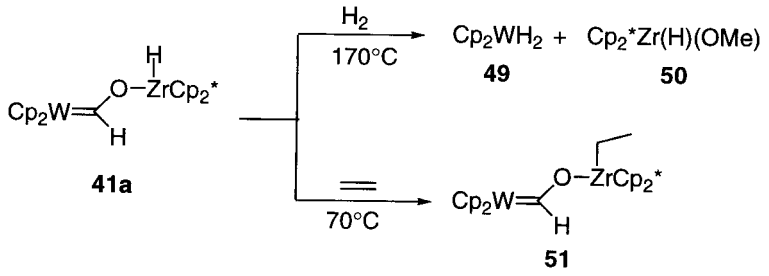
general routes may be mentioned. These are nucleophilic attack to coordinated carbon monoxide, known as the Fischer route, and zirconium-mediated reductive cyclodimerization of metal carbonyls and unsaturated systems such as alkenes, alkynes, or dienes.

4.1. The Fischer route

Bercaw et al. have used bis(pentamethylcyclopentadienyl)-zirconium(IV) dihydride **40** as a nucleophilic reagent for carbene complex synthesis. Zirconoxycarbene complexes **41** may be prepared in this way with very good yields (75–90%) by treatment of the corresponding metal carbonyl **1** with **40** (Scheme 12).[32–35] The reaction fails if **1** [L_nM=Cp(CO)Co, Cp(CO)Rh, and Cp(CO)(H)Ru] are used as starting materials and, in these cases, the mixed-metal dimers **42** and hydrogen are obtained.[36,37] The reductive elimination of hydrogen from **40** leading to the formation of **42** may be prevented by replacement of one of the zirconium hydrides by a halide (F, Cl). Thus, treatment of an excess of **1** [L_nM=Cp(CO)Co, Cp(CO)Rh, and Cp(CO)(H)Ru] with zirconocene(halide)(hydride) **43** at room temperature affords the zirconoxycarbene complexes **44** in good yields (Scheme 12).[37] Finally, reaction of the binuclear ruthenium complex **45** with **40** at 25°C produces the carbene complex **46** in 70% yield, in which the zirconoxycarbene occupies a bridging position and the ruthenium cyclopentadienyl ligands are mutually *trans*.[38] Alternatively, **46** can be smoothly obtained by the reaction of hydrogen with the complex **47**, which is in equilibrium



Scheme 12.



Scheme 13.

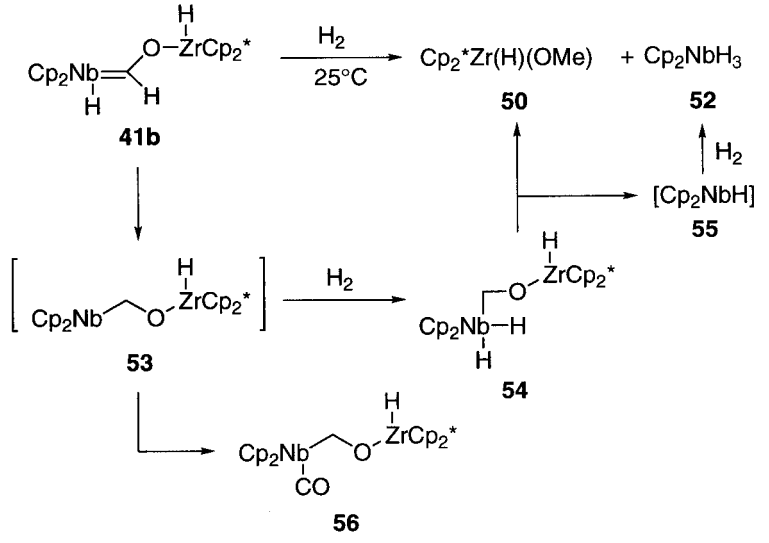
with a small amount of **45** and permethylzirconocene.[39] The latter adds hydrogen to form **40**, which rapidly reacts with **45** to produce **46**. Addition of a second equivalent of **40** to **46** yields the highly insoluble biscarbene complex **48** (Scheme 12).

The complex **41a** ($L_nM{=}Cp_2W$) exhibits a remarkable thermal stability and remains unchanged after hours at 150°C. When treated with hydrogen (1 atm) at 170°C, bis(cyclopentadienyl)tungstendihydride **49** and (methoxy)-permethylzirconocenehydride **50** are obtained in 50% yield.[32] Excess ethylene reacts smoothly with **41a** at 70°C to afford only the corresponding ethyl derivative **51**, there being no evidence of addition to the zirconoxycarbene moiety (Scheme 13).[32]

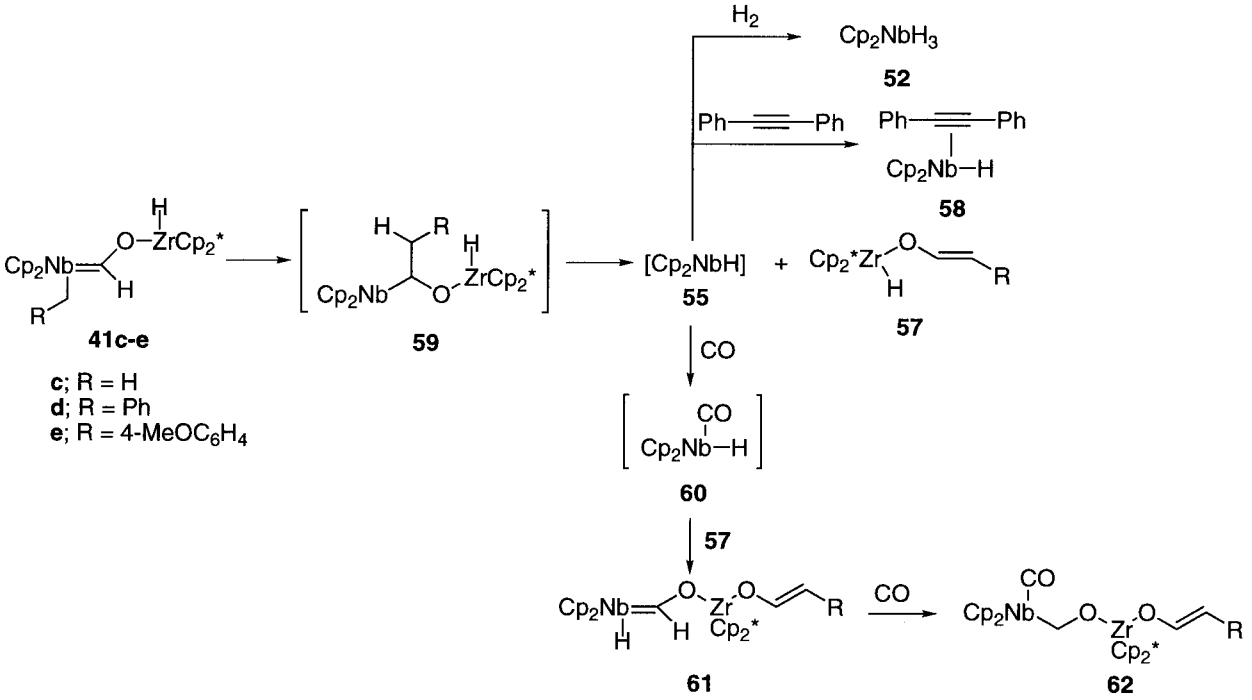
The carbene complex **41b** [$L_nM{=}Cp_2(H)Nb$] also undergoes a smooth reaction with hydrogen (1 atm) at 25°C to yield **50** and niobocenetrihydride **52**.[32] The higher reactivity of **41b** compared to **41a** may be attributed to its availability to undergo a migratory insertion generating the formal 16-electron Nb(III) intermediate **53**. Further oxidative addition of hydrogen to the coordinatively unsaturated **53** leads to **54**, which by subsequent reductive elimination yields **50** and **52**, by addition of hydrogen to the resultant niobocenemonohydride **55**.[34] The intermediate **53** has been detected by ^{1}H NMR spectroscopy and chemically characterized by trapping with carbon monoxide, affording the complex **56** (Scheme 14).

The alkyl-substituted niobocene carbene complexes **41c–e** [$L_nM{=}Cp_2(RCH_2)Nb$, **c**, R=H, **d**, R=Ph, **e**, R=4-$MeOC_6H_4$] afford the *trans*-zirconium enolate **57** and either niobocenetrihydride **52** or niobocene(diphenylacetylene)-hydride **58** in the presence of hydrogen or diphenylacetylene, respectively.[34] A plausible mechanism leading to these products would involve insertion of the zirconoxycarbene into the niobium alkyl bond to give the complex **59**, followed by rapid β-hydride elimination to yield **57** and the monohydride complex **55**. Subsequent trapping of this reactive intermediate by hydrogen or diphenylacetylene gives the complexes **52** or **58**, respectively. When carbon monoxide is the promoting ligand, a secondary reaction is also observed. The initially generated products, niobocene-(carbonyl)hydride **60** and **57**, react further by nucleophilic attack of the zirconium hydride **57** on the coordinated carbonyl ligand of **60** to yield the zirconoxycarbene complexes **61**, which by subsequent hydride transfer in the presence of carbon monoxide leads to the complex **62** (Scheme 15).[34] Unlike the carbene complexes **41c–e**, **41f** [$L_nM{=}Cp_2(Ph)Nb$] decomposes when it is warmed under a carbon monoxide atmosphere or it reacts with hydrogen to give undetermined products.

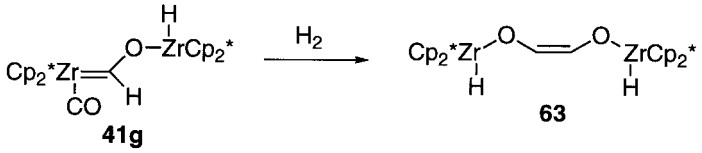
The homobimetallic carbene complex **41g** [$L_nM{=}Cp^*_2(CO)Zr$] is very unstable and decomposes to a myriad of products. In the presence of a hydrogen atmosphere, however, it evolves to form the *cis*-zirconiumenediolate complex **63** (Scheme 16).[33,35] This result is in marked



Scheme 14.



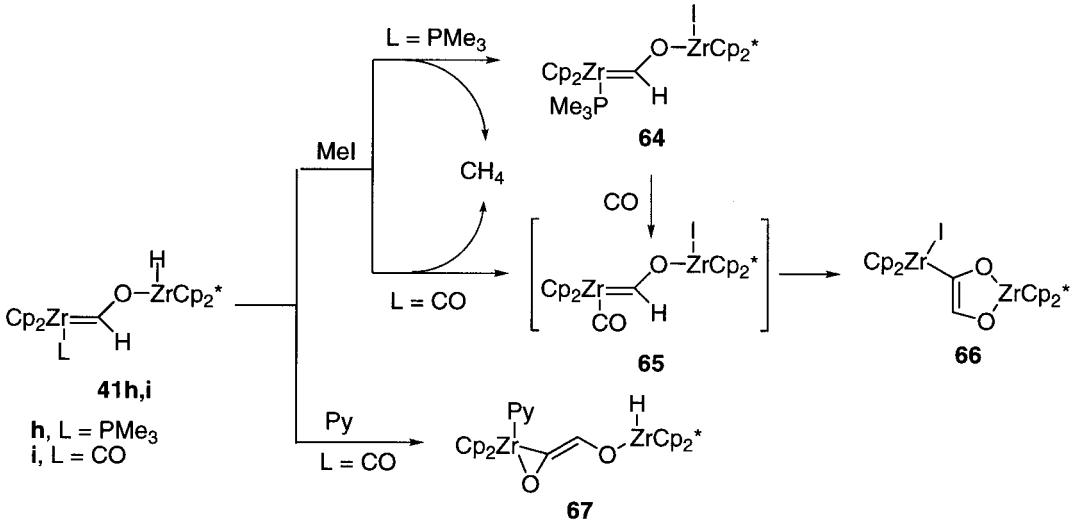
Scheme 15.



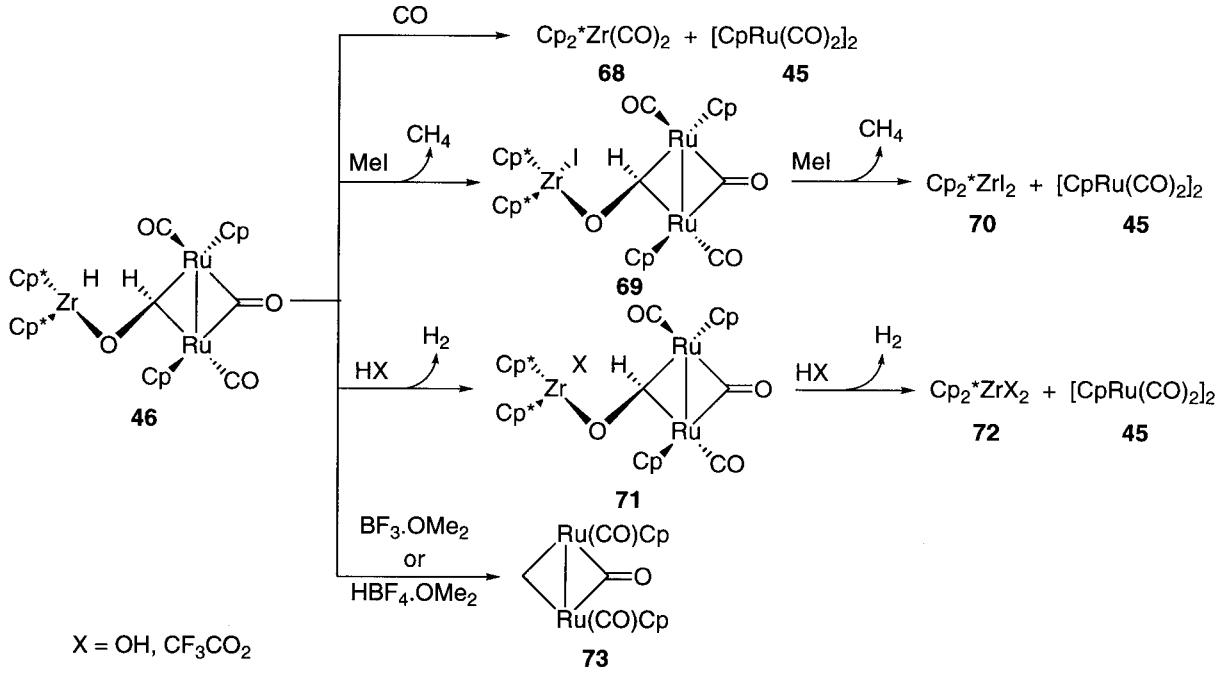
Scheme 16.

contrast to that obtained in the reaction of permethylzirconocenedihydride and free carbon monoxide, in which the *trans*-zirconium enediolate analogous to **63** is exclusively formed.[40]

In contrast to **41g**, **41h**,**i** [$L_nM{=}Cp_2(L)Zr$, **h**, L=PMe_3, **i**, L=CO] are more stable, presumably owing to the presence of the less sterically hindered cyclopentadienyl ligand, and they can be easily isolated. Treatment of **41h** with an excess of methyl iodide liberates 1 equiv. of methane and yields the zirconoxycarbene complex **64** in 83% yield. The same treatment carried out with **41i**, however, generates, with the



Scheme 17.



Scheme 18.

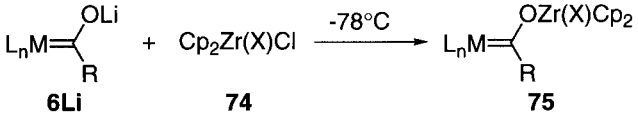
liberation of methane, the carbene complex **65**, which leads to the dioxazirconacyclopentene derivative **66**, involving a carbonyl insertion in the zirconoxycarbene followed by a rearrangement. The same results are obtained by carbonylation of **64**. The reactivity of **41i** with bases is also of interest. Addition of an excess of pyridine to **41i**, for example, affords a pyridine-trapped zirconium ketene complex **67** in 82% yield (Scheme 17).[35]

With regard to the reactivity of **46**, its treatment with carbon monoxide (4 atm) at 25°C generated the dicarbonylzirconocene **68**, the binuclear ruthenium complex **45**, and presumably hydrogen, indicating the apparent reversibility of the carbonyl reduction. The reaction of **46** with methyl iodide results in the rapid formation of methane and the new carbene complex **69**, which then reacts further with methyl iodide to produce zirconocene diiodide **70** and **45**. Protonation of **46** with HX (X=CF_3CO_2, OH) results in the formation of the complex **71**, isolated for X=OH, which reacts further with HX to give rise to **72** and **45**. Although reaction of HX with **46** involves protonation of the hydride position, Lewis acids ($BF_3{\cdot}OMe_2$) or stronger protic acids ($HBF_4{\cdot}OMe_2$) react in a different manner with **46**, and the bridging methylene complex **73** is obtained as a mixture of *cis* and *trans* isomers in 60–70% yield (Scheme 18).[38] In the formation of **73**, cleavage of an oxygen–carbene carbon bond is invoked, this reaction having been previously described for the cleavage of bridging carbenes of iron with electrophiles (Scheme 18).[41]

Following the Fischer route, zirconoxycarbene complexes are also available by the reaction of acyl metallates with zirconocene chlorides. In this way, treatment of lithium acyl metallates **6Li** (M′=Li) with an equimolecular amount of the corresponding zirconocene chloride **74** at −78°C leads to the zirconoxycarbene complexes **75** in over 60% yield (Scheme 19).[21,22] Attempts to transform **75a** [$L_nM{=}(CO)_5Cr$, R=Me, X=Cl] into the four-membered zirconoxycarbene complex analogous to the titanium derivative **21** (see Scheme 7) by deprotonation with sodium hexamethyldisilazide and intramolecular alkylation were unsuccessful, although zirconocene ketene is a known compound.[42]

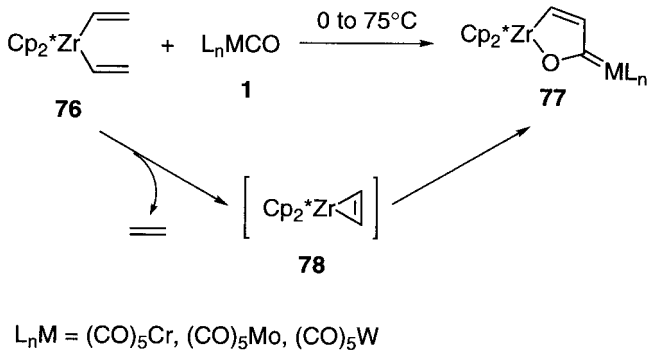
4.2. Insertion reactions of metal carbonyls in unsaturated zirconium complexes

4.2.1. η^2-Alkyne zirconium complexes. Reactive metal alkyne or diene π-complexes can be appropriate starting materials for the synthesis of zirconium-stabilised carbene complexes avoiding nucleophilic addition to metal carbonyls. In this context, divinylzirconocene **76** is thermally converted in the presence of metal carbonyls **1** into the metallacyclic Fischer carbene complexes **77** in 65–80% yield.[43] Unlike divinylpermethyltitanocene **23a**, on warming at temperatures between 0 and 75°C **76** undergoes loss of ethylene through a cyclometallation reaction[44] affording the zirconacyclopropene complex **78**, which reacts in situ with **1** by insertion of the coordinated carbon monoxide into the zirconium–carbon bond to furnish carbene complexes **77** (Scheme 20).



$L_nM = (CO)_5Cr, (CO)_5W$
R = Me, Ph
X = Cl, OPh

Scheme 19.



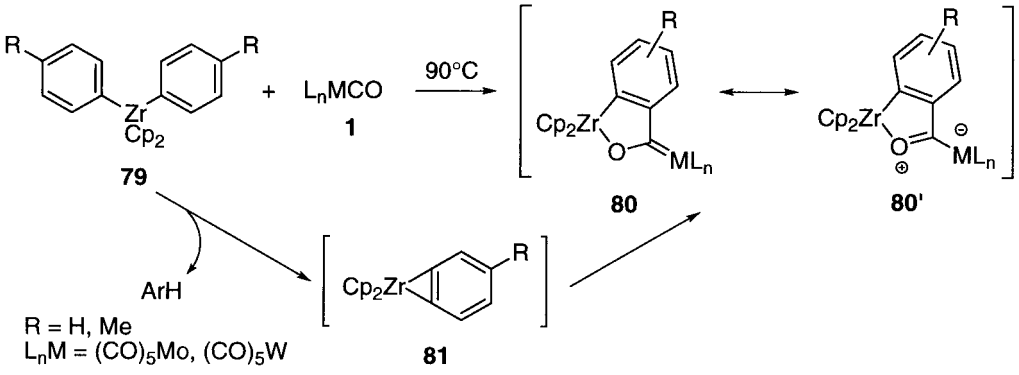
Scheme 20.

Similarly, diphenylzirconocene **79a** (R=H) reacts smoothly with **1** at 90°C to give the benzannelated five-membered metallacyclic zirconoxycarbene complexes **80a**,**b** [**a**, $L_nM=(CO)_5Mo$, R=H, **b**, $L_nM=(CO)_5W$, R=H] in good yields (Scheme 21).[21,45] X-Ray structure analysis shows that **80b** exhibits the characteristic properties of a Fischer-type carbene complex but the carbene carbon–oxygen bond is remarkably short, indicating again the importance of the dipolar resonance structure **80′b**.

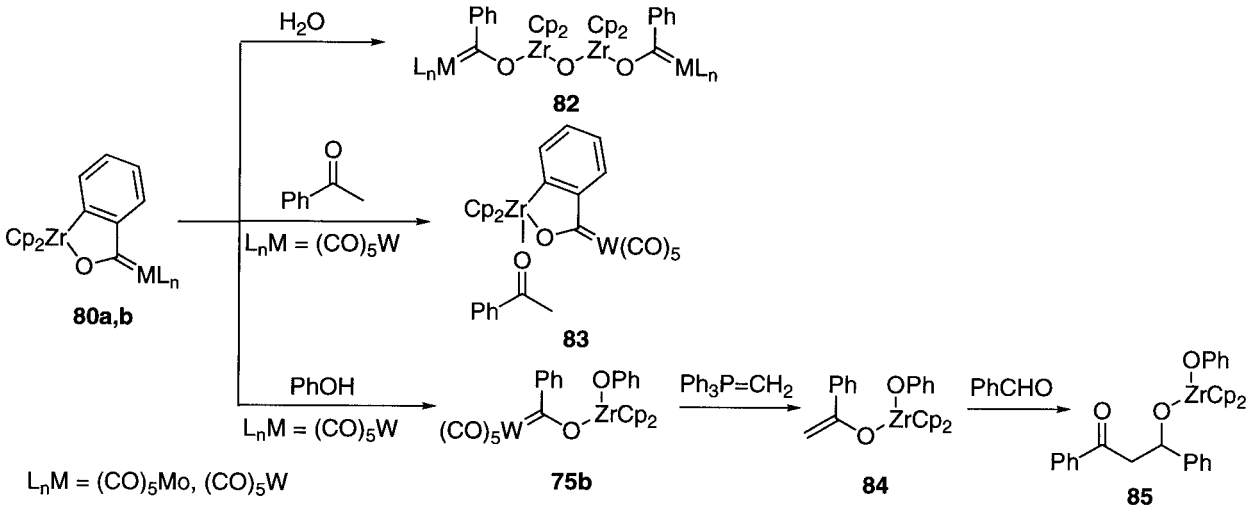
These results are explained by invoking the formation of the benzyne zirconocene derivative **81a** (R=H),[46] which reacts readily with **1** to form **80a**,**b**. Formation of **81a** is supported by the generation of a 40:60 mixture of the two regioisomers of **80c** [$L_nM=(CO)_5W$, R=Me on C(4) and C(5) of the aromatic benzene ring, respectively], derived from the alternative insertion of the carbonyl ligand of **1** into the zirconium–carbon bond of the unsymmetrical benzyne derivative **81b** (R=Me) (Scheme 21).

The complexes **80** are extremely moisture sensitive. Thus, controlled hydrolysis of **80** leads to opening of the five-membered metallacyclic structures by reaction of the zirconium–carbon bond with formation of the bis(zirconoxycarbene) complexes **82** containing four metal centres and a μ-oxo-bridged $Cp_2Zr–O–ZrCp_2$ unit, as determined by X-ray diffraction.[47] Despite the extreme sensitivity of the carbene complexes **80** to hydrolysis, their reluctance to undergo carbon–carbon coupling with common electrophiles is remarkable. The zirconoxycarbene complex **80b** [$L_nM=(CO)_5W$] is unreactive towards a variety of alkyl halides, aldehydes, ketones and esters. Only in its reaction with acetophenone has the 1:1 adduct **83** been observed. In contrast, the zirconium–carbon σ-bond of **80** is rapidly cleaved at room temperature by protic reagents. Addition of phenol to **80b** furnishes the zirconoxycarbene complex **75b**, analogous to that obtained according to the procedure indicated in Scheme 19. The complex **75b** rapidly reacts with 1 equiv. of methyltriphenylphosphorane[48] at room temperature to give the zirconium enolate **84**. It is interesting to note that the presence of zirconium in the carbene complexes gives this reaction a new dimension compared with the classical alkoxycarbene complexes, because zirconium enolates are produced and these can be further manipulated. Thus, subsequent reaction of **84** with benzaldehyde affords the zirconium aldol derivative **85** (Scheme 22).[21]

4.2.2. η^4-Diene zirconium complexes. Erker et al. have used butadiene zirconocene extensively in the synthesis of zirconoxycarbene complexes.[49] Butadiene zirconocene exists at room temperature as two isolable isomers, (*s-trans*-η^4-butadiene)- and (*s-cis*-η^4-butadiene)zirconocene **86a** and **86′a** (R=H), respectively.[50] The equilibration **86a:86′a** can be considered to proceed through the coordinatively unsaturated intermediate (η^2-butadiene)zirconocene **86″a** and is presumably responsible for the coupling reactions with unsaturated compounds.[51] In the same way **86a/86′a** slowly react at room temperature with metal carbonyls derived from vanadium,[52] chromium,[53] molybdenum,[53] tungsten,[53] iron,[54] cobalt,[55] rhodium,[56] and platinum[57] to yield the zirconoxycarbene complexes **87** in moderate to good yields (Scheme 23). The thermally induced addition of isoprenezirconocene **86b/86′b**



Scheme 21.

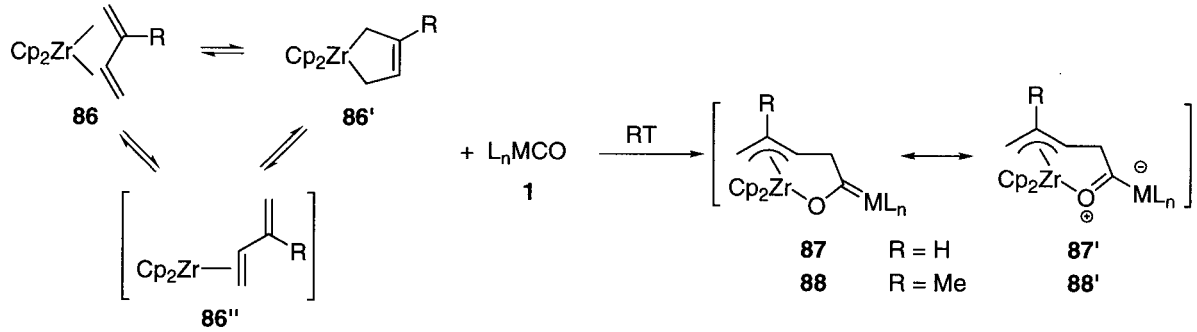


Scheme 22.

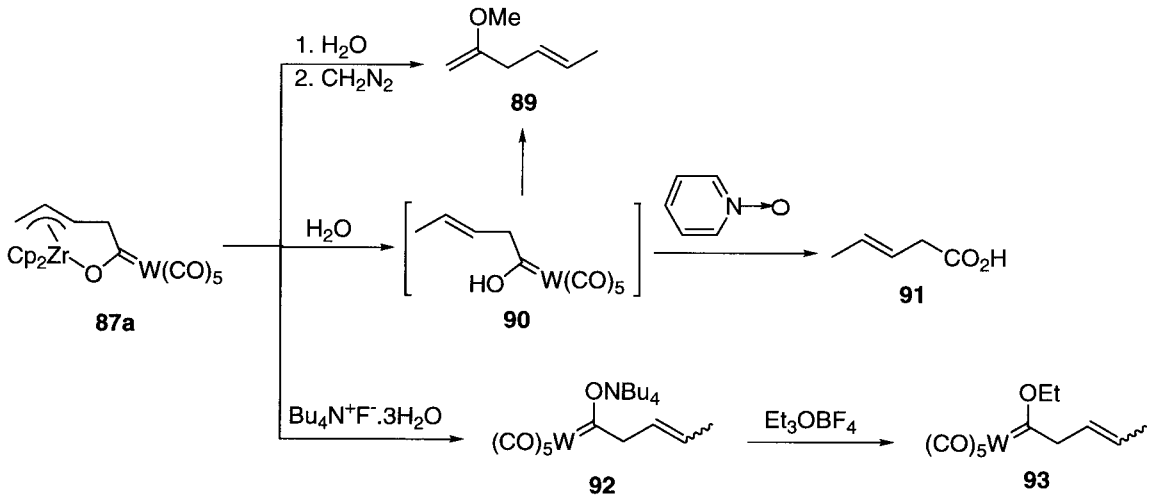
(R=Me)[58] to metal carbonyls **1** at 50°C proceeds similarly and the complexes **88** are obtained as a single regioisomer. The coupling takes place between the coordinated carbonyl group of complexes **1** and the unsubstituted carbon–carbon double bond of the coordinated isoprene of **86b/86′b**.[59]

The zirconoxycarbene complexes **87** and **88** have a much reduced carbene complex reactivity as compared with alkoxy carbene complexes. For example, **87** do not appear to react with amines, enol ethers, alkenes, or alkynes. The low electrophilic reactivity of the metal carbene moiety in the complexes **87** and **88** underlines the pronounced metal acyl type character of these complexes, as indicated by **87′** and **88′** in Scheme 23. Complexes **87** and **88** can be converted to metal-free organic products, however, by a combination of reactions involving hydrolytic removal of the zirconium moiety and conventional transformations of Fischer carbene complexes. Thus, treatment of **87a** [L_nM=$(CO)_5W$] with water, followed by diazomethane[60] leads to *trans*-2-methoxy-1,4-hexadiene **89** in ca. 30% yield.[61] In this reaction a hydroxycarbene complex intermediate **90** is initially formed by hydrolytic cleavage of carbon–zirconium and zirconium–oxygen bonds. This hydroxycarbene complex **90** can also be trapped by oxidizing reagents.[62] Oxidation of **90**, formed previously by hydrolytic treatment, with pyridine *N*-oxide at room temperature yields *trans*-3-pentenoic acid **91** in over 50% yield.[61] The zirconoxycarbene complexes **87** and **88** can also be used for the preparation of conventional Fischer carbene complexes. Treatment of **87a** with tetrabutylammonium fluoride trihydrate at 0°C instead of water affords the tetrabutylammonium acyl tungstate **92** as a mixture of *cis*/*trans* isomers in 70% yield. Further addition of triethyloxonium tetrafluoroborate to **92** produces the neutral tungsten carbene complex **93** isolated in 50% yield as a 40:60 mixture of *cis*/*trans* isomers (Scheme 24).[61]

Complexes **87** and **88**, which contain a zirconium–bound π-allyl ligand, can undergo nucleophilic addition reactions to organic carbonyl compounds.[63] Reaction of complexes **87** with aldehydes or ketones at room temperature produces the metallacyclic nine-membered zirconoxycarbene complexes **94** as a variable mixture of *trans*- and *cis*-isomers in over 70% yield (Scheme 25).[52b,64] Most of the reactions with



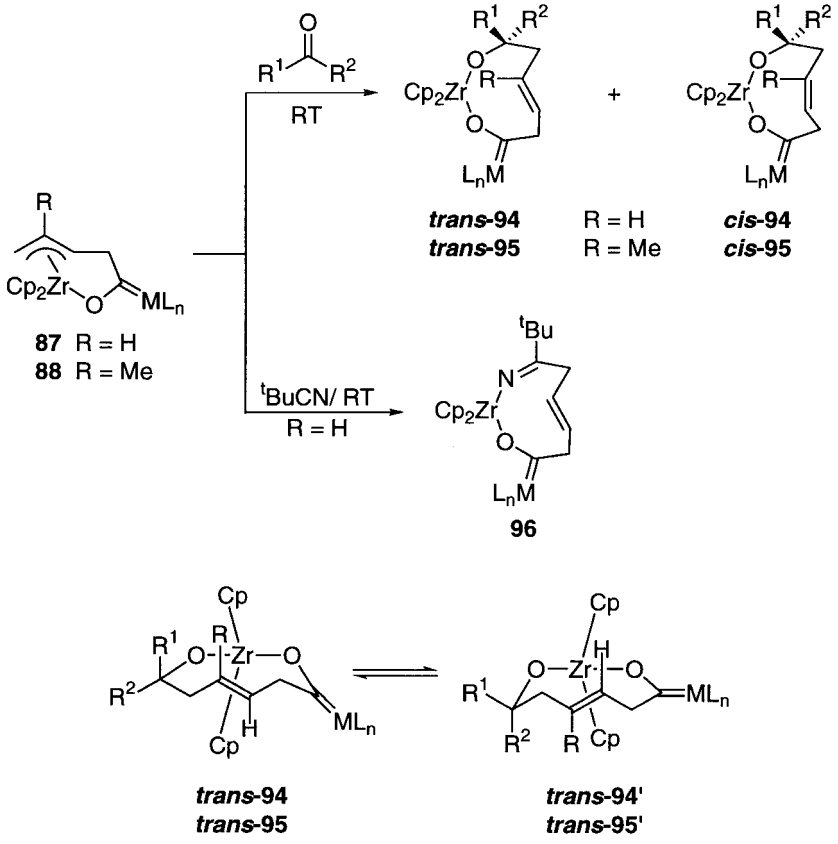
Scheme 23.



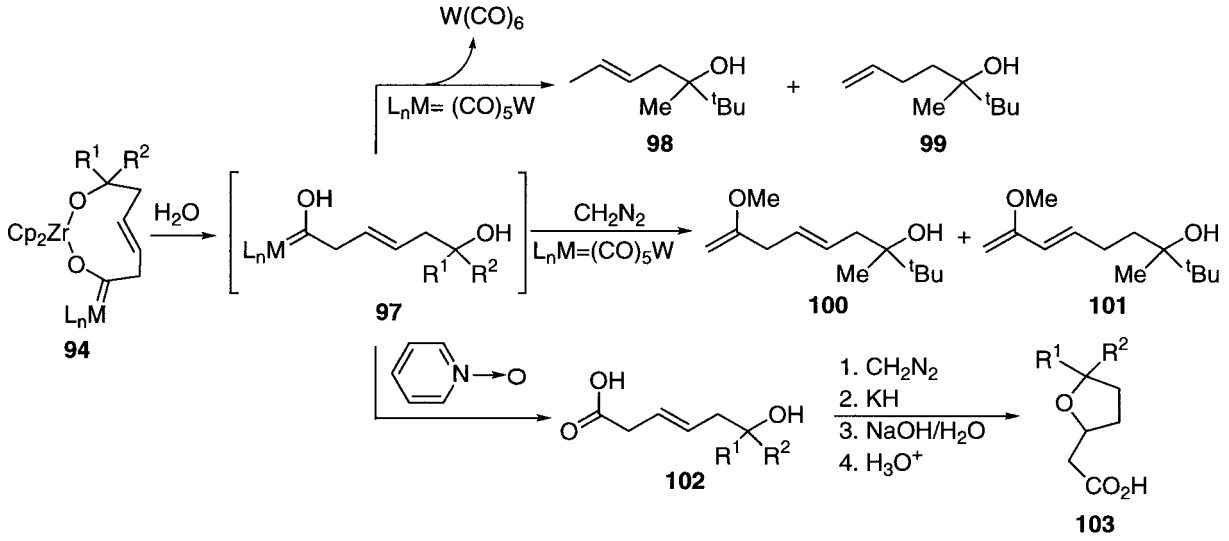
Scheme 24.

ketones lead to two diastereoisomeric compounds *trans*-**94** and *trans*-**94′**, and the *cis*-**94**-isomers are not observed. The *trans*-nine-membered ring metallacycles **94** and **94′**, which can be regarded as organometallic *trans*-cycloalkene analogues, are chiral and exhibit a very similar ring topomerisation behaviour. According to solid state and dynamic NMR studies,[65] *trans*-**94** are the major diastereoisomers present in the mixture and the activation barrier for the *trans*-**94**→*trans*-**94′** rearrangement can be calculated. When ketones with bulky goups are used, only the respective *trans*-**94** isomers have been found. In this context, it is interesting to point out that when **87** are treated with chiral ketones (camphor[64b] or steroid ketone derivatives[64c]) exclusive formation of one of the four possible diastereoisomeric products is observed.

On the other hand, starting from aldehydes with less sterically demanding alkyl groups, mixtures of the *trans*-**94** compounds and their *cis*-**94** isomers are obtained. Using the bulkier bis(*t*-butylcyclopentadienyl)zirconium moiety for coupling reactions with aldehydes, however, a large excess of the *trans*-isomers is obtained.[64b] When



Scheme 25.



Scheme 26.

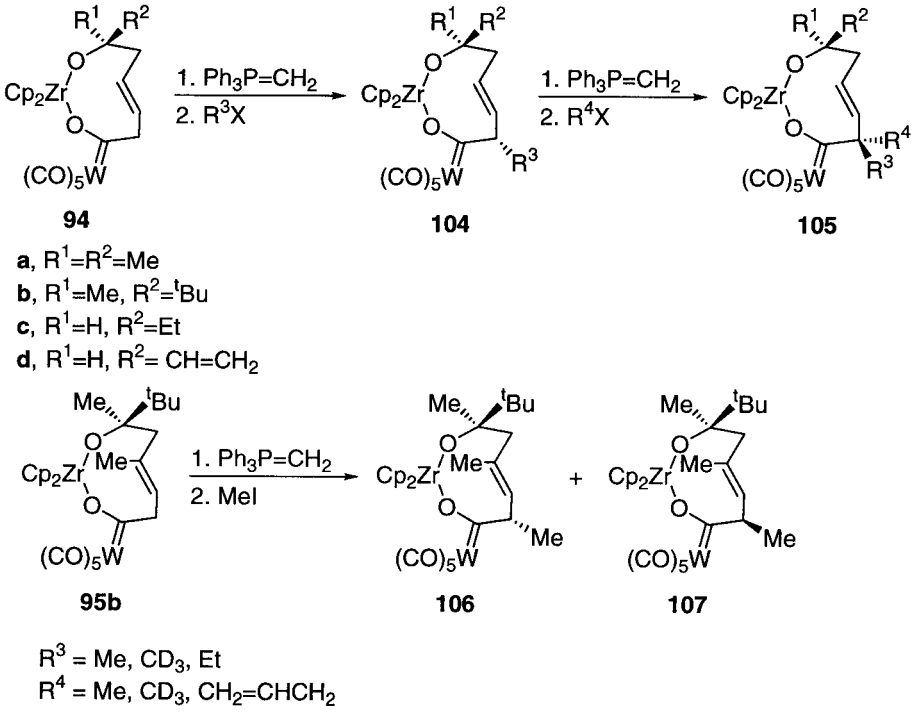
α,β-unsaturated aldehydes or -ketones are used, the nine-membered ring systems **94** derived from a 1,2-addition to the carbonyl group are exclusively formed and the eleven-membered rings derived from a 1,4-addition are not observed.

The reaction of **88** with carbonyl compounds proceeds similarly and a mixture of stereoisomeric complexes *trans*-**95** and *trans*-**95′** is obtained (Scheme 25).[59] The presence of a methyl group attached to C(4), however, results in a decrease of the ring inversion activation barrier, as observed for **95a** [$L_nM=(CO)_5W$, $R^1=R^2=Me$] relative to **94a** [$L_nM=(CO)_5W$, $R^1=R^2=Me$]. In the reaction of the complex **88a** [$L_nM=(CO)_5W$] with pinacolone, in which, in principle, two diastereoisomeric *E*-configuration conformers could be formed, only the *trans*-**95b** isomer [$L_nM=(CO)_5W$, $R^1=Me$, $R^2={}^tBu$] is obtained. The ^1H NMR spectra of this compound remain essentially unchanged even at low temperatures and this indicates that only a single isomer is present under equilibrium conditions.[59]

The complexes **87** also react with pivalonitrile at room temperature to afford the nine-membered metallacyclic zirconoxycarbene complexes **96** in good yields (52–75%), which also exhibit a chiral *trans*-cycloalkene oxazametalla-*trans*-cyclononene framework, as deduced from their ^1H and ^{13}C NMR spectra (Scheme 25).[51b,66]

The complexes **94** and **95**, as with **87** and **88**, also show a reduced carbene complex reactivity as compared to classical alkoxycarbene complexes. They can, however, be converted to metal-free organic products by hydrolytic removal of the zirconium moiety followed by conventional transformation of Fischer-type carbene complexes. Hydrolysis of the carbene complexes **94** leads to the unstable hydroxycarbene complexes **97**, which in the absence of a trapping reagent decompose by loss of the metal fragment.[67] Thus, **97a** [$L_nM=(CO)_5W$, $R^1=Me$, $R^2={}^tBu$] gives mainly hexacarbonyltungsten and a 45:55 mixture of the heptenol derivatives **98** and **99**.[61] The hydrolytic reaction is cleaner, however, in the presence of a trapping reagent. When the reaction is carried out in the presence of diazomethane **97a** is converted into a 85:15 mixture of the methoxydienol isomers **100** and **101** in 90% yield.[61] The hydroxycarbene complexes **97** also react with pyridine *N*-oxide and the corresponding substituted 6-hydroxy-3-hexenoic acids **102** are formed in good yields (60–90%).[61,64c,68] The compounds **102** can be used as templates for the synthesis of substituted tetrahydrofuran systems. Esterification of **102** with diazomethane followed by treatment with potassium hydride in refluxing tetrahydrofuran affords, after basic hydrolysis and neutralization, the 2-tetrahydrofurylacetic acid derivatives **103** in reasonable yields (47–75%) (Scheme 26).[64c]

As with the base-promoted alkylation of alkoxycarbene complexes,[69] deprotonation of metallacyclic zirconoxycarbene complexes **94** by the ylide methylenetriphenylphosphorane takes place at the α-position to the carbene carbon atom. Further treatment with alkyl halides leads regioselectively to the α-alkylation products **104** and starting from **94b** the corresponding α-alkylated complex **104b** is obtained with 70% diastereoselectivity. Both major and minor diastereoisomers exhibit a *trans*-carbon–carbon double bond and the spectroscopic data and X-ray crystal structure determination on the major diastereoisomer of **104b** reveal that its structure corresponds to the α-alkylation product, in which the alkyl group has been incorporated on the opposite side to the bulkier R^2 group (^tBu) (Scheme 27).[70] Remarkably, this result is obtained in the alkylation of a steroid ketone-derived zirconoxycarbene complex **94**, in which a 94% de is achieved.[64c] Repetition of the deprotonation/alkylation reaction sequence starting from **104**, stereoselectively yields the α,α-dialkylated carbene complexes **105**. The diastereoselectivity of the second alkylation step is >80% de, which represents an even more effective 1,5-asymmetric induction than that observed for the first α-alkylation step. α-Alkylation of aldehyde-derived nine-membered metallacyclic zirconoxycarbene complexes **94c**,**d** also proceeds with effective stereochemical 1,5-induction. Thus, the deprotonation/alkylation sequence starting from **94c** or **94d** (mixture of *cis*- and *trans*-isomers)

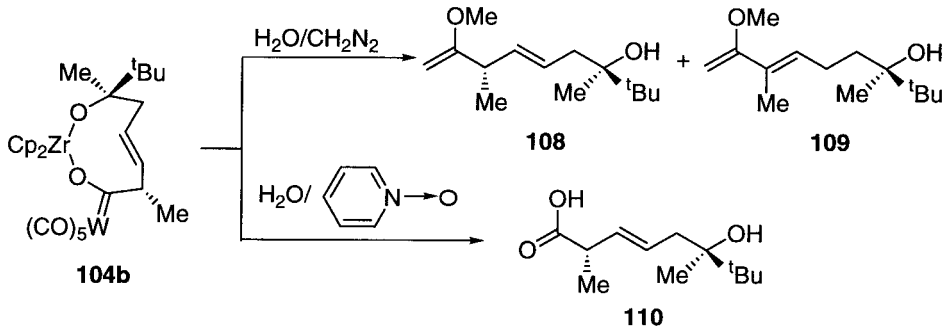


Scheme 27.

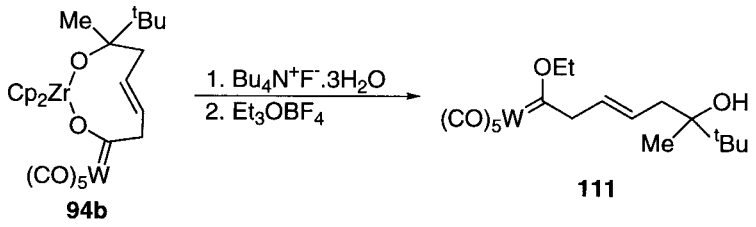
yields a mixture of two major isomers (*cis*-**104c**,**d** and *trans*-**104c**,**d**, respectively, with a similar *cis*/*trans* ratio to the starting complexes **94**), which is formed by addition of the alkyl group at the same side as the small hydrogen substituent (R^1=H) (Scheme 27).[70] These results represent an interesting example of 1,5-asymmetric induction in which it is not the direct steric influence of the asymmetric carbon centre that determines the side discrimination at the newly formed stereogenic centre, but rather that the stereochemical information is rather transferred across such a large distance by means of the rigid chiral conformation of the nine-membered metallacyclic ring system. A key feature of this process is the evidence that the anionic intermediate formed by deprotonation of **94** adopts a chiral metallacyclic conformation, which is very similar to that of the neutral starting material.

On the other hand, the reaction of complex **95b** with methylenetriphenylphosphorane followed by treatment with methyl iodide is similar to the base-induced alkylation of **94** and products of α-methylation are smoothly obtained. The α-methylation reaction of **95b**, however, shows some differences from the butadienezirconocene-derived carbene complexes **94** with respect to the stereochemical outcome. Whereas the alkylation of **94** is rather diastereoselective, an almost equimolecular mixture of the respective diastereoisomers **106** and **107** is isolated at temperatures above 0°C (Scheme 27).[59]

The new zirconoxycarbene complexes **104**–**107** which are generated can be transformed, as described above, into metal-free organic products by convenient cleavage of both metal centres. Reaction of an 85:15 diastereoisomeric mixture of the α-methylated zirconoxycarbene complex **104b** (R^3=Me) with water and then with an ethereal solution of diazomethane furnishes a 80:20 regioisomeric mixture of the enol ethers **108** and **109** in a combined yield of 88%. Spectroscopic analysis of **108** reveals the presence of two diastereoisomers in an 85:15 ratio. In a similar process, treatment of the same diastereoisomeric mixture of complex **104b** (R^3=Me) with water in the presence of pyridine *N*-oxide leads to the unconjugated



Scheme 28.



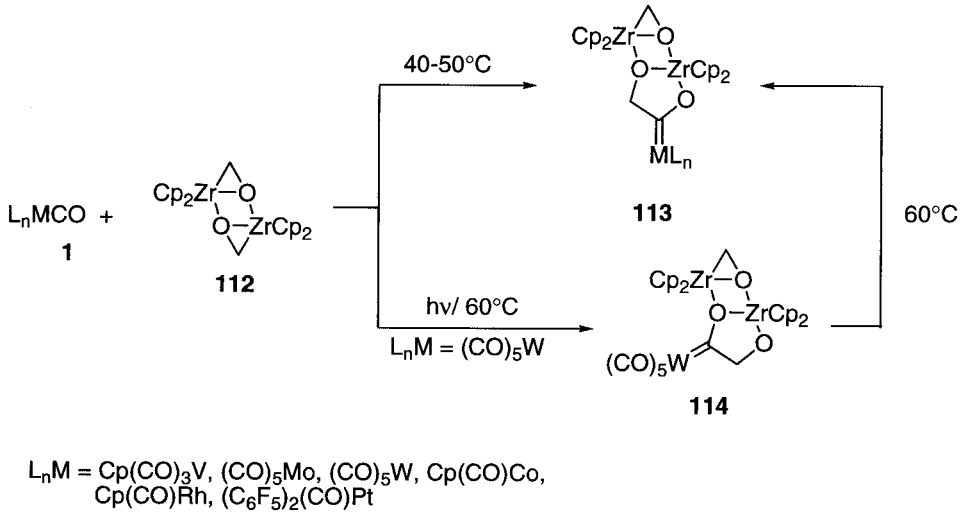
Scheme 29.

6-hydroxyoctenoic acid **110**, isolated as a 80:20 mixture of diastereoisomers (Scheme 28).[70] It is interesting to note that the stereochemical information present in the organometallic system has been practically retained during the formation of the final organic reaction products.

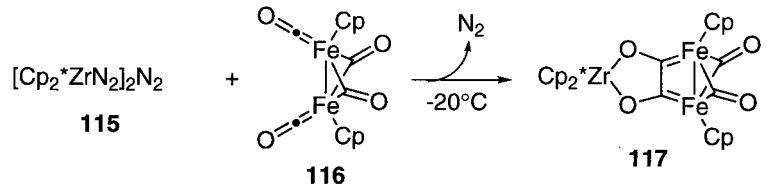
The complexes **94** can also be transformed into alkoxycarbene complexes by successive treatment with tetrabutylammonium fluoride and triethyloxonium tetrafluoroborate and in this way **94b** provides the ethoxycarbene complex **111** (Scheme 29).[61] In the different transformations described up to now, the zirconoxycarbene moiety is rather unreactive, although it can be converted into a normal alkoxycarbene functional group. Zirconoxycarbene complexes can thus be regarded as protected Fischer carbene complexes. The presence of the zirconocene-protecting group at the carbene oxygen atom allows a variety of selective transformations to be carried out at other parts of the molecules without interfering with the zirconoxycarbene moiety.

4.2.3. η^2-Formaldehyde zirconium complexes. The different methods described for the preparation of zirconoxycarbene complexes up to now do not allow the direct introduction of functional groups and chemical functionalities are usually attached in subsequent reactions, as in the formation of **94**, **95** and **96** (see Scheme 25). (η^2-Formaldehyde)zirconocene, which exhibits a pronounced metallaoxirane character,[71] offers the possibility of being used as starting material to prepare functionalised zirconoxycarbene complexes. The thermal reaction of cyclodimeric (η^2-formaldehyde)zirconocene **112** with metal carbonyls **1** at temperatures between 40 and 50°C leads to the zirconoxycarbene complexes **113**, which contain two atoms of zirconium per carbene metal, in very good yields (80–90%).[72] Increasing the **1/112** ratio does not result in any more metal being incorporated into the product.[73] The reaction can also be photochemically assisted and the same results are observed. A different situation exists for the corresponding reaction of **112** with hexacarbonyltungsten **1** [$L_nM{=}(CO)_5W$]. When this reaction is carried out at 60°C with sun lamp irradiation under kinetic control a 1:1 mixture of regioisomeric zirconoxycarbene complexes **113** [$L_nM{=}(CO)_5W$] and **114** is formed. Subsequent thermolysis at 60°C leads to a rapid rearrangement of **114** to **113** [$L_nM{=}(CO)_5W$] (Scheme 30).[72]

4.2.4. Other insertion reactions. In all of the preceding methods to prepare zirconoxycarbene complexes involving insertion reactions, a carbonyl ligand is coupled with an unsaturated organic substrate. A zirconium-promoted direct coupling of two carbonyl ligands of a binuclear transition–metal complex may be used to prepare a new type of zirconoxycarbene complexes. Treatment of $[Cp^*_2ZrN_2]_2N_2$ **115**, as a precursor of permethylzirconocene,[74] with the dinuclear iron complex **116** above −20°C results in evolution of nitrogen and the formation of over 95% yield of the zirconoxybiscarbene diiron complex **117**, according to X-ray diffraction data (Scheme 31).[39] The formation of **117** may be viewed as a reductive coupling of the two terminal carbonyl ligands of **116** with oxidation of zirconium from the divalent to the tetravalent state.



Scheme 30.

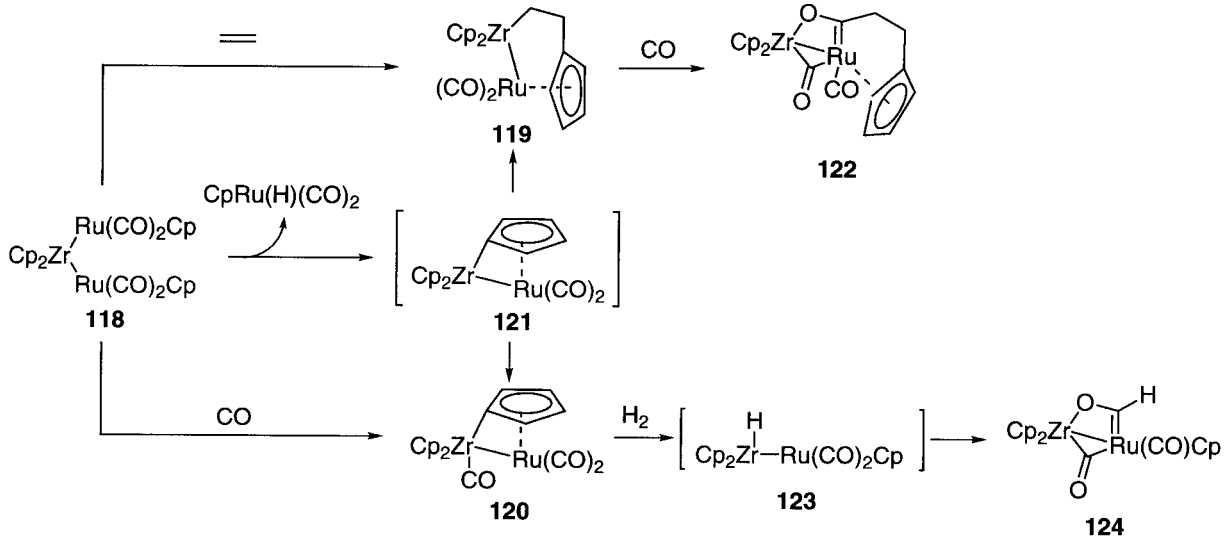


Scheme 31.

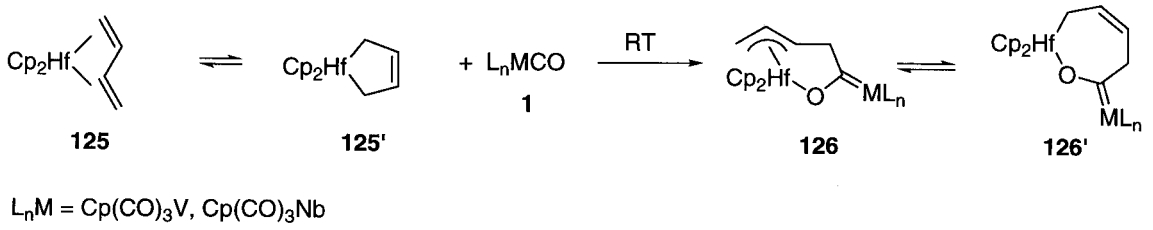
Finally, the trimetallic compound **118**[75] can be used as a starting material to prepare precursors of zirconoxycarbene complexes. This zirconium–diruthenium complex **118** is thermally stable but it reacts with a variety of ligands at room temperature, such as ethylene or carbon monoxide, to form the strained intermediates **119** and **120**, respectively. Both reactions involve expulsion of dicarbonylcyclopentadienylruthenium hydride and formation of the unsaturated complex **121**, which is trapped by the ethylene or carbon monoxide.[76] The intermediates **119** and **120** can be now transformed into the corresponding zirconoxycarbene complexes. When the ethylene product **119** is treated with carbon monoxide at room temperature, the carbene complex **122** is formed in 80% yield. The adduct **120** reacts similarly with hydrogen (1 atm) at room temperature to afford the hydrido–zirconoxycarbene complex **124**. Although no intermediates are observed, the reaction is suggested to proceed by hydrogenolysis of the strained zirconium–carbon bond of **120** to give a reactive intermediate **123**. Formation of the carbene complexes **122** and **124** is consistent with the initial insertion of carbon monoxide into the zirconium–methylene bond of **119** or into the zirconium–hydrogen bond of **123** to form an η^2-acyl intermediate, followed by rapid transfer of the very electrophilic η^2-acyl carbon to the electron-rich ruthenium atom (Scheme 32).[77]

5. Hafnoxycarbene Complexes

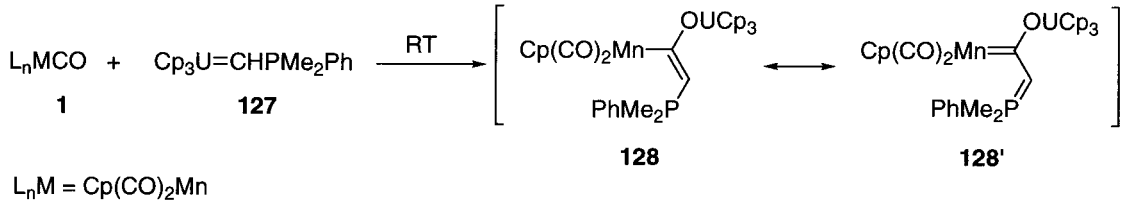
The synthesis of hafnoxycarbene complexes parallely that of the zirconium analogues. For example, the readily accessible equilibrium mixture of *s-trans*- and *s-cis*-(η^4-butadiene)hafnocene **125** and **125′**, respectively,[78] reacts readily with metal carbonyls **1** by coupling of the butadiene ligand with a coordinated carbonyl group to give rise to the metallacyclic hafnoxycarbene complexes **126** in over 60% yield. In contrast to the analogues of zirconium **87**, the hafnoxycarbene complexes **126** are not in equilibrium with the educts **1** and **125** in solution at room temperature



Scheme 32.



Scheme 33.



Scheme 34.

but rather with the seven-membered ring σ-allyl isomer **126′** (Scheme 33).[51] The equilibrating system of isomeric (σ-/π-allyl)hafnoxycarbene complexes **126/126′** behaves as a carbon nucleophile and reacts with ketones and nitriles to give the nine-membered metallacyclic hafnoxycarbene complexes analogous to the zirconium derivatives **94** and **96** (see Scheme 25).[51b]

6. Uranoxy and Thoroxycarbene Complexes

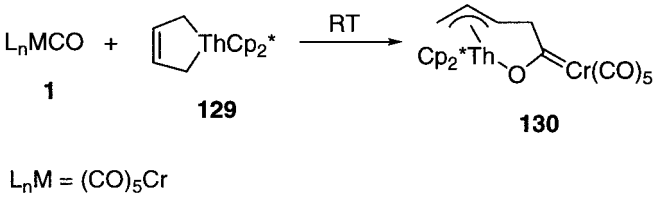
The development of the chemistry of the uranium–carbon multiple bond has allowed entry into a set of products by the insertion of polar, unsaturated molecules.[79] The reactivity of the uranium–carbon double bond with coordinated carbon monoxide is extraordinary and the complex **127** is able to interact with the dinuclear iron complex **116** to form an η^1:η^3-allyl group bonded to two iron atoms by insertion of the carbonyl ligand into the uranium–carbon double bond accompanied by coupling with a bridging carbonyl.[80] The reaction with the metal carbonyl complex **1**, [L_nM=Cp(CO)$_2$Mn], however, which contains only terminally bonded carbonyls, at room temperature leads to a complex which, according to the X-ray crystal structure, can be written as two limiting resonance forms, **128**, an enolate, and **128′**, a uranoxycarbene complex, to describe the bonding (Scheme 34).[81]

On the other hand, the organometallic chemistry of the actinide element thorium shows some remarkable similarities to the group 4 oxophilic transition metals, especially zirconium and hafnium.[82] Taking into account the extraordinary possibilities exhibited by the group 4 dienemetallocene complexes for synthesising the metalloxycarbene complexes described above the readily available butadienepermethylthorocene **129** can be used to prepare thoroxycarbene complexes. Thus, the very reactive metal–diene complex **129**, which exhibits a substantial metal alkyl character, reacts smoothly at room temperature with the metal carbonyl complex **1**, [L_nM=(CO)$_5$Cr], to afford the metallacyclic thoroxycarbene complex **130** in 85% yield (Scheme 35).[83]

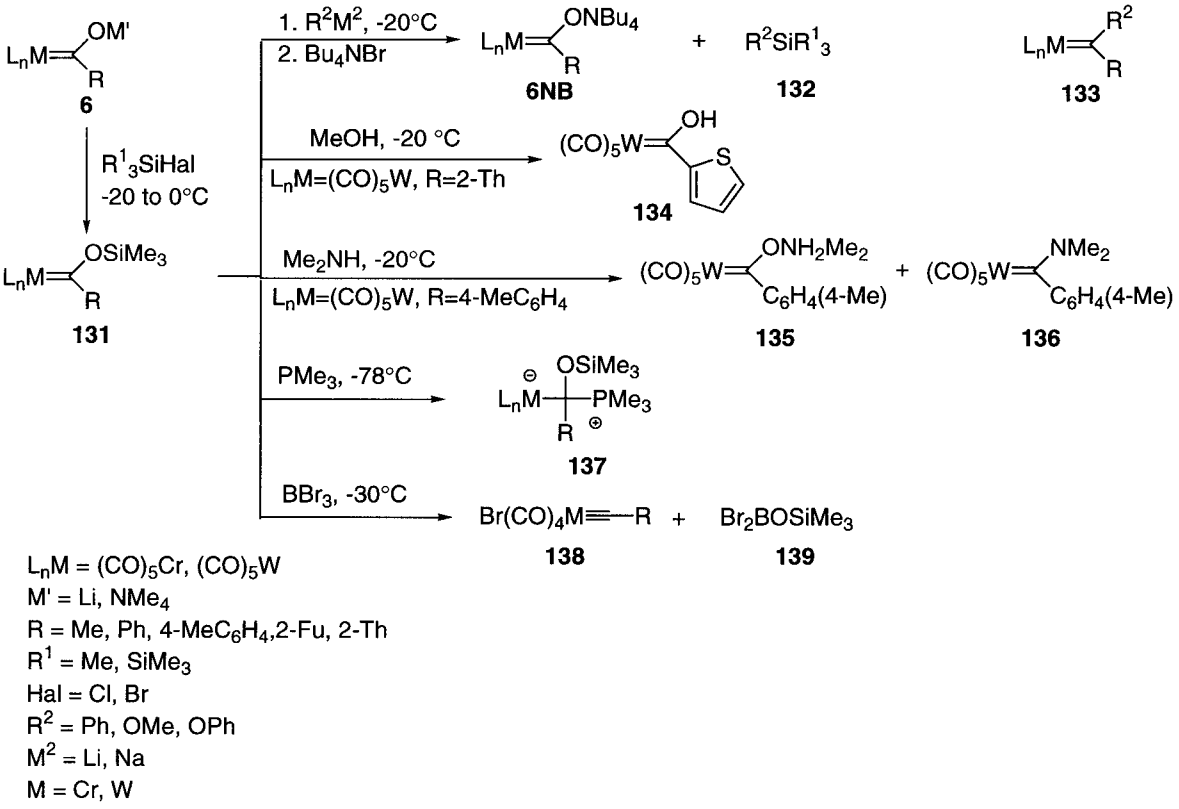
In the previous sections the presence of a transition metal directly bound to the carbene oxygen atom in metalloxycarbene complexes has been shown to modify the carbene reactivity and to confer upon them peculiar properties compared to the classical alkoxycarbene complexes. The synthesis of metalloxycarbene complexes, in which the carbene oxygen is bound to a non-transition metal such as silicon, tin, boron, aluminium, or phosphorous, and their chemical behaviour, will now be discussed.

7. Siloxycarbene Complexes

Lithium or tetramethylammonium acyl metallates **6** react with trimethylsilyl chloride[84] or tris(trimethylsilyl) bromide[85] at temperatures from −20 to 0°C to give the thermally unstable siloxycarbene complexes **131** in 40–80% yield (Scheme 36). These complexes **131** are extremely sensitive to nucleophiles, traces of moisture, and alcohols. Thus, the reaction of **131** with nucleophiles (phenyllithium or sodium alkoxides) at −20°C leads to the corresponding acyl metallates, isolated as their tetrabutylammonium complexes **6NB**, (M′=Bu$_4$N), and the substituted trimethylsilanes **132**. The corresponding phenyl or alkoxycarbene complexes **133** are not observed. When methanol is used instead of sodium methoxide, the complex **131a**, [L_nM=(CO)$_5$W, R=2-thienyl], is quantitatively converted to the hydroxycarbene complex **134**. Treatment of **131b**, [L_nM=(CO)$_5$W, R=4-MeC$_6$H$_4$], with dimethylamine at −20°C, however, leads to formation of the dimethylammonium pentacarbonyl tungstate **135** in 85% yield and small amounts of the aminocarbene complex **136**. On the other hand, reaction of **131** with trimethylphosphine at −78°C affords the ylide complexes **137**, according to the spectrocopic data. Finally, when the complexes **131** are treated with boron tribromide at −30°C *trans*-bromotetracarbonylcarbyne complexes **138** are isolated in over 80% yield along with dibromoboroxytrimethylsilane **139** (Scheme 36).[84b] The chemical behaviour of the complexes **131** is clearly different from that known for the corresponding alkoxycarbene complexes. As a consequence of the d_π–p_π silicon–oxygen interaction, an increase in the electrophilicity of the carbene carbon is produced in the complexes **131** compared with the alkoxycarbene complexes and, therefore, they are more



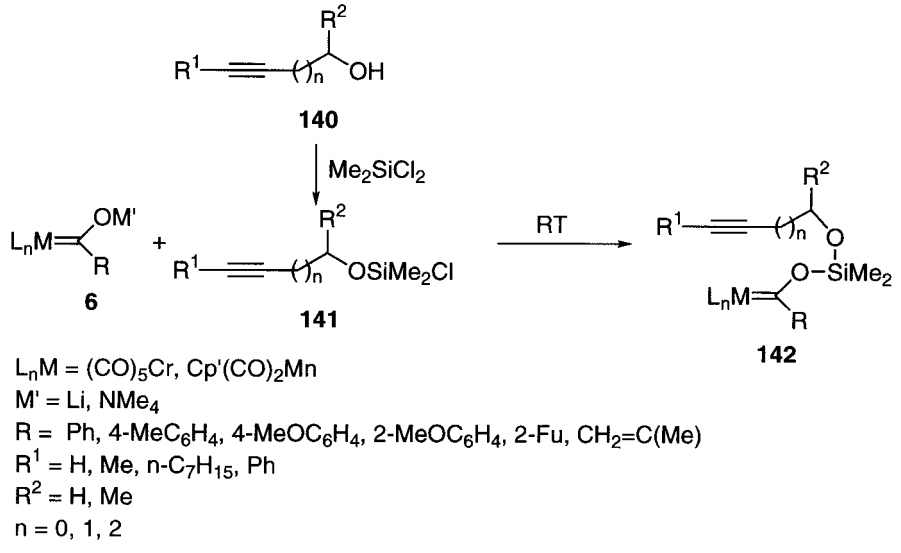
Scheme 35.



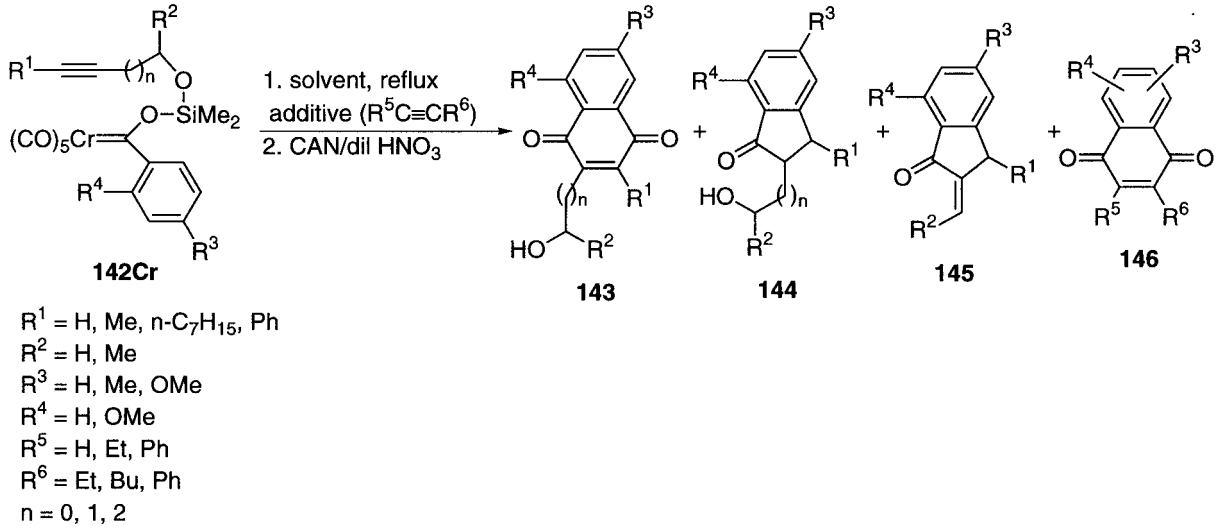
Scheme 36.

reactive towards a nucleophilic attack at the carbene carbon. The silicon atom, however, can also act as electrophilic centre in the complexes **131** and can compete with the carbene carbon towards nucleophiles. Thus, the complexes **131** can undergo both nucleophilic addition at the carbene carbon (reaction with trimethylphosphine and boron tribromide) and nucleophilic substitution of the trimethylsilyl group (reaction with phenyllithium, sodium alkoxides, methanol, or dimethylamine).

The use of dichlorodimethylsilane instead of chlorotrimethylsilane allows the linkage of acetylenic alcohols to acyl metallates in a convenient fashion to provide siloxycarbene complexes which can undergo intramolecular benzannulation reactions. The siloxycarbene complexes **142** are prepared in quantitative yield from the alkynyloxydimethylsilyl chlorides **141**, which were previously generated by treatment of the acetylenic alcohols **140** with dichlorodimethylsilane and the appropriate acyl metallate **6** as shown in Scheme 37.[86]



Scheme 37.

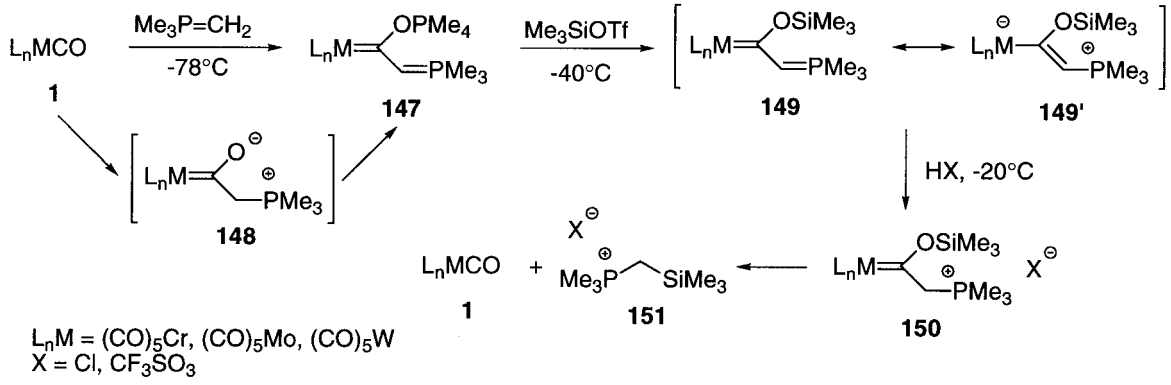


Scheme 38.

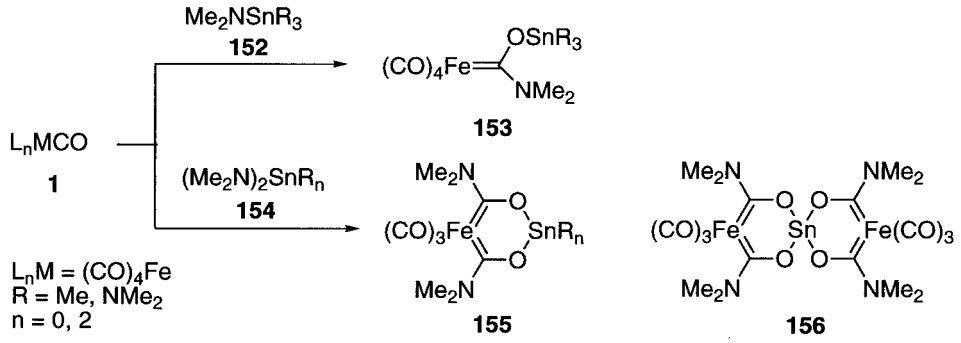
The siloxycarbene complexes **142** undergo benzannulation reactions under photochemical conditions[86a] and also upon heating in various solvents under an inert atmosphere.[86b] Thus, warming of **142Cr**, [$L_nM{=}(CO)_5Cr$], followed by oxidative work-up [ceric ammonium nitrate (CAN) in dilute aqueous nitric acid] leads to the substituted naphthoquinones **143** in moderate yields (20–25%) along with variable amounts (2–16%) of the substituted indanones **144** and the α-methyleneindanones **145**, the latter being produced for propargylic substrates (n=0) from **144** during acidic oxidative work-up (Scheme 38). The intramolecular benzannulation reaction in the absence of alkyne additives is insensitive to the concentration of the chromium complex and variations in the solvent and tether chain length also produce little change in the product yields. Low yields of annulated compounds are typically accompanied by benzil and benzoin-type decomposition products derived from the coupling of two carbene fragments, as observed in the benzannulation reactions carried out with the titanoxycarbene complexes **7a**,**b**.

The allochemical effect of added alkyne substrates in the intermolecular benzannulation reactions described by Wulff[87] is also observed in the intramolecular benzannulation reactions of siloxycarbene complexes.[88] The addition of 10 equiv. of alkyne (diphenylacetylene, 3-hexyne, or 1-hexyne) to the complexes **142Cr** in hexane significantly enhances the yield of the desired quinone derivatives **143** (from 20–25% to 40–85%) while that of the indanone products is relatively unaffected by the presence of the alkyne additive. Moreover, the products of the intermolecular benzannulation reaction **146** only compete to a minor extent (Scheme 38). The beneficial action of the added alkyne is manifested in non-polar solvents (hexane, benzene), but is completely suppressed in tetrahydrofuran. The presence of 1 atm of carbon monoxide severely inhibits the action of the alkyne, reducing the yield of **143**. The excellent regioselectivity observed for all of the intramolecular benzannulation reactions is remarkable, including those carried out in the absence of external alkyne. For complexes bearing substituted aromatic groups, only one out of the two possible isomers of each product is detected. Kinetic measurements demonstrate that the benzannulation reactions are initiated by dissociative carbon monoxide loss and that the alkyne additives presumably act by coordination to vinylcarbene intermediates produced by intramolecular alkyne insertion.[86b,89]

Reaction of phosphorous ylides with metal carbonyls allows entry into a new type of siloxycarbene complexes.



Scheme 39.



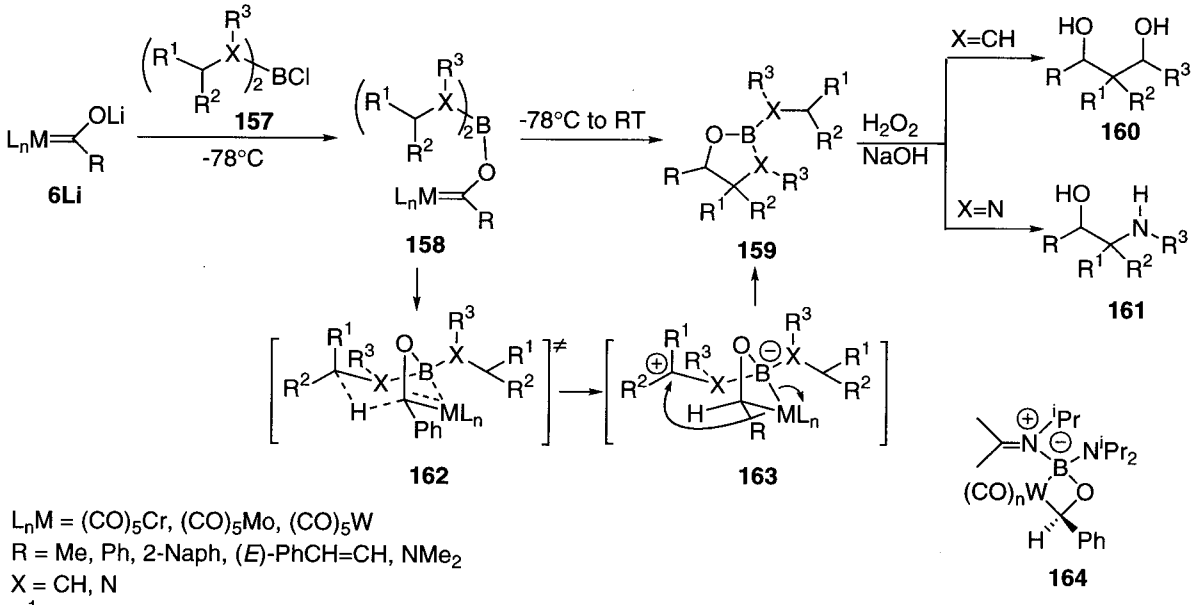
Scheme 40.

Treatment of the carbonyl metal compounds **1** with 2 equiv. of trimethylmethylenephosphorane at −78°C yields the phosphonium acylmetallate-phosphorous ylides **147**. The reaction proceeds by initial formation of the adducts **148**, which are transformed to the complexes **147** by the second equivalent of the phosphorous ylide.[90] Further reaction of **147** with trimethylsilyl triflate at −40°C leads via *O*-silylation to the formation of neutral siloxy(ylidecarbene) complexes **149** in ca. 50% yield (Scheme 39).[91]

According to the spectroscopic data and the X-ray crystal structure determinations, the limiting trimethylphosphoniovinyl resonance structure **149′** describes the bonding in these complexes better than the Fischer carbene structure **149**. The complexes **149** are protonated by protic acids HX (X=Cl, CF_3SO_3) at −20°C to give the thermolabile carbene complexes **150**, which decompose to the metal carbonyls **1** and the trimethyl(trimethylsilylmethyl)-phosphonium salts **151** above this temperature (Scheme 39).[91]

8. Stannoxycarbene Complexes

It has been shown in Scheme 2 that tetrakis(dimethylamino)titanium **4** is able to react with coordinated carbon monoxide. Considering that tin amides are very similar to the corresponding amides of titanium in their reactions with polar, unsaturated systems, they should be suitable starting materials to synthesize stannoxycarbene complexes by addition to carbonyl ligands of metal carbonyls. Dimethylaminotrimethyltin **152a** (R=Me) reacts with an equimolecular amount of the metal carbonyl **1**, [L_nM=$(CO)_4Fe$], at 0°C to form the carbene complex **153a** (R=Me) in 87% yield by addition of the tin–nitrogen bond to a carbonyl group. The reaction of **152b** (R=NMe_2) with **1**, [L_nM=$(CO)_4Fe$], under the same conditions leads also to the 1:1 addition product **153b** (R=NMe_2) in 94% yield. If the complex **153b** is kept in solution, it is smoothly transformed into the stannoxybiscarbene complex **155a** (R=NMe_2, n=2) by addition of a second tin–nitrogen bond to an adjacent carbonyl group of the complex **153b**.



Scheme 41.

When the reaction of pentacarbonyliron **1**, [$L_nM{=}(CO)_4Fe$], with **152b** is carried out in a 2:1 ratio, the complex **156**, which contains four carbene units connected to the central tin atom by a double OSnO bridge, is isolated in 90% yield. Likewise, treatment of the tin amides **154**, bearing two amide moieties, and derived from both tin(IV) (n=2) and also tin(II) (n=0), with **1**, [$L_nM{=}(CO)_4Fe$], affords the biscarbene complexes **155** in 52–90% yield (Scheme 40).[92]

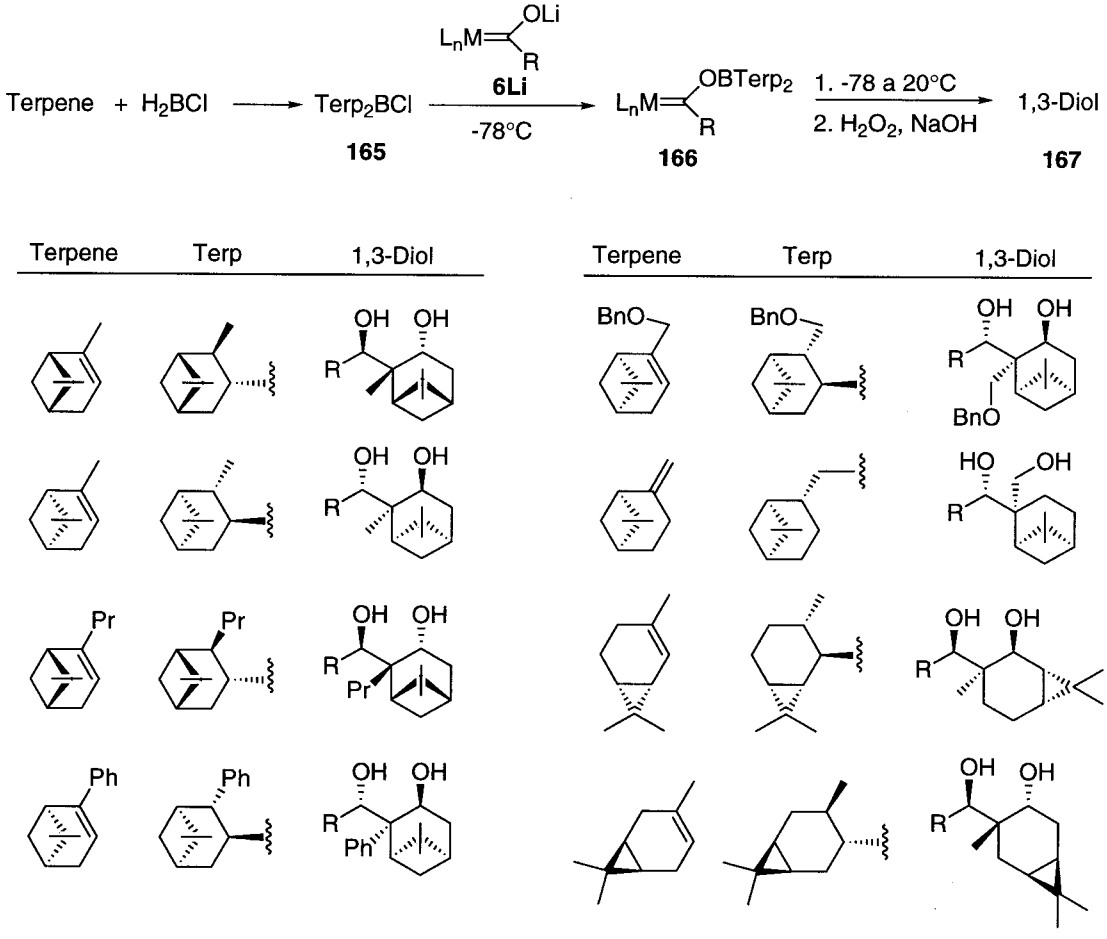
9. Boroxycarbene Complexes

The Fischer route is the more important method to prepare boroxycarbene complexes using haloboranes as electrophilic reagents to transform the acyl metallate intermediates.[60a,92] The chemical behaviour of these boroxycarbene complexes is strongly dependent on the substituents bound to the boron atom. Therefore, the dialkyl- and difluoroboroxycarbene complexes will be considered in the following discussion.

9.1. Dialkyl- and dialkylaminoboroxycarbene complexes

Treatment of the acyl metallate intermediates **6Li** with dialkylchloroboranes **157** (X=CH)[93] at −78°C leads readily to the dialkylboroxycarbene complexes **158**.[94–96] On warming to room temperature, these compounds undergo loss of the metal fragment to afford the oxaborolane derivatives **159** (X=CH). This transformation involves insertion of the carbene ligand into the boron C_β–H bond.[97,98] Further oxidation of **159** (X=CH) with hydrogen peroxide in basic media yields the 1,3-diols **160** (49–64%) as mixtures of diastereoisomers (11–24% de).[96] The oxaborolanes **159** (X=CH) are produced in moderate yield when either R^1 and R^2 are alkyl groups or R^1 and R^2 are H and an electron–donor group, respectively. Conversely, the reaction does not proceed for R^1=H and R^2=alkyl or electron-withdrawing groups, and metal carbonyl and R-boranes (R=NMe_2)[94] or complex mixtures[95] are obtained. On the other hand, starting from the diaminochloroborane **157** (X=N),[99] the oxazaborolidines **159** (X=N) and 1,2-aminoalcohols **161** can be prepared in over 65% yield. Alternatively, the carbene complexes **158** (X=N) and, therefore, the oxazaborolidines **159** (X=N) and 1,2-aminoalcohols **161** can also be obtained indirectly in similar yields by successive treatment of the acyl metallates **6Li** with boron tribromide at −78°C and an excess of dialkylamine at the same temperature (Scheme 41).[96]

Formation of the oxaborolanes **159** is believed to proceed by intramolecular hydride transfer to the carbene carbon atom in the complex **158**, presumably favoured by an initial interaction between the boron atom and the metal of the



Scheme 42.

carbene complex (as depicted in the transition state **162**), to give formally the carbocation intermediate **163**, which rapidly affords the oxaborolane derivatives **159**, most likely by simultaneous formation of a carbon–carbon bond and loss of the metal fragment. The hydride transfer is, in fact, only observed in the cases in which the early developing carbocation can be stabilised. Support for this mechanism is found in the NMR characterization of intermediate the **164** in the transformation of **158** [$L_nM{=}(CO)_5W$, X=N, $R^1{=}R^2{=}$Me, $R^3{=}{}^i$Pr] (Scheme 41). In addition, theoretical calculations show the presence of a boron-metal interaction, which could be the key step for the C–H insertion reaction.[96b]

This process is of interest for synthesising enantiomerically pure compounds using chiral dialkylchloroboranes. The reaction of acyl metallates **6Li** with the commercially or readily available (by hydroboration of the corresponding terpene with monochloroborane[100]) diterpenylchloroborane **165** at −78°C leads to the corresponding chiral boroxycarbene complexes **166**, which were clearly identified by NMR spectroscopy. Warming the reaction mixture to room temperature followed by oxidative work-up gives rise to the 1,3-diols **167** in good chemical yields (65–85%) and diastereoselectivities of over 80%, these being in many cases only one diastereoisomer observed within the limits of ^{1}H NMR detection (Scheme 42).[96b]

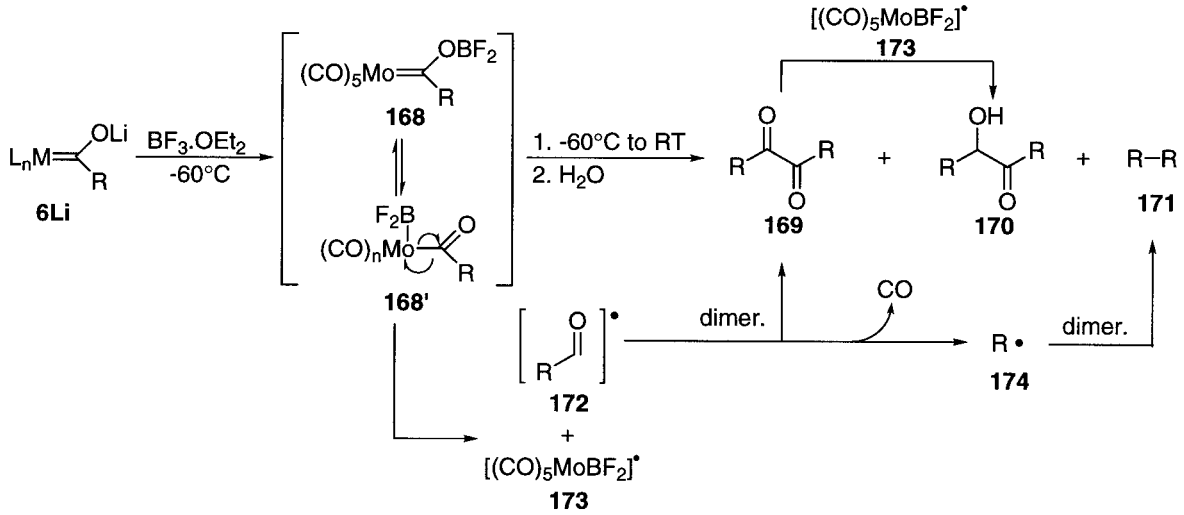
This diastereoselective terpene transformation always results in the enantioselective formation of a quaternary carbon centre,[101] it being diastereoselectivity exclusively dependent on the way that the C–H approaches the metal–carbon double bond.

9.2. Difluoroboroxycarbene complexes

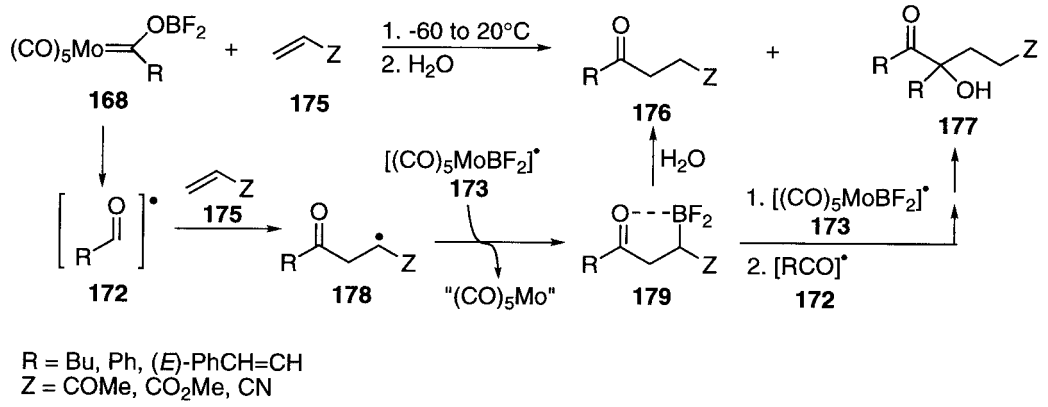
Preparation of difluoroboroxycarbene complexes proceeds in a similar way to that of the aforementioned dialkylboroxycarbene complexes using boron trifluoride as the electrophilic reagent instead of the dialkylhaloborane in the reaction with acyl metallates. The difluoroboroxycarbene complexes **168** are formed by treatment of the pentacarbonyl acyl metallate intermediates **6Li** with boron trifluoride diethyl ether complex at −60°C. The complexes **168** are stable at this temperature but, upon warming to room temperature, they undergo loss of the metal fragment affording, after hydrolysis, mixtures of the 1,2-diketones **169** and 1,2-hydroxyketones **170** (for R=alkyl and aryl) and the dimers **171** (for R=alkenyl and alkynyl) (Scheme 43).[102] The products **169** and **170** are similar to the by-products found by Finn in the evolution of complexes **7a**,**b** and **142Cr**.

The formation of the products described above is considered to proceed via the pathway shown in Scheme 43. Homolytic scission of the carbon–molybdenum bond of the acylmolybdenum complexes **168′** leads to the acyl radicals **172** and the radical species **173**.[103] Dimerization of the acyl radical **172** affords the 1,2-diketones **169**. Generation of the 1,2-hydroxyketones **170** may be understood by considering the reaction of **169** and the radical species **173** by a double electron transfer with release of '$Mo(CO)_5$' and further hydrolysis. On the other hand, formation of the dimers **171** can be understood as the result of decarbonylation[104] of **172** and dimerization of the radical species **174** thus obtained.

When the carbene complexes **168** are warmed from −60°C to room temperature in the presence of an excess of the electron-deficient alkenes **175** (2–10 equiv.), the expected formal Michael addition products **176** are isolated in ca. 50% yield.[105] In addition, when the olefins **175** (Z=CO_2Me, CN) are used as trapping agents, hydroxyketone derivatives **177** (29–32%) were isolated together with the corresponding Michael adducts **176** (31–32%) (Scheme 44).[102] Formation of the products **176** as well as the hydroxyketone derivatives **177** involves direct addition of the acyl radicals **172**, generated following the pathway shown in Scheme 43, to the alkenes **175** leading to the radical intermediates **178**.[106] Further electron transfer from **173** to intermediates **178** produces loss of '$Mo(CO)_5$' with formation of the boronenolates **179**. Hydrolysis of **179** leads to the formal 1:1 Michael-addition products **176**. Otherwise, formation of **177** can be understood by considering a second



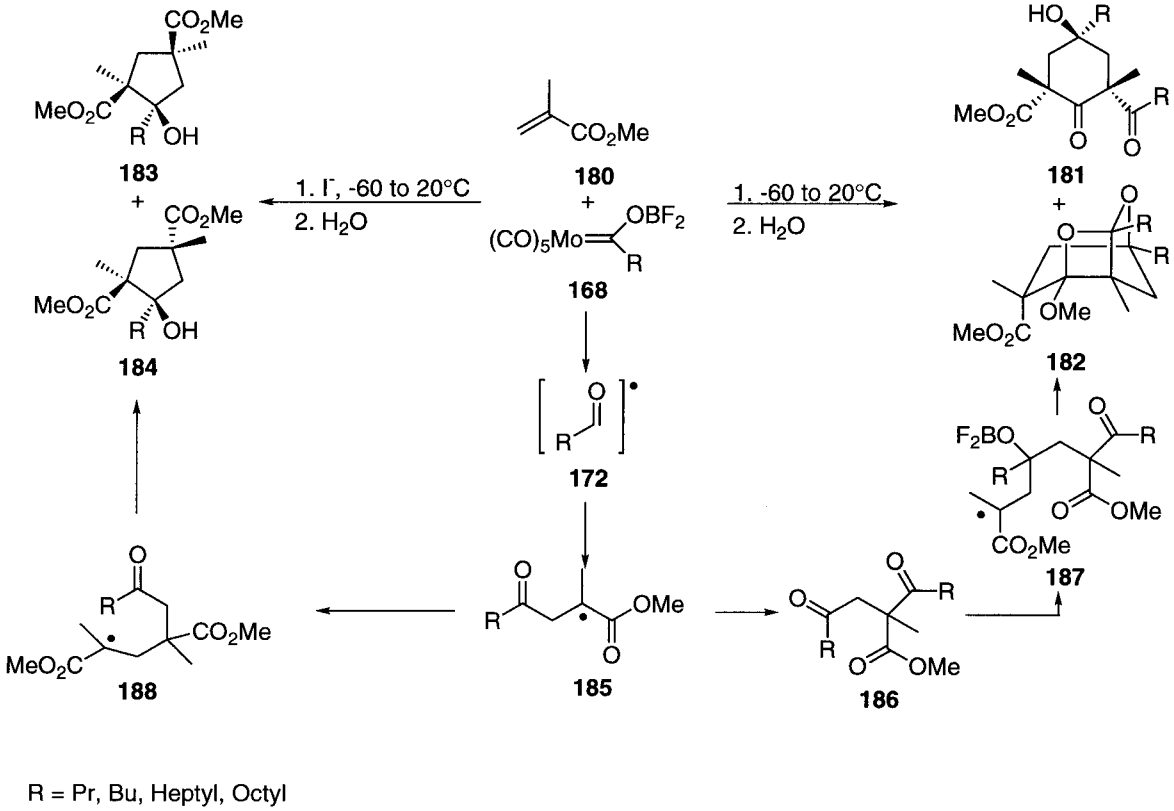
Scheme 43.



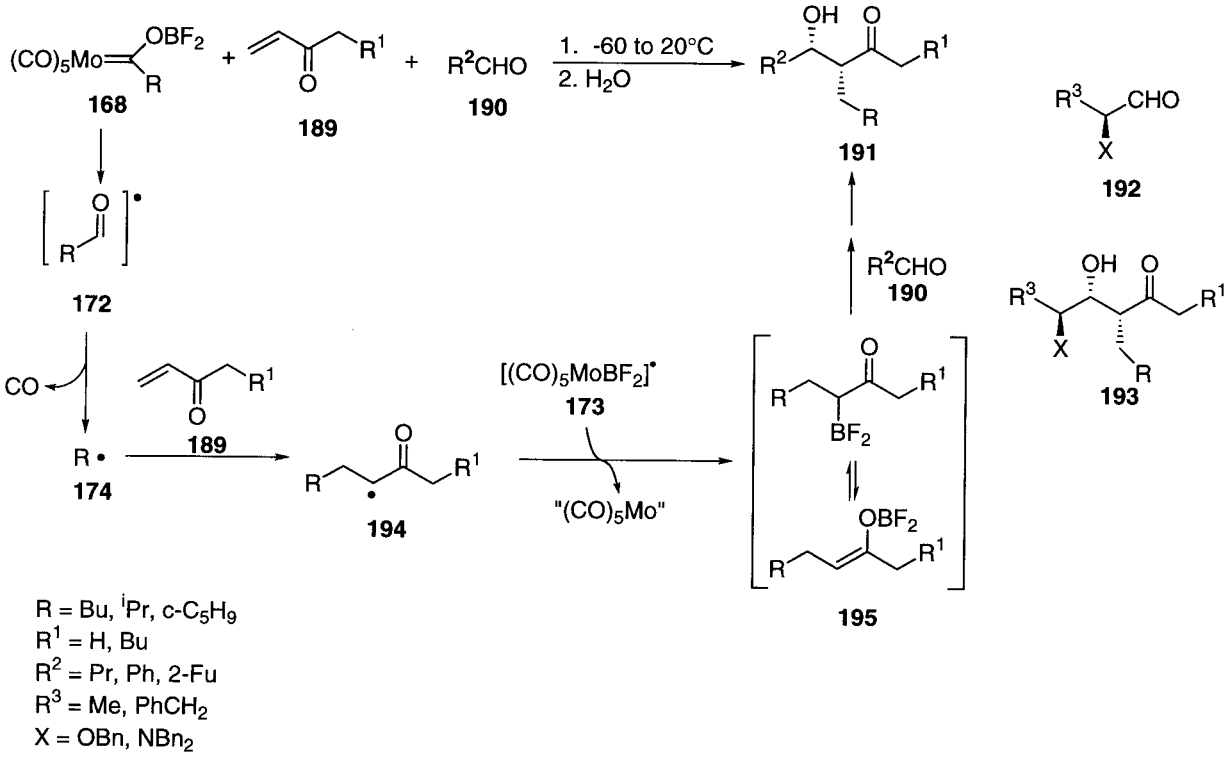
Scheme 44.

electron transfer from the radical species **173** to the boronenolates **179** followed by coupling with another molecule of the acyl radical **172** to generate, after hydrolysis, the hydroxyketone derivatives **177** (Scheme 44).[102]

A completely different outcome was observed when methyl methacrylate **180** was used as trapping agent in the decomposition of the difluoroboroxymolybdenum carbene complexes **168**. In these cases only small amounts (<10%) of the Michael adducts analogous to **176** were obtained and the main reaction products were a mixture of the cyclohexanone derivatives **181** (36–40%) and the tricyclic compounds **182** (25–30%). Surprisingly, if the reaction described above is performed in the presence of iodide anions (LiI, NaI), a mixture of diastereoisomers of the cyclopentanedicarboxylate derivatives **183** and **184** is isolated (Scheme 45). On the other hand, the formation of compounds **181**–**184** is only observed when the R groups in the difluroboroxymolybdenum carbene complexes **168** are primary alkyl groups. If, however, R is a secondary alkyl group (R=*c*-C_5H_9) the reaction leads only to the Michael adduct methyl 4-cyclopentyl-2-methyl-4-oxo-butanoate (54%) analogous to **176**. The compounds **181** and **182** are the products of a four-component coupling reaction, two fragments originating from the carbene complex **168** and the other two from the methyl methacrylate **180**. On the other hand, the cyclopentanedicarboxylate derivatives **183** and **184** are the products of a three-component coupling reaction, two fragments coming from the methyl methacrylate **180** and the other one from the carbene complex **168**.



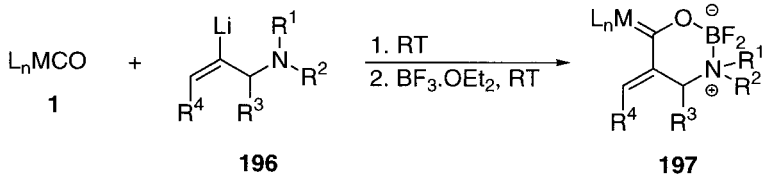
Scheme 45.



Scheme 46.

The more stable tertiary radicals **185** have been invoked to explain the different reaction outcome when methyl methacrylate **180** is used to trap the acyl radicals **172**. In the absence of iodide anions, the radicals **185** collapse with a second molecule of the acyl radical **172** to form the tricarbonyl compounds **186**. Further electron transfer from **173** to the most accessible carbonyl group of **186** followed by addition to another molecule of methyl methacrylate **180** gives rise to the new radical intermediates **187**. A ring-closing reaction, electron transfer from **173** and final hydrolysis furnish **181** and **182**, depending on the relative stereochemistry of the new chiral centres generated in the reaction (Scheme 45).[102b] In the presence of iodide anions, however, the intermediates **185** are added to a further molecule of methyl methacrylate **180**, presumably due to the lower concentration of the acyl radicals **172** provoked by the iodide anion, to form the new tertiary radicals **188**. A ring-closing reaction, electron transfer from **173**, and hydrolysis generates the cyclopentanedicarboxylate derivatives **183** and **184** (Scheme 45).[102b] Finally, the reluctance to form the three and four-component coupling products when R are secondary alkyl groups may be understood, on the basis of the proposed mechanism, as the result of the steric hindrance of the R group in the reaction of **185** either with **172** or **180**. Instead, the electron transfer from **173** followed by hydrolysis is preferred and the Michael adduct is generated.

Addition of a new component to the mixture containing the difluoroboroxycarbene complex and the electron-deficient alkene results in the formation of a new type of products. Thus, treatment of the pentacarbonyl difluoroboroxymolybdenum carbene complexes **168** with the vinylketones **189** and aldehydes **190** at temperatures from −60 to 20°C leads exclusively to the *syn* 3-hydroxyketone derivatives **191** (44–54%). The diastereofacial selectivity of this process, when chiral aldehydes **192** are used, is remarkable. Thus, when the reagents are mixed at −60°C, allowed to warm up to −20°C, and the reaction kept at this temperature for 72 h, the hydroxyketone derivatives **193** are produced in over 40% yield and diastereoselectivities above 99% are found in most cases (Scheme 46).[107] This process represents an interesting alternative to the aldol reaction where the main problem of the lack of regioselectivity for nearly symmetrical ketones is solved. A plausible explanation for the formation of the 3-hydroxyketones **191** is presented in Scheme 46. Unlike the observed outcome of the decomposition of the complexes **168** in the sole presence of electron-deficient alkenes (see Schemes 44 and 45), the acyl radicals **172** surprisingly suffer decarbonylation to generate the alkyl radicals **174**, which then add to the vinylketones **189** in a Michael fashion to generate the radical intermediates **194**. Further electron transfer from **173** to the intermediate **194** with loss of the $(CO)_5Mo$ fragment produces the boron-enolates **195**, which by addition to the aldehydes **190** afford, after hydrolysis, the 3-hydroxyketone derivatives **191**.[107] An explanation of the 1,2-*syn* induction in the aldol reaction is possible considering the well-known Zimmermann–Traxler chair-like transition state model,[108] if the geometry of the formed enolate is assumed to be exclusively *Z*. In this case, the small size of the fluorine atoms would favour the formation of the (*Z*)-isomer.[109] The preference for the Felkin-type products (3,4-*anti*) when the chiral aldehydes **192** were used can be explained by assuming a non-chelated transition state[110] as observed in similar reactions.[111] These results reflect a very high degree of substrate control in the aldol addition of achiral boron-enolates to chiral aldehydes.[111]



$L_nM = (CO)_5Cr, (CO)_5Mo, (CO)_5W$
$R^1 = Me, Et, PhCH_2$
$R^2 = Et, PhCh_2, Ph, 4\text{-}^tBuC_6H_4, 4\text{-}MeOC_6H_4$
$R^3 = R^4 = H$
$R^3\text{-}R^4 = (CH_2)_3$

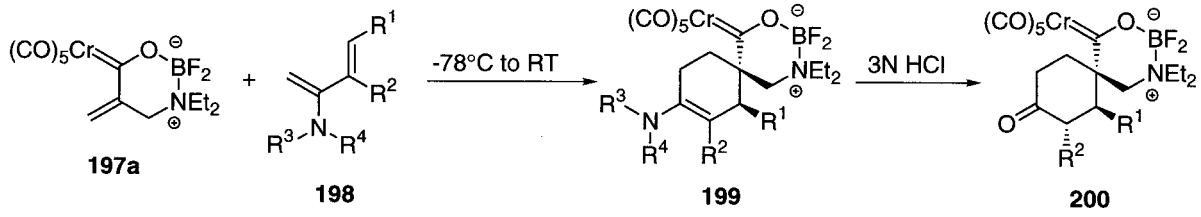
Scheme 47.

The presence of a nitrogen atom adequately positioned in the structure of the difluoroboroxycarbene complexes dramatically increases their stability and results in an unusual chemical behaviour. The boroxycarbene complexes **197** are synthesized in moderate yields (40–45%) by addition at room temperature of the appropriate β-nitrogen-functionalised organolithium compound **196**[112] to a solution of the corresponding metal carbonyl **1**, followed by treatment with an excess of boron trifluoride etherate at the same temperature.[113] The structure of these compounds, determined from their spectral data and by single-crystal X-ray diffraction, shows the formation of a six-membered ring oxazaboracycle that locks the vinylcarbene complex into an *s-cis* conformation (Scheme 47).

Owing to the remarked particularity in their structure, the complexes **197** are appropriate candidates to act as dienophiles in Diels–Alder reactions. In fact, the complex **197a** [$L_nM=(CO)_5Cr$, $R^1=R^2=Et$, $R^3=R^4=H$] reacts with 2-amino-1,3-dienes[114] at temperatures from −78°C to room temperature to give rise to the corresponding [4+2] cycloadduct **199** in good yields (80–85%) and as a single regio- and diastereoisomer. The stereochemistry of the adducts **199** corresponds to an *exo* diene-dienophile orientation. Subsequent acid hydrolysis of the enamine group of **199** affords the spiro carbene complexes **200** as a single diastereoisomer in quantitative yield (Scheme 48). The reaction of other carbene complexes **197** proceeds similarly. Starting from the complexes **197** with R^1–R^2 (two different substituents at the nitrogen atom), however, the Diels–Alder adducts similar to **199** are formed as mixture of diastereoisomers due to the presence of a stereogenic centre at the nitrogen atom.[113b]

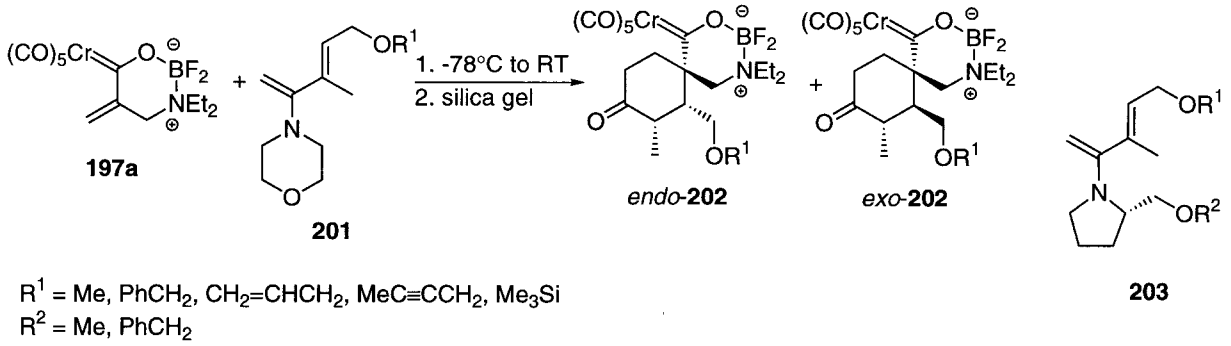
The results of the above-mentioned Diels–Alder reactions are strongly dependent on the substitution pattern of the aminodiene employed. While the reactions of the BF_2-chelated carbene complex **197a** with nonheteroatom 4-substituted 2-aminodienes **198** affords exclusively the corresponding *exo* cycloaddition products (Scheme 48), the reactions of the same carbene complex with 2-morpholino dienes **201** bearing an alkoxy-containing group at the C-4 position leads directly to the corresponding ketocarbene complexes as a mixture of formal *endo*-**202** and *exo*-**202** Diels–Alder adducts in which the former is generally the major or even the exclusive isomer isolated under otherwise analogous reaction conditions (Scheme 49).[113b]

The outcome of the reaction of the chelated boroxycarbene complexes **197** with the enantiomerically pure 2-aminodienes **203** derived from (*S*)-prolinol *O*-alkyl ether is interesting. Treatment of the carbene complex **197a** with the chiral dienes **203** under the above conditions affords exclusively, and in sharp contrast to the results obtained with the structurally similar 2-morpholino dienes **201**, the corresponding Diels–Alder *exo*-adduct **202** in moderate yields (30–60%) but with a high level of enantioselectivity (>90% ee) (Scheme 49). This different behaviour is presumably attributed to the presence of an alkoxy group at the C-2 position of the amine, which could favour the *exo* approximation by a greater number of close contacts of the metal centre with the prolinol unit.[113b] These [4+2]

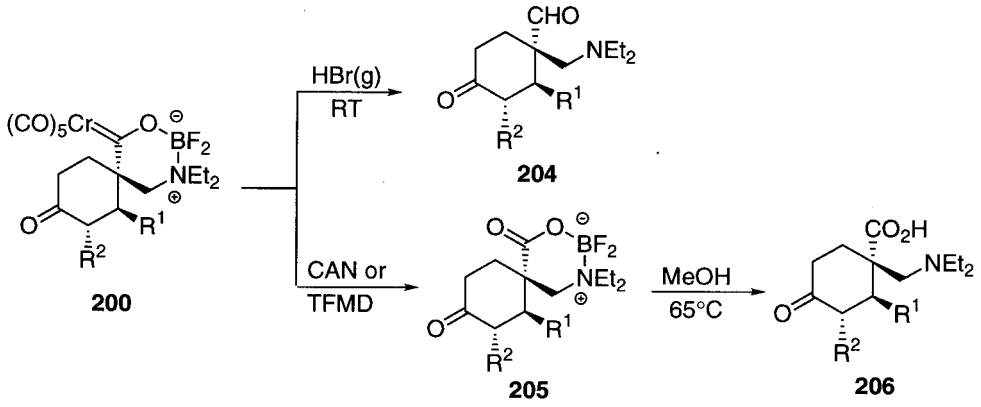


$R^1 = H, R^2 = Me$
$R^1\text{-}R^2 = (CH_2)_3, (CH_2)_4$
$R^3 = Me, R^4 = Ph$
$R^3\text{-}R^4 = [(CH_2)_2]_2O$

Scheme 48.



Scheme 49.



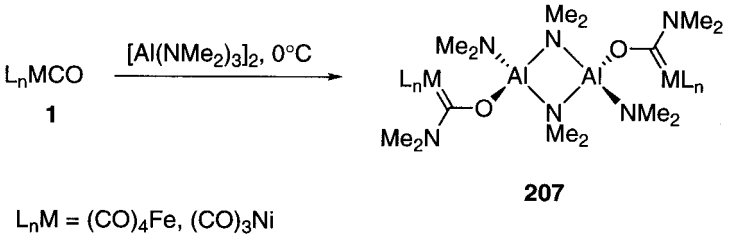
Scheme 50.

cycloaddition reactions generate with a high enantioselectivity spiranic carbene complexes[115] containing three contiguous stereogenic centres, one of which is a quaternary carbon atom.[101,116]

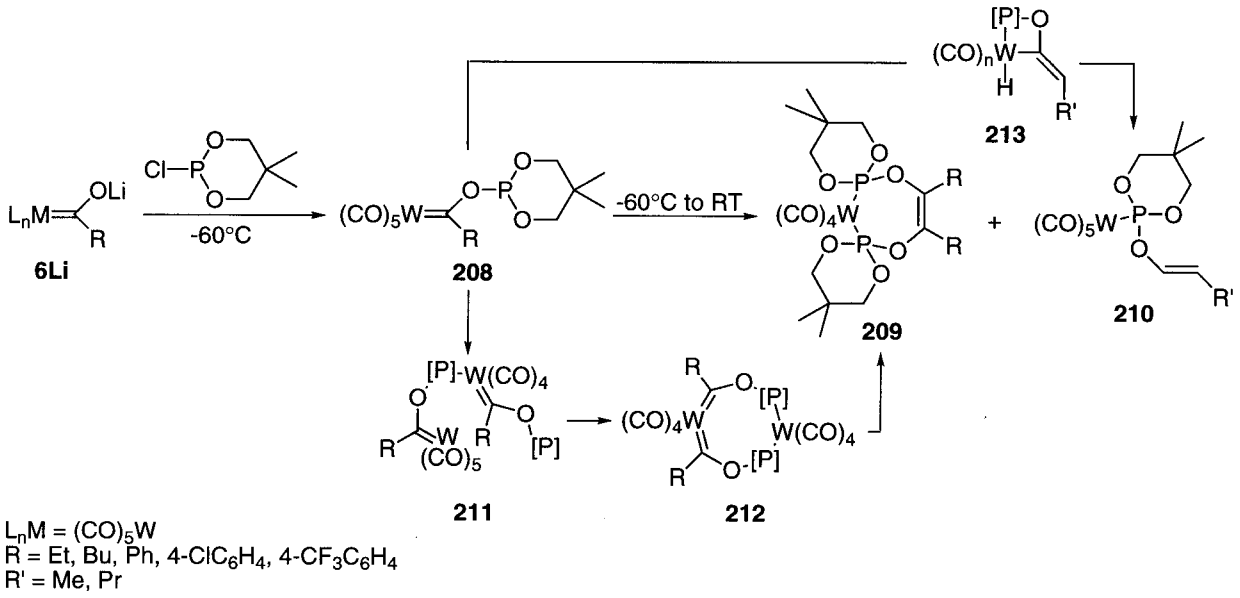
The formation of metal-free organic products from the spiro BF_2-chelate metal-complexed cycloadducts is carried out by employing known reactions of Fischer carbene complexes. Thus, simultaneous removal of both the metal fragment and the BF_2 group is readily achieved by treatment with hydrogen bromide.[117] Bubbling this gas into a solution of the carbene complexes **200** furnishes the corresponding aminoaldehydes **204** (85–89%) as diastereoisomerically pure compounds. Alternatively, the formation of metal-free organic products is accomplished in a two-step sequence. Firstly, the metal fragment is selectively removed by oxidative cleavage either with CAN[118] or methyl(trifluoromethyl)dioxirane (TFMD).[119] The complexes **200** are easily oxidized to the corresponding BF_2-protected β-amino acids **205** by treatment with either of these oxidants in good yields (75–90%). Secondly, heating the adducts **205** in refluxing methanol leads to the corresponding α,α-disubstituted β-amino acids **206** as a single diastereoisomer (Scheme 50).[113b]

10. Alanoxycarbene Complexes

Aminoaluminum derivatives like aminotitanium or aminotin compounds are able to add to coordinated carbon monoxide and, therefore, the metal carbonyls **1** react with the tris(dimethylamino)aluminum dimer at 0°C to give the alanoxycarbene complexes **207** in 70–84% yield (Scheme 51). Spectroscopic data and molecular weight determinations indicate the dimeric nature of the complexes **207**. Formation of these complexes occurs by direct nucleophilic attack of the amino group of the aluminum compound on the carbonyl carbon, this presumably being favoured by an interaction between the aluminum atom and the carbonyl oxygen, in a synchronic mechanism.[120]



Scheme 51.



Scheme 52.

11. Phosphitecarbene Complexes

Treatment of the lithium acyl metallates **6Li** with 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane at temperatures ranging between −60 and −30°C allows the synthesis of the highly unstable phosphitecarbene complexes **208**.[121] On warming to room temperature, the complexes **208**, where R is an aryl group, undergo loss of the metal fragment affording the (*Z*)-1,2-diphosphite alkene tetracarbonyl tungsten complexes **209** (50–60%) as a single diastereoisomer, according to their NMR spectra and X-ray structural analysis. This transformation involves dimerization of the carbenes **208** under very mild conditions.[122] On the contrary, starting from the carbene complexes **208**, which contain α-hydrogen atoms, formation of the (*E*)-vinyl phosphite pentacarbonyl tungsten complexes **210** (60–68%) along with a small amount of the dimeric carbene complexes **209** (8–12%) is observed (Scheme 52).[121]

Formation of the dimeric complexes **209** is considered to proceed by initial generation of the bimetallic complexes **211** through CO dissociation in the complexes **208** and reaction with another molecule of **208**, via coordination to phosphorous. Subsequent carbene ligand transfer forms **212**, which decomposes to the carbene dimers **209**. According to this mechanism, the double coordination of the tungsten atom to the phosphorous in the complexes **212** favours the *cis* arrangement in the carbene ligand transfer leading exclusively to the (*Z*)-diastereoisomers. On the other hand, the formation of the vinylic phosphites **210** probably proceeds by a migration of the acidic proton α to the carbene carbon atom to the tungsten in the metal carbene complexes **208** to give the complexes **211**, followed by a reductive elimination furnishing the vinylic phosphites **210**. This intramolecular coordination of the phosphorous atom to the tungsten is presumably responsible for the stereoselective formation of the (*E*)-isomer, in contrast with the results observed for the base-catalyzed decomposition of carbene complexes, in which mainly the (*Z*)-isomer is obtained.[123]

12. Conclusions

Described in this review are a variety of methods to prepare, from the corresponding metal carbonyls, heteroatom stabilised carbene complexes, in which a second metal is directly bound to the carbene heteroatom. The more general methods involve either nucleophilic attack to a carbonyl ligand, the conventional Fischer method, or routes which avoid the nucleophilic addition by using unsaturated transition metal complexes, which undergo carbonyl insertion reactions. The presence of two metals in the structure of the metalloxycarbene complexes allows the development of the characteristic chemistry of each metal and also that derived from the mutual action of both metals. The acyl resonance structure in metalloxycarbene complexes usually has a large contribution and consequently decreases the carbene reactivity, which permits the carrying out of reactions at other parts of the molecules without interfering with the carbene moiety. The metalloxy complexes can thus be regarded as protected Fischer carbene complexes. On the other hand, these systems undergo a series of transformations rarely observed in classical alkoxycarbene complexes. In summary, the presence of a second metal directly bound to the carbene heteroatom represents a way of modulating the carbene reactivity and it is doubtless expected that new and surprising transformations will be found for related compounds.

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Biographical Sketch

José Barluenga was born in 1940 in Tardienta, Spain. He received his doctoral degree at the University of Zaragoza in 1966 under the direction of Prof. Gómez Aranda. Following this, he spent three and a half years as a postdoctoral research fellow working on aluminium chemistry in Prof. H. Hoberg's group at the Max Planck Institut für Kohlenforschung, Mülheim a.d. Ruhr, Germany. In 1970, he took a position as a Research Associate at the University of Zaragoza, where he was promoted to Associate Professor in 1972. In 1975, he moved to the University of Oviedo as Professor of Organic Chemistry, where he is now Director of the Instituto Universitario de Química Organometálica 'Enrique Moles'. Prof. Barluenga is recipient of the Research Award of the Foundation Alexander von Humboldt (1989), the Solvay Award from Spanish CEOE (1990), the First DuPont Award (1991), the Iberdrola Award (1997), and the Gold Medal of Real Sociedad Española de Química (1999). His major research interest is focused on various topics related to selective organic synthesis and organometallic chemistry.

Francisco J. Fañanás was born in 1952 in Huesca, Spain. He received his BS degree from the University of Zaragoza in 1974 and his Ph.D in chemistry in 1979 from the University of Oviedo under the supervision of Professor Barluenga and Professor Yus. He was a post-doctoral fellow of Prof. H. Hoberg's laboratory at the Max Planck Institut für Kohlenforschung, Mülheim a.d. Ruhr, Germany, from 1982–1984 working on nickel chemistry. In 1985 he joined the Instituto Nacional del Carbón in Oviedo as a Research Assistant. Thereafter, in 1987, he joined the Organic Department at the University of Oviedo as an Associate Professor. His research interest is focused in organic synthesis mediated by transition metals of groups 4 and 6.