Electrophilic Half-Sandwich (Carbene)metal (Metal = Fe, Ru, Os) Complexes: Recent Developments in Synthesis and Applications

Véronique Guerchais[a]

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This review covers synthetic and structural aspects of electrophilic half-sandwich (carbene)metal complexes of Group-8 metals as well as the use of these complexes in transformations of organic molecules. These species, including chelate complexes, are involved in C–C bond-forming reactions in stoichiometric or catalytic processes.

Contents

1. Introduction

The chemistry of electrophilic (carbene)metal complexes is an area of current interest because of the wide applications in organic synthesis.[1,2] Their potential to mediate novel C−C bond-forming reactions has generated the development of new synthetic methodologies. In this context, the (carbene)ruthenium complexes, that are highly active metathesis catalysts able to generate polymeric materials and five-, six-, seven-, and eight-membered carbocycles or heterocycles, have seen rapid developments.[3] In addition, (carbene)metal complexes attract considerable attention since they offer the possibility of the development of new types of organometallic intermediates that may have unusual reactivity.

This review deals with electrophilic half-sandwich complexes of iron, ruthenium, and osmium containing the C_5R_5 (R = H, Me, Ph), $C_9H_4R_3$ (R = H, Me), or Tp [Tp = hydrotris(pyrazolyl)borate] ligand and covers the literature from January 1995 up to June 2001. We will focus our attention on the synthesis, the structural features, and the role of these carbene complexes in C−C bond-forming reactions. The discussion will emphasise our ongoing research on chelate (carbene)iron derivatives that are involved in bond-activation reactions. We are interested in investigating the chemistry of electrophilic (carbene)iron complexes containing a labile or hemi-labile ligand. The presence of a potential vacant coordination site allows the introduction of a substrate capable of reacting with the carbene ligand within the coordination sphere of the metal centre. Finally,

[a] Institut de Chimie de Rennes, UMR 6509 CNRS-Université de Rennes 1 "Organométalliques et Catalyse",
Campus de Beaulieu, 35042 Rennes Cedex, France

Véronique Guerchais is a CNRS researcher at the Institut de Chimie de Rennes, unit "Organometallics and Catalysis". She received her PhD under the supervision of Prof. D. Astruc on "electron reservoir" complexes. She carried out postdoctoral studies on the activation of alkynes at diruthenium centres at the University of Bristol (U. K.) with Prof. S. A. R. Knox. Her current research interests are focused on iron complexes, including carbene species, for bond activation and C−C bond formation.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

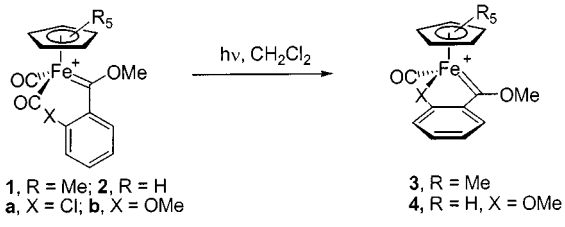
we will describe the catalytic reactions of (carbene)-ruthenium complexes.[4] Cyclopentadienyl complexes $[Ru(C_5R_5)(L)_2Cl]$ and related species were found to be effective catalyst precursors in C−C coupling reactions involving diazo compounds,[5] including insertion, carbene dimerisation, and carbene transfer reactions to alkenes and alkynes.

2. Preparation and Structural Characterisation

2.1. Iron Complexes

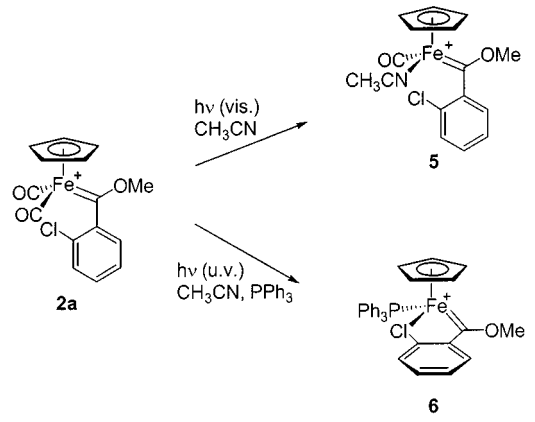
The reaction of an acyl complex with an electrophile is a common route to alkoxycarbene complexes of iron $[Fe(C_5R_5)(CO)_2\{C(OR^2)R^1\}]^+$ (R = H, Me). The required alkyl- and aryl-substituted acyl derivatives $[Fe(C_5R_5)(CO)_2\{C(O)R^1\}]$ are in turn accessible by the reaction of the ferrate complex $[M][Fe(C_5R_5)(CO)_2]$ (M = Na, K) with the appropriate acyl chloride.[6]

ortho-Substituted arylcarbene complexes are good precursors of chelate carbene species.[7] Thus, the cationic κ^2-(*C*,*X*) chelate complexes $[Fe(C_5R_5)(CO)\{C(OMe)C_6H_4$-*o*-$X\}(Fe-X)][OTf]$ (**3**) (R = Me; **a**: X = Cl; **b**: X = OMe)[7a] and **4** (R = H; X = OMe)[7b] are obtained upon irradiation of the corresponding dicarbonyl species in a non-coordinating solvent such as CH_2Cl_2 (Scheme 1). In contrast with the C_5Me_5 analogue, coordination of the chlorine atom of **2a** does not take place. When irradiation of **2a** is performed in CH_3CN, the stable acetonitrile complex $[Fe(C_5H_5)(CO)(CH_3CN)\{C(OMe)C_6H_4$-*o*-$Cl\}][OTf]$ (**5**) is obtained (Scheme 2). Substitution of one carbonyl ligand by PPh_3 allows the isolation of the κ^2-(*C*,*Cl*) chelated derivative **6** (Scheme 2).[7b] The phosphane ligand has the same effect on the nature of the product as the permethylation of the C_5 ring. The formation of the chelate structure can easily be established by ^{13}C NMR spectroscopy. The signal of the aryl carbon atom which bears the heteroatom is shifted downfield upon coordination of the *ortho* substituent X. There is a marked shift difference of 20 ppm in both the C_5H_5 and C_5Me_5 series, in agreement with a decrease in electronic density. The chlorine and the oxygen atoms act as neutral two-electron donor ligands allowing the formation of a five-membered metallacycle. This has been confirmed by the crystallographic analyses of **3a** and **4**.

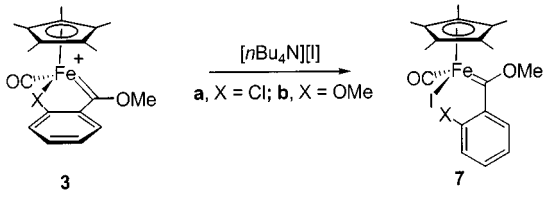


Scheme 1. Synthesis of chelate arylcarbene complexes

The neutral iodo derivatives **7a**,**b** are obtained on treating **3a**,**b** with $[nBu_4N][I]$, due to the lability of the chelating group X (Scheme 3). In contrast with the dicarbonyl species, the competitive *O*-demethylation reaction that leads to the acyl complex and methyl iodide does not take place.[8]

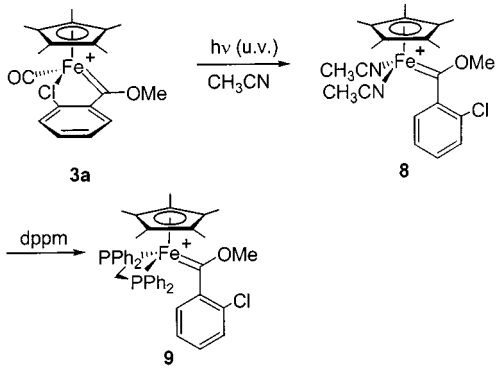


Scheme 2. Synthesis of (chloroaryl)carbene complexes containing a labile or hemi-labile ligand



Scheme 3. Synthesis of iodo carbene complexes **7**

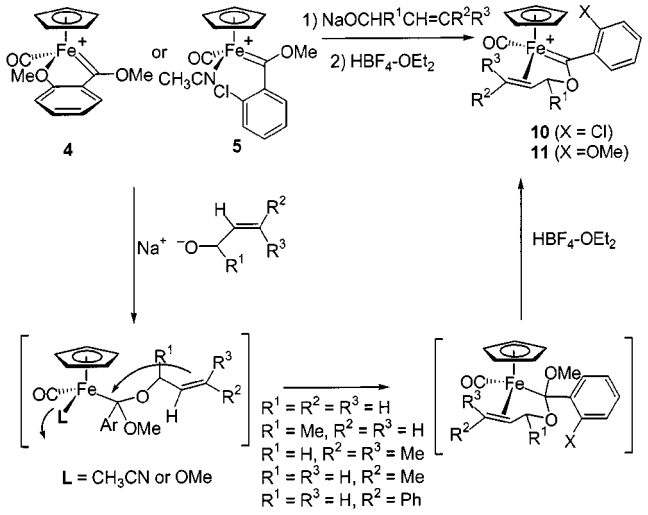
Carbene complexes containing two labile ligands can also be obtained. For example, UV irradiation of **3a** gives **8**, and then addition of dppm [dppm = bis(diphenylphosphanyl)-methane] provides **9** (Scheme 4).



Scheme 4. Ligand exchange reactions of **3a**

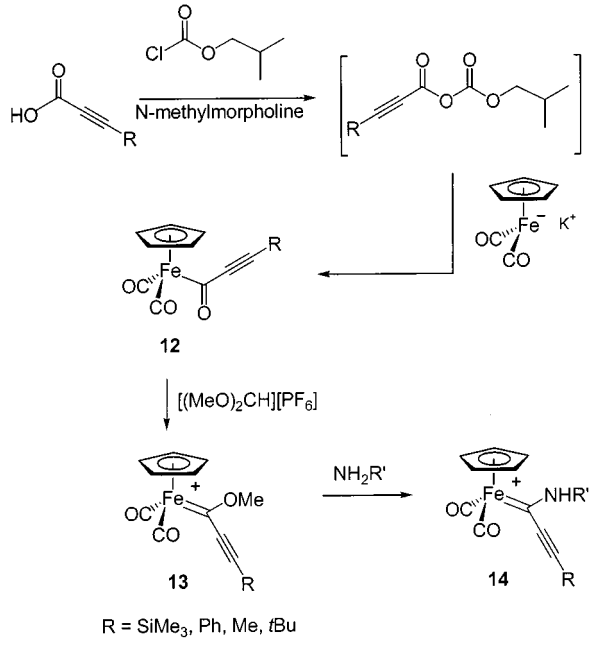
The presence of a labile or hemi-labile ligand in carbene complexes **4** and **5** allows the chelation of the C−C double bond of an allyloxy group, and the chelate (allyloxy)carbene complexes **10** and **11** are thus accessible (Scheme 5).[9] They are prepared in a two-step one pot procedure, by treating **4** or **5** with the appropriate allyl oxide followed by protonation. This sequence conveniently gives access to various substituted complexes. The iron moiety, which is sterically not encumbered, is able to coordinate a di- and trisubstituted C−C double bond. We found that this preparation

requires pre-coordination of the allyloxy group, otherwise the synthesis fails.

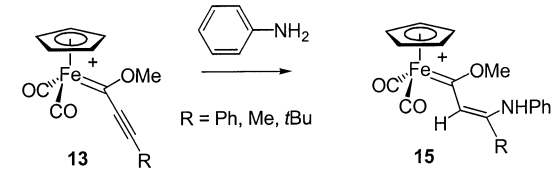


Scheme 5. Synthesis of chelate (allyloxy)carbene complexes **10** and **11**

The preparation of the alkynyl-substituted acyl complexes **12** has been achieved by using mixed anhydrides [*i*PrCH$_2$OC(O)OC(O)C≡CR] (Scheme 6).[10] Compounds **12** are obtained in high yields and can be converted into the respective methoxy- and aminocarbene complexes **13** and **14** (Scheme 6). Some of the methoxycarbene complexes **13** undergo a Michael-type addition of aniline at room temperature to give the (2-aminoethenyl)methoxycarbene complexes **15** (Scheme 7).[10d]

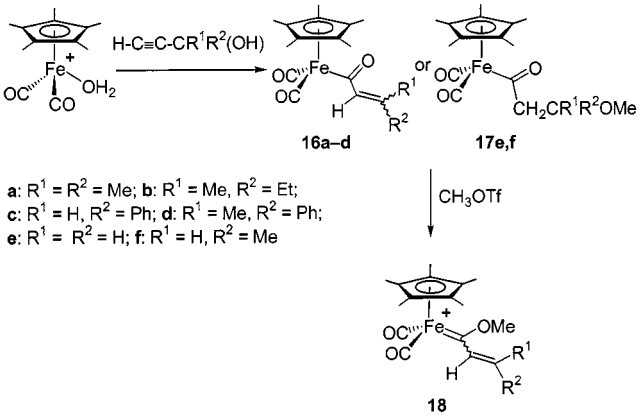


Scheme 6. Synthesis of (alkynyl)acyl complexes and the corresponding methoxy- and aminocarbene complexes



Scheme 7. Synthesis of (2-aminoethenyl)methoxycarbene complexes **15**

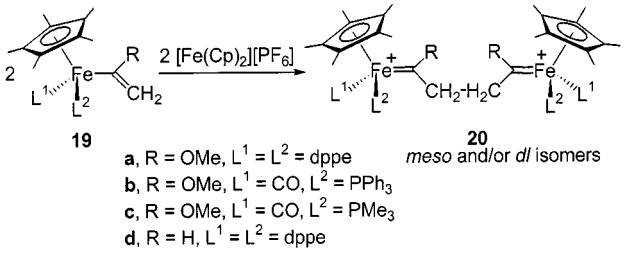
We have found that the activation of propargylic alcohols by [Fe(C$_5$Me$_5$)(CO)$_2$(H$_2$O)][BF$_4$] in the presence of methanol leads to the isolation of the α,β-unsaturated acyl complexes **16** or the Michael adducts **17** (Scheme 8).[11] The expected methoxycarbene complexes [Fe(C$_5$Me$_5$)(CO)$_2${=C(OMe)CH=CR^{1}R^2}] (**18**) are not obtained directly, and *O*-alkylation of **16** or **17** with methyl triflate generates **18**. This may be due to a spontaneous demethylation reaction of methoxycarbene complexes in solution, a feature already described.[8]



Scheme 8. Synthesis of (alkenyl)carbene complexes **18** by activation of propargylic alcohols

Alkylation of formyl transition metal complexes constitutes a route to secondary alkoxycarbene complexes. Thus, methylation of the stable formyl complex [Fe(C$_5$Ph$_5$)(CO)(PMe$_3$)(CHO)] and addition of [NH$_4$][PF$_6$] afford the secondary methoxycarbene complex [Fe(C$_5$Ph$_5$)(CO)(PMe$_3$)(=CHOMe)][PF$_6$] in high yield.[12]

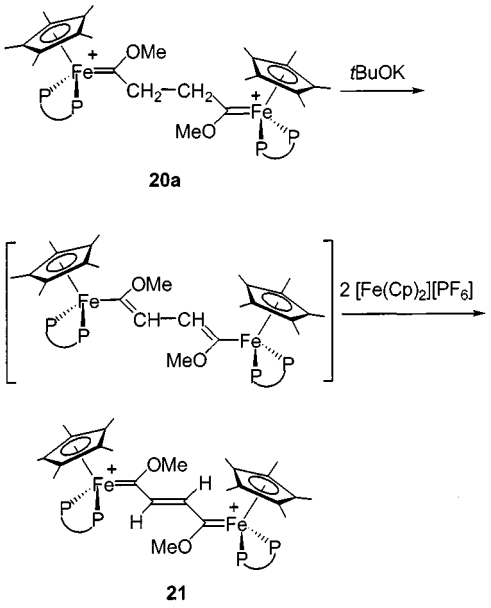
Dinuclear bis(carbene) complexes have been synthesised from mononuclear species through a carbon−carbon ligand coupling.[13] The 18-electron (vinyl)iron(II) derivatives **19** undergo oxidative coupling via 17-electron **19**$^+$ (Fe^{III}) to produce [μ-bis(methoxycarbene) or μ-bis(ethylidene)]diiron



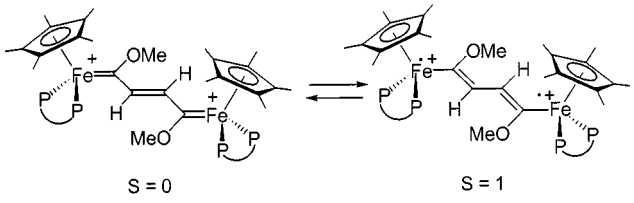
Scheme 9. Synthesis of bridged bis(carbene) complexes

complexes **20** in good yields (Scheme 9). The coupling reaction is sensitive to steric effects of the ancillary ligands at the metal centre, and the *meso* and *dl* couples of the bis(carbene) dimers are formed with good diastereoselectivities.

The dinuclear butadienediyl-bridged bis(carbene) complex **21** is then accessible through deprotonation of **20a**, followed by a two-electron oxidation with 2 equiv. of ferricenium (Scheme 10).[14] Complex **21** is diamagnetic in solution. However, variable-temperature Mössbauer spectroscopy allows the observation of the singlet and triplet spin isomers and their interconversion (Scheme 11).[14,15]



Scheme 10. Synthesis of the butadienediyl-bridged bis(carbene) complex **21**

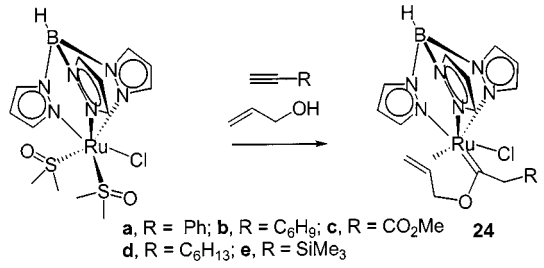


Scheme 11. Interconversion of the singlet and triplet spin isomers of **21**

2.2. Ruthenium and Osmium Complexes

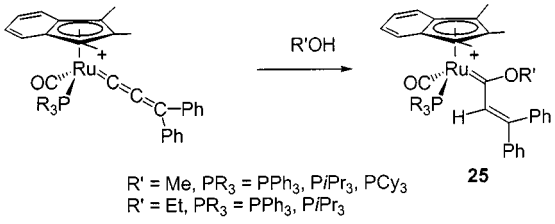
(Carbene)ruthenium complexes are accessible from vinylidene and allenylidene precursors but the formation of the carbene ligand depends on both the ligand sphere of the metal centre and on the nature of the substituents of the unsaturated ligand.[16]

For instance, the methoxycarbene complex [Ru(Tp)(dippe){=C(OMe)CH_2CO_2Me}][BPh_4] (**22**) [dippe = bis(diisopropylphosphane)ethane] is formed by the addition of MeOH to the corresponding vinylidene complex [Ru(Tp)(dippe)(=C=$CHCO_2$Me)][BPh_4].[17] Similar alkoxycarbene complexes have not been obtained from [Ru(Tp)(dippe)(=C=CHR)][BPh_4] when R is different from CO_2Me. Complex [Ru(Tp)(Haapy)(Cl)] (Haapy = 2-acetamido-4-methylpyridine) reacts with HC≡CR to give the cyclic amidocarbene complexes [Ru(Tp)(Cl)(=CCH_2R-aapy)] (**23**) (**a**: R = Ph; **b**: R = *n*Bu).[18] The formation of **23** presumably proceeds via vinylidene intermediates. Although such intermediates could not be isolated or detected spectroscopically, such a process would be facile when the nucleophilic attack occurs in an intramolecular, chelate-assisted fashion. This can explain the addition of the weakly nucleophilic nitrogen atom of the amide. Similarly, addition of allyl alcohol to terminal alkynes mediated by [Ru(Tp)$(dmso)_2$(Cl)] gives the (allyloxy)carbene complexes **24** (Scheme 12).[19]



Scheme 12. Synthesis of (allyloxy)carbene complexes **24**

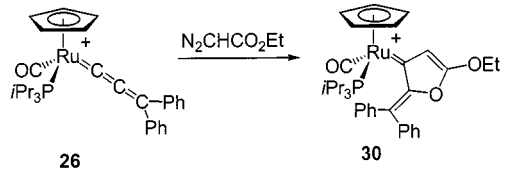
Addition of nucleophiles to allenylidene complexes is a general route to Fischer-type α,β-unsaturated carbene complexes of ruthenium. The reactivity of allenylidene complexes has recently been reviewed.[20] For example, the addition of methanol or ethanol to the trimethylindenyl complex [Ru(η^5-1,2,3-$Me_3C_9H_4$)(L^1)(L^2){=C=C=CPh_2}][BF_4] (L^1 = CO and L^2 = PPh_3, P*i*Pr_3, PCy_3) takes place to afford the corresponding alkoxy derivatives **25** (Scheme 13).[20,21] Unstable allenylidene derivatives can be trapped in situ by methanol, and this allows the complexes [Ru(η^5-C_9H_7)(L^1)(L^2){=C(OMe)−CH=CHR}][PF_6] (R = Ph, L^1 = L^2 = dppe, dppm; R = H, L^1 = L^2 = dppm) to be isolated.[22] By contrast, the bis(triphenylphosphane)-substituted carbene derivatives are not formed, presumably because the PPh_3 ligands offer a steric protection of the allenylidene group towards nucleophilic addition.



Scheme 13. Synthesis of alkoxy(alkenyl)carbene complexes **25**

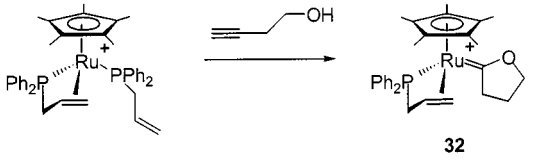
The acetone complex [Ru(C_5H_5)(CO)(P*i*Pr_3){OC-$(CH_3)_2$}][BF_4] reacts with 1,1-diphenyl-2-propyn-1-ol to afford the allenylidene derivative [Ru(C_5H_5)(CO)(P*i*Pr_3){C=C=CPh_2}][BF_4] (**26**) which adds water, alcohols, and thiols, at the $C_\alpha-C_\beta$ double bond of the allenylidene group to afford diphenyl-α,β-unsaturated-hydroxycarbene, -alkoxycar-

bene, and -(alkylthio)carbene complexes, respectively.[23] Complex **26** reacts with alcohols such as allyl alcohol (without pre-coordination of the olefinic moiety) and propargyl alcohol affording $[Ru(C_5H_5)(CO)(P\mathit{i}Pr_3)\{C(OCH_2CH{=}CH_2)CH{=}CPh_2\}][BF_4]$ (**27**)[24] and $[Ru(C_5H_5)(CO)(P\mathit{i}Pr_3)\{C(OCH_2C{\equiv}CH)CH{=}CPh_2\}][BF_4]$ (**28**),[25] respectively. Treatment of **26** with secondary and primary amines affords azoniabutadienyl derivatives $[Ru(C_5H_5)(CO)(P\mathit{i}Pr_3)\{C(CH{=}CPh_2){=}NR^1R^2\}][BF_4]$ (**29**).[26] Addition of ethyl diazoacetate to **26** affords the cyclic carbene complex $[Ru(C_5H_5)(CO)(P\mathit{i}Pr_3)\{{=}[-CCH{=}C(OEt)-O-C(=CPh_2)-]\}][BF_4]$ (**30**), which results from a formal 1,3-addition of the organic reagent at the $C_\alpha-C_\beta$ double bond (Scheme 14).[27]



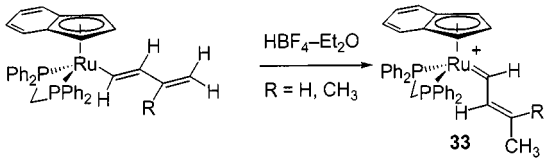
Scheme 14. Synthesis of the cyclic carbene complex **30**

The common approach to cyclic Fischer-type carbene complexes is the metal-assisted cycloisomerisation of ω-alkynols to oxacycloalkylidenes.[28] Such a reaction has been used for the preparation of $[Ru(C_5Me_5)(\kappa^1\text{-DPVP})_2\{{=}C^a(CH_2)_3O(C^a{-}O)\}][PF_6]$ (DPVP = diphenylvinylphosphane) starting from $[Ru(C_5Me_5)(\kappa^1\text{-DPVP})(\kappa^3\text{-DPVP})][PF_6]$.[29] In contrast, the formation of $[Ru(C_5Me_5)(\kappa^3\text{-ADPP})\{{=}C^a(CH_2)_3O(C^a{-}O)\}][PF_6]$ (**32**) (ADPP = allyldiphenylphosphane) from $[Ru(C_5Me_5)(\kappa^1\text{-ADPP})(\kappa^3\text{-ADPP})][PF_6]$ is accompanied by the loss of one phosphane ligand (Scheme 15).[30]



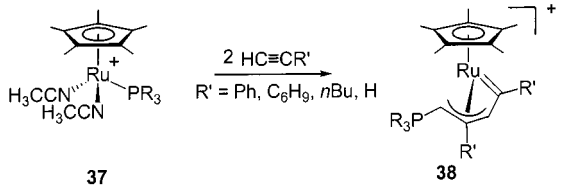
Scheme 15. Synthesis of cyclic oxycarbene complex **32**

The synthesis of (alkenyl)carbene complexes **33** has been achieved by protonation of the readily available (vinyl)alkenyl derivatives $[Ru(\eta^5\text{-}C_9H_7)(dppm)\{CHCH{=}CR^1R^2\}]$ (Scheme 16).[31] The formation of these α,β-unsaturated alkylidene complexes proceeds through regioselective protonation at either the C_γ or C_δ atom revealing the high electron density on these positions of the vinylalkenyl ligand.



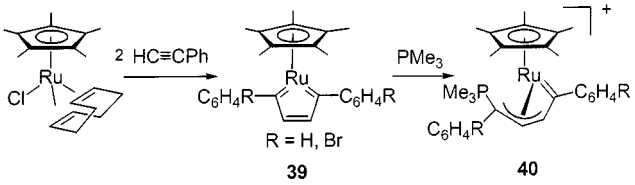
Scheme 16. Synthesis of vinylcarbene complexes **33**

(Allyl)carbene complexes are accessible through alkyne coupling reactions. The labile complexes $[Ru(C_5H_5)(PR_3)(CH_3CN)_2][PF_6]$ (**37**) (R = Me, Ph, Cy) react with alkynes HC≡CR′ and 1,6-heptadiyne to afford the (allyl)carbene complexes **38** and $[Ru(C_5H_5)\{{=}CH\text{-}\kappa^3\text{-}C(CH_2)_3CCHPR_3\}][PF_6]$ in high yields.[32] For the substituted derivatives, the substituents are exclusively in the 1- and 3-positions (Scheme 17).



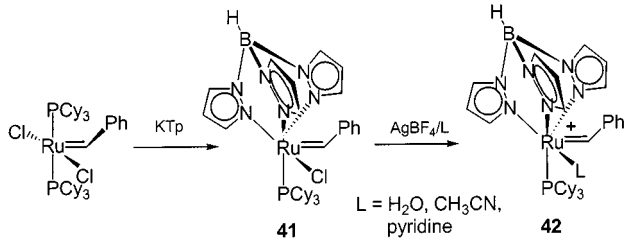
Scheme 17. Synthesis of the (allyl)carbene complexes **38** from **37**

A possible mechanism may involve a metallacyclopentatriene intermediate, from which subsequent migration of the phosphane to one of the electrophilic carbene carbon atoms occurs to give the observed carbene complex. This proposal is supported by the formation of **40** by treating the isolated ruthenacyclopentatriene **39** with PMe_3.[33] Addition of the phosphane occurs at the electrophilic α-carbon atom. Note that the substituents of **40** are located on the 1,4-positions due to a head-to-head coupling of the alkynes (Scheme 18). The ruthenacyclopentatriene complexes are prepared from $[Ru(C_5Me_5)(Cl)(TMEDA)]$ [34] or $[Ru(C_5Me_5)(cod)(Cl)]$ [33] in the presence of alkynes.



Scheme 18. Synthesis of (allyl)carbene complex **40** via **39**

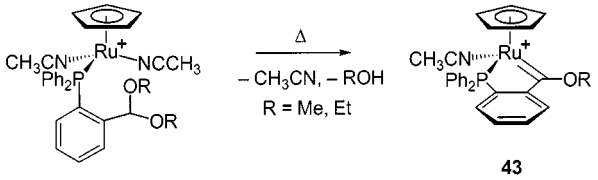
The complex $[Ru(Tp)(PCy_3)(Cl)(=CHPh)]$ (**41**) has been synthesised by the reaction of $[Ru(PCy_3)_2(Cl)_2(=CHPh)]$ and KTp (Scheme 19).[35] The cationic species **42** are then obtained by treatment of **41** with $AgBF_4$ or $AgSbF_6$ in the presence of various coordinating solvents L (L = H_2O, CH_3CN, pyridine).



Scheme 19. Synthesis of benzylidene complexes **41** and **42**

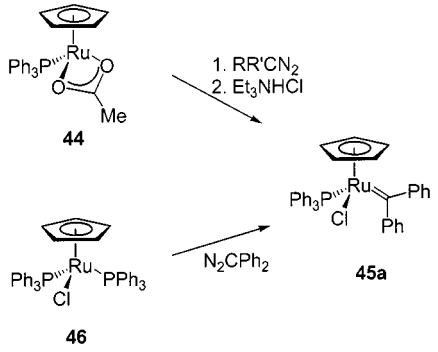
The synthesis of alkoxycarbenes **43** from an acetal derivative has been described.[36] Heating the acetal complexes

$[Ru(C_5H_5)(CH_3CN)_2\{\kappa^1\text{-}Ph_2PCH(OR)_2C_6H_4\}][OTf]$ (R = Me, Et) at 60−95 °C results in loss of one CH_3CN ligand and the alcohol ROH resulting from C−O bond cleavage, leading to carbene complex **43** in high yield (Scheme 20).



Scheme 20. Synthesis of alkoxycarbene complexes **43** from an acetal derivative

The diarylcarbene complexes $[Ru(C_5H_5)(PPh_3)(Cl)(=CRR')]$ (**45**) (**a**: R = Ph, R′= Ph; **b**: R = Ph, R′= *p*-C_6H_4Me; **c**: R = *p*-C_6H_4Cl, R′= *p*-C_6H_4Cl; **d**: R = *p*-C_6H_4OMe, R′= *p*-C_6H_4OMe) can be readily prepared by reaction of the acetato complex $[Ru(C_5H_5)(\kappa^2\text{-}O_2CMe)(PPh_3)]$ (**44**) with diaryldiazomethanes N_2CRR', followed by treatment with Et_3NHCl (Scheme 21).[37]

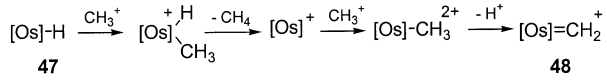


Scheme 21. Synthesis of the (diphenylcarbene)Ru complex **45a**

Complex **45a** is also obtained from $[Ru(C_5H_5)(PPh_3)_2(Cl)]$ (**46**) by direct reaction with diphenyldiazomethane. The dissociation of one triphenylphosphane ligand from **46** occurs at 65 °C in a non-polar solvent such as toluene (Scheme 21).[38] An excess of N_2CPh_2 has to be added during the reaction to obtain complete conversion of **46** into **45a**, because of the slow decomposition of N_2CPh_2. Similarly, facile displacement of one phosphane ligand in $[Ru(C_5H_5)\{PPh_2(2\text{-}MeC_6H_4)\}_2(Cl)]$ leads to the formation of $[Ru(C_5H_5)\{PPh_2(2\text{-}MeC_6H_4)\}(Cl)(=CPh_2)]$.[38] The (methyl-substituted aryl)phosphane appears to be more weakly bound to the ruthenium centre compared to PPh_3 and therefore more prone to dissociation. Complex **46** is also a good precursor for the aminocarbene complex $[Ru(C_5H_5)(PPh_3)_2(=CNHPh-CH_2Ph)]$ via the vinylidene complex $[Ru(C_5H_5)(PPh_3)_2(=C=CHPh)]$[40] by addition of benzylamine.[39]

Well-characterised examples of methylidene complexes remain relatively rare. One example has recently been described; complex **48** is obtained by treatment of the osmium hydride **47** with 2 equiv. of methyl triflate (Scheme 22).[41] The mechanism depicted in Scheme 23 is proposed to account for the formation of **48**. Methylation of the hydride precursor **47** generates the methyl/hydride intermediate, which then undergoes reductive elimination of methane. Attack of a second molecule of methyl triflate would give a methyl dication that provides **48** by loss of a proton.

Scheme 22. Synthesis of the (methylidene)osmium complex **48**



Scheme 23. Proposed mechanism for the formation of **48**

2.3. Conformational and Structural Features

Table 1 lists the M=C and C−X (X = O, N) bond lengths of structurally characterised (carbene)metal complexes (M = Fe, Ru, Os). These piano-stool complexes adopt a classical pseudo-octahedral geometry around the metal centre. The carbene ligand of such piano-stool complexes is generally oriented perpendicular to the plane of the C_5 ligand, the so-called "upright" conformation. This is for example the case for the ethylidene complex $[Fe(C_5Me_5)(dppe)(=CHMe)][CF_3SO_3]$ (**49**) in which the hydrogen atom is directed towards the C_5 ring.[13] The aminocarbene complex **14a** was found to exist in an "upright" conformation, whereas the related derivative **14b** shows an "orthogonal" conformation.[10b] Moreover, it has been shown that **14a** and **14b** exist in the solid state as *anti* isomers with respect to the C−N bond.

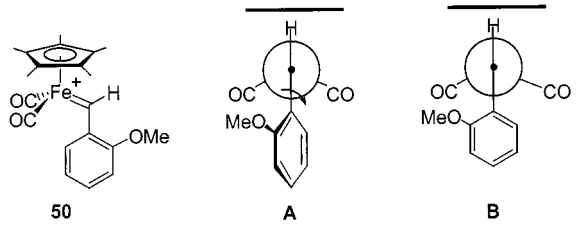
In solution, dynamic studies show that the arylcarbene complex **50** exists as two isomers in solution at −80 °C. Since the rotation around the Fe−C_α bond usually cannot be frozen out in such complexes, this feature most likely arises from restricted rotation about the C_α−C_{ipso} bond. Therefore, these two geometric isomers differ from each other in the orientation of the anisyl group [$\Delta G^{\ddagger}$ = 9.7 kcal·mol^{-1}, T_C(300 MHz) = 211 K].[7a] The conformation in which the aryl group is aligned with the Fe−C_α−C_{ipso} plane (rotamer **A**) provides the better electronic delocalisation of the positive charge (Scheme 24). On the basis of the NMR spectroscopic data of the carbonyl ligands, we assume that conformation **B** is preferred for the methoxycarbene derivatives **1**, **2**, and **9**; steric interactions appear to govern the carbene conformation. A twisted orientation of the carbene ligand is expected for the unsymmetrically substituted carbene complex **2a**.

X-ray structures of (alkylidene)iron complexes are scarce. The only complex that has been structurally characterised is the ethylidene complex **49**. The Fe−C_α bond length [1.787(8) Å] reflects the double-bond character of the iron−carbon bond.[13] The Fe−C bond lengths of het-

Table 1. Selected bond lengths [Å] of (carbene)metal complexes (M = Fe, Ru, Os)

Complex	$M-C_{carbene}$	$C_\alpha-X$ (X = O, N)	Ref.
$[Fe(C_5Me_5)(CO)(\kappa^2\text{-}C(OMe)\text{-}o\text{-}C_6H_4Cl][OTf]$ (**3a**)	1.857(6)	1.304(7)	[7a]
$[Fe(C_5H_5)(CO)\{\kappa^2\text{-}C(OMe)\text{-}o\text{-}C_6H_4OMe\}][OTf]$ (**4**)[a]	1.859(6)	1.299(7)	[7b]
	1.879(5)	1.303(6)	
	1.870(5)	1.299(7)	
$[Fe(C_5H_5)(CO)\{\kappa^3\text{-}C(OCH_2CH{=}CMe_2)\text{-}o\text{-}C_6H_4Cl\}][BF_4]$ (**10c**)	1.828(11)	1.344(14)	[51]
$[Fe(C_5H_5)(CO)_2\{C(OMe)CH{=}CRNHR'\}][PF_6]$ (**15**)			[10d]
a: R = Me, R′ = $CH(CH_3)CO_2tBu$	1.961(7)	1.361(10)	
b: R = *t*Bu, R′ = Ph	1.968(6)	1.336(7)	
c: R = Me, R′ = Ph	1.960(4)	1.323(5)	
$[Fe(C_5H_5)(CO)_2\{C(NHR')C{\equiv}CR\}][PF_6]$ (**14**)			[10b]
a: R = $SiMe_3$, R′ = C_6H_5	1.928(4)	1.305(6)	
b: R = $SiMe_3$, R′ = $p\text{-}C_6H_5CH_3$	1.940(5)	1.303(6)	
$[Fe(C_5Me_5)(dppe)(=CHMe)][OTf]$ (**49**)	1.787(8)		[13]
$[Ru(C_5H_5)(CO)(PiPr_3)\{C(OCH_2C{\equiv}CH)CH{=}CPh_2\}][BF_4]$ (**28**)	1.965(4)	1.321(4)	[25]
$[Ru(C_5H_5)(CO)(PiPr_3)(C{=}CH{=}(OEt)OC{=}CPh_2)][BF_4]$ (**30**)	2.017(6)		[27]
$[Ru(C_5H_5)(CO)(PiPr_3)(C{=}CH{=}(Me)OC{=}CPh_2)][BF_4]$ (**31**)	2.010(6)		[27]
$[Ru(C_5Me_5)(\kappa^3\text{-}ADPP)\{{=}C(CH_2)_3O\}][PF_6]$ (**32**)	1.956(4)		[29]
$[Ru(Tp)(dippe)\{{=}C(OMe)CH_2CO_2Me\}][BPh_4]$ (**22**)	1.86(2)	1.43(2)	[17]
$[Ru(Tp)(Cl)\{{=}CCH_2Ph(aapy)]$ (**23a**)	1.897 2)	1.387(3)	[18]
$[Ru(Tp)(Cl)\{\kappa^3\text{-}C(OCH_2CH{=}CH_2)(CH_2Hex)]$ (**24d**)	1.928(2)	1.329(3)	[19]
$[Ru(Tp)(Cl)\{\kappa^3\text{-}C(OCH_2CH{=}CH_2)(CH_2SiMe_3)]$ (**24e**)	1.918(7)	1.331(8)	[19]
$[Ru(Tp)(PCy_3)_2(H_2O)(=CHPh)][BF_4]$ (**42**)	1.878(4)		[35]
$[Ru(C_5H_5)\{{=}CH\text{-}\kappa^3\text{-}C(CH_2)_3CCHPMe_3\}][PF_6]$ (**38**)	1.897(2)		[32]
$[Ru(C_5H_5)\{{=}C(C_6H_5)\text{-}\kappa^3\text{-}CHCHC(C_6H_5)PMe_3\}][PF_6]$ (**40**)	1.934(3)		[33]
$[Ru(C_5H_5)\{{=}C(p\text{-}C_6H_4Br)\text{-}\kappa^3\text{-}CHCHC(pC_6H_4Br)P(OMe_3\}][PF_6]$	1.928(2)		[33]
$[Os(C_5Me_5)(dppm)(=CH_2)]$ (**48**)	1.926(9)		[41]

[a] Three independent molecules per unit cell.



Scheme 24. Conformers of complex **50**

eroatom-stabilised carbene complexes are typically in the range 1.83−1.97 Å. We can note that the Fe−C bond lengths are shorter in the case of chelated structures (Table 1, complexes **3a** and **4**). The $C_{carbene}-O$ bond length ranges from 1.30 to 1.36 Å. In the case of chelated complexes, the C−O bond lengths are shortened. Similarly, the C−N bond lengths of aminocarbene complexes of iron reflect the π-bonding between the amino substituent and the carbene carbon atom.

The chelate κ^2-(*C*,*Cl*) complex **3a** is characterised by an Fe−Cl bond length of 2.310(2) Å.[7a] The Fe−O bonds [2.045(5), 2.043(4), 2.043(4) Å, three independent molecules][7b] in κ^2-(*C*,*O*) complex **4** are similar to those found for other oxygen-containing iron complexes,[42] such as $[Fe(C_5Me_5)(dppe)(O{=}CMe_2)][OTf]$[42a] [2.031(4) Å] and $[Fe(C_5Me_4Et)(CO)_2(H_2O)][BF_4]$ [2.022(8), 2.043(9) Å, two independent molecules].[42c]

For ruthenium complexes, the bond lengths Ru−C(carbene) are typically in the range 1.90−1.97 Å. The $Ru-C_\alpha$ bond length in **22** is rather short,[17] compared with that of other (alkoxycarbene)Ru complexes, and found to be even shorter than that of the benzylidene complex **42**.[35] The longest bond length was found in the cyclic carbene complexes $[Ru(C_5H_5)(CO)(PiPr_3)\{{=}C^aCH{=}C(R)\text{-}OC^b(=CPh_2)(C^\alpha\text{-}C^b)\}][BF_4]$ (R = OEt, Me),[27] for which the Ru−C bond order is between that of a single and double bond. This suggests a significant contribution of the alkenyl resonance form.

X-ray diffraction studies and calculations on $[Ru(C_5H_5)(CO)(PiPr_3)\{C(CH{=}CPh_2){=}NEt_2\}][BF_4]$ (**29a**) show that the contribution of the carbene form is not relevant.[26] The $Ru-C_\alpha$ [2.063(6) Å] and the $C_\alpha-N$ [1.306(7) Å] bond lengths correspond rather to an Ru−C single bond and a C=N double bond, respectively. Complexes **29** can be considered as azoniabutadienyl rather than carbene complexes.

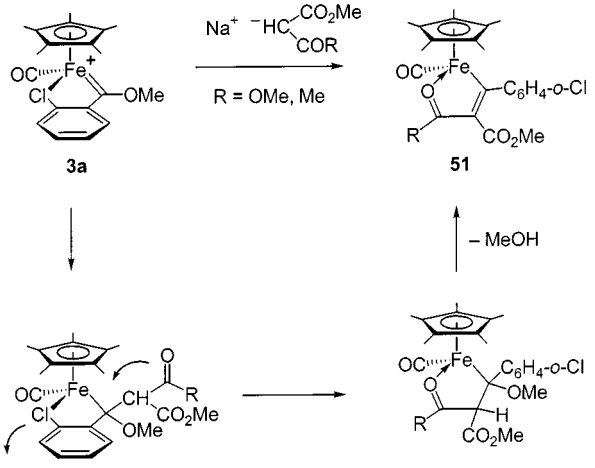
3. Reactivity of Carbene Complexes in Stoichiometric Reactions

3.1. Chelated Carbene Complexes: Bond-Activation and -Formation Reactions

Hemilabile ligands in carbene complexes may stabilize reactive intermediates or influence catalytic activity. For instance, the importance of chelated carbene complexes has been pointed out for diastereoselective cyclopropanation reactions of electronically neutral alkenes with chromium

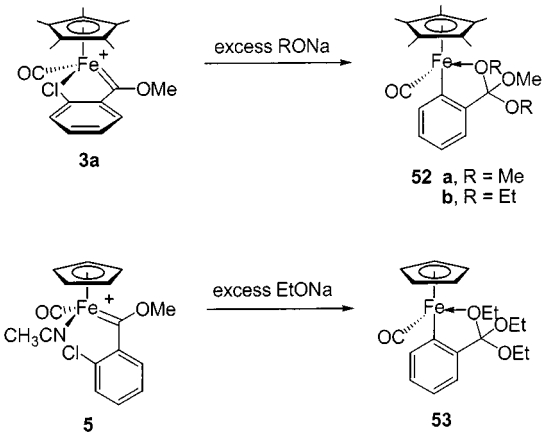
complexes.[43] The chelate isopropoxy derivative $[Ru(Cl)_2(PCy_3)(\kappa^2\text{-CH-}o\text{-}C_6H_4OiPr)]$ was found to be efficient in Ring Closing Metatheses (RCM) reactions for the formation of five- to eight-membered carbo- and heterocycles and it can be recovered through simple chromatography in high yield.[44] The importance of the chelated structure was also found for arylcarbene complexes **3a**,**b** which are involved in bond-activation and -formation reactions.

Nucleophilic attack of Lewis bases at the halocarbon atom gives rise to substitution reactions.[45] However, addition of stabilized carbanions $NaCH(CO_2Me)(COR)$ (R = OMe, Me) to **3a** affords oxametallacycles **51** (Scheme 25).[46] The substitution of the chlorine atom does not take place in these cases. The formation of **51** results from an α-attack by the nucleophile to give the C−C-bonded adduct, followed by displacement of the chlorine ligand by the coordinating carbonyl group to form a new five-membered ring. Eventually, spontaneous elimination of MeOH produces a more stable conjugated ring in the final product.



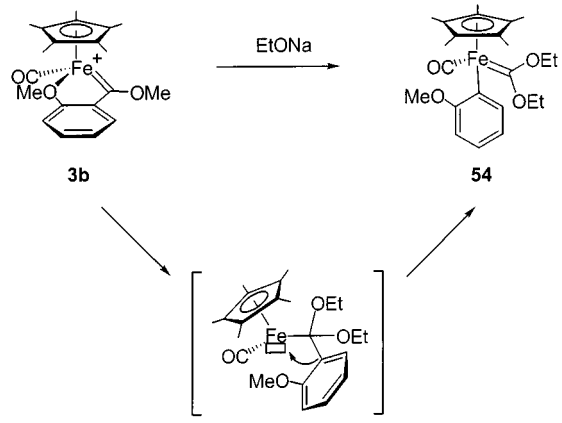
Scheme 25. Formation of oxametallacycles **51**

The chelated chloro derivative **3a** cleanly reacts with ethoxide or methoxide affording **52** which contains a chelated orthoester group (Scheme 26).[47] Similarly, complex **53** is formed upon treatment of **5** with EtONa (Scheme).[7b] The formation of **52**−**53** involves the cleavage of the Ar−Cl bond, which can be promoted by the coordination of the chlorine atom or the presence of a vacant coordination site. In contrast, the Ar−Cl bond cleavage does not occur for the dicarbonyl(carbene) complex **1a**. The reaction with RO^- affords the ketal derivatives $[Fe(C_5Me_5)(CO)_2\{C(OMe)(OR)(C_6H_4\text{-}o\text{-Cl}\}]$ by addition at the electrophilic carbene centre. Although the formation of an orthoester group from a carbene species has already been reported,[27] such a rearrangement process is without precedent.



Scheme 26. Activation of the Ar−Cl bond of (chloroaryl)carbene complexes

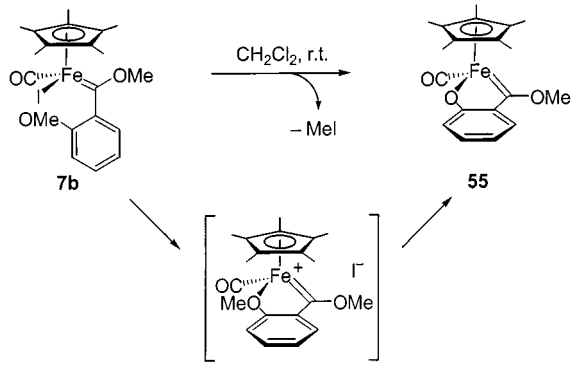
The related anisyl derivative $[Fe(C_5Me_5)(CO)\{\kappa^2\text{-C-}(OMe)C_6H_4\text{-}o\text{-}O^aMe\}(Fe-O^a)][OTf]$ (**3b**) affords the bis-(ethoxy)carbene complex **54** upon treatment with ethoxide (Scheme 27).[47] The Lewis base interaction in **3b** appears not to weaken the Ar−OMe bond to the same extent as the Ar−Cl bond in the chloroaryl derivative **3a**. Therefore, a different rearrangement process takes place. We assume that the formation of **54** results from an initial formation of the chelate ketal intermediate $[Fe(C_5Me_5)(CO)\{C(OMe)(OEt)\text{-}(C_6H_4\text{-}o\text{-}O^aMe)\}(Fe-O^a)]$ followed by deinsertion/migration of the anisyl substituent to the metal centre. This final step is promoted by the presence of a labile ligand. Such migrations of alkyl or aryl groups to give carbenes are rare,[48,49] and are relevant to C−C bond activation. The C−C bond formation corresponds to the insertion/migration of an alkyl or aryl group to a carbene ligand (Scheme 28).



Scheme 27. C−C bond cleavage of complex **3b**

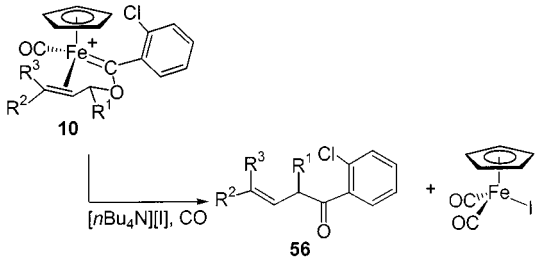
Scheme 28. Alkyl migration in carbene complexes

In this system, the Me−O bond is cleaved in the presence of halide anions.[7a] The (anisylcarbene)iodo complex **7b** spontaneously rearranges in dichloromethane or chloroform solution into the chelate aryloxy complex **55** along with the formation of methyl iodide (Scheme 29). We assume that the neutral iodo complex **7b** is in equilibrium with the cationic chelated form. The iodide counter-anion reacts as a demethylation reagent. The organometallic fragment plays the role of a Lewis acid to activate the C−O bond. Related sp^3-sp^3 C−O bond cleavage has previously been reported in the case of a palladium complex.[50]



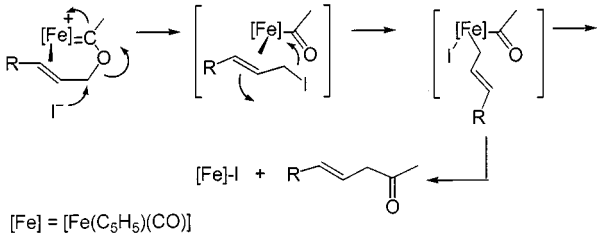
Scheme 29. Formation of the (aryloxy)carbene complex **55**

We found that chelate [(allyloxy)carbene]iron complexes **10** are involved in regioselective C−C bond-coupling reactions. Complex **10** reacts with [*n*Bu$_4$N][I] to give the corresponding β,γ-unsaturated ketones **56** (Scheme 30).[51] The organometallic fragment is recovered as the iodo derivative [Fe(C$_5$H$_5$)(CO)$_2$(I)] when the reaction is carried out under CO. Remarkably, no rearrangement of the initial allyl substituent is observed. Moreover, the C−C coupling is regioselective, since the carbon atom that is involved in the C−O bond cleavage recombines to form the new C−C bond.



Scheme 30. Formation of β,γ-unsaturated ketones **56** from (allyloxy)carbene complexes **10**

We propose that the formation of **56** results from an initial nucleophilic attack of the iodide, the rupture of the C−O bond thus leads to a coordinated η^2-(*C*,*C*)-allyl iodide. Oxidative addition of the latter and decoordination of the olefinic unit provide a transient Fe^{IV} species. Reductive elimination of the acyl and allyl ligands affords the observed ketone (Scheme 31).

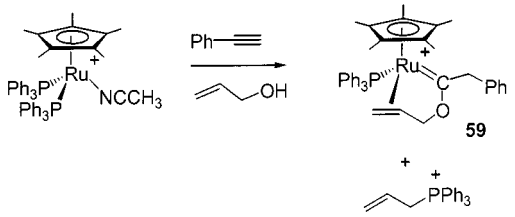


Scheme 31. Postulated mechanism for the formation of **56** showing the participation of the iodide anion

This study provides the direct evidence of the formation of unsaturated ketones from *chelate* (allyloxy)carbene complexes by an intramolecular regioselective C−C coupling reaction. Such (allyloxy)carbene complex intermediates have been postulated in the Ru-catalysed synthesis of β,γ-unsaturated ketones from terminal alkynes and allyl alcohols.[52,53]

The β,γ-unsaturated ketone complex [Ru(Tp)(Cl)(κ^3-C$_7$H$_{15}$C(O)CH$_2$CH=CH$_2$)] (**57**) as well as the free ketone 4-dodec-1-enone (**58**) are formed during the synthesis of the chelate carbene complex [Ru(Tp)(Cl){κ^3-C(OCH$_2$CH=CH$_2$)(C$_7$H$_{15}$)}] (**24d**).[19] Although this result is also in agreement with the proposed intermediary of chelate (allyloxy)carbene complexes, it is only observed for **58**, and the yields of **57** and **58** are low.

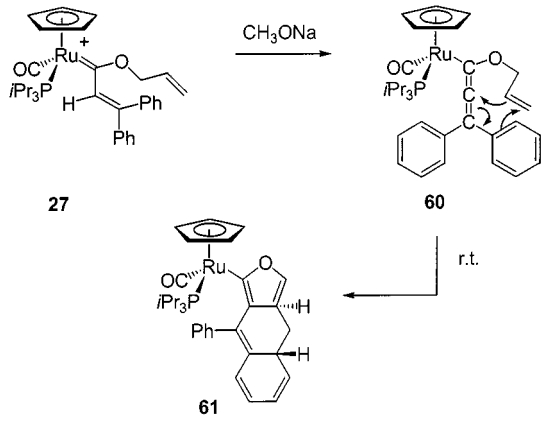
We attempted to synthesise the parent (carbene)(C$_5$Me$_5$)Ru complex **59** from the acetonitrile derivative [Ru(C$_5$Me$_5$)(PPh$_3$)$_2$(CH$_3$CN)][PF$_6$] in the presence of PhC≡CH and CH$_2$=CH−CH$_2$OH, but a mixture of the expected (allyloxy)carbene complex **59** [Ru(C$_5$Me$_5$)(PPh$_3$){(κ^3-*C*,*C*,*C*)-C(OCH$_2$CH=CH$_2$)CH$_2$Ph}][PF$_6$] and the allylphosphonium salt [CH$_2$=CH−CH$_2$PPh$_3$][PF$_6$] was obtained (Scheme 32).[54] The formation of the latter results from nucleophilic attack of free PPh$_3$ at the terminal carbon atom of the coordinated olefinic fragment, precluding the isolation of the pure carbene complex.



Scheme 32. Synthesis of the [(allyloxy)carbene]ruthenium complex **59**

When the allyloxy group is not coordinated to the metal fragment such as in **27**, it can be involved in an intramolecular reaction. The phenylallene fragment of the deprotonated complex [Ru(C$_5$H$_5$)(CO)(P*i*Pr$_3$){C(OCH$_2$CH=CH$_2$)=C=CPh$_2$}] (**60**) reacts with the free C=C double bond (Scheme 33).[25] In solution at room temperature, **60** isomerised into the tricyclic tetraenyl complex **61** by an intramolecular Diels−Alder reaction where the C$_\beta$−C$_\gamma$ double bond and one of the two phenyl groups of the al-

lenyl unit acts as an inner-outer sphere diene and the CH=CH_2 double bond of the alkoxy fragment act as a dienophile.

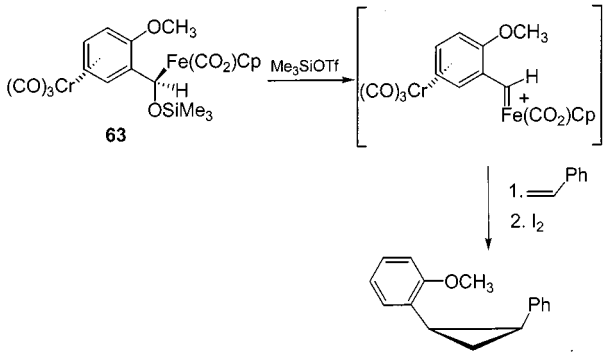


Scheme 33. Intramolecular Diels–Alder reaction involving a free allyloxy group

3.2. Transient Carbene Species: Cyclopropanation and Intramolecular C–H Bond-Insertion Reactions

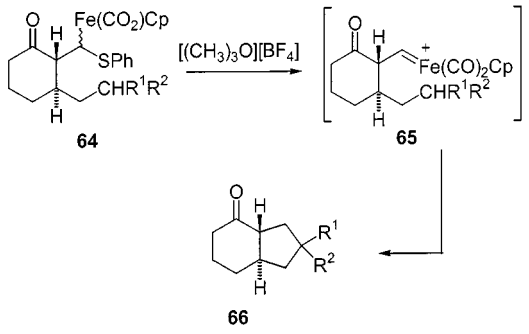
Non-heteroatom-stabilised carbene complexes of iron are good cyclopropanating agents of alkenes.[55,56] These transient species can be generated from (α-siloxyalkyl)iron derivatives [Fe(η^5-ligand)$(CO)_2${CH(OSiMe)R}] (η^5-ligand = C_5H_5, C_9H_7). They are readily accessible from saturated or unsaturated aldehydes RCHO (R = Ph, CH_3, *p*-C_6H_4OMe, *p*-C_6H_4Cl, *p*-C_6H_4Me, *p*-$C_6H_4CF_3$, *o*-C_6H_4OMe, CH=CMe_2) by addition to the iron metallate [Na][Fe(η^5-ligand)$(CO)_2$] and subsequent capture with $ClSiMe_3$.[57]

Asymmetric cyclopropanation reactions involving a chiral carbene ligand have been performed using the dimetallic Fe/Cr complex **63** (Scheme 34).[58] Reaction with styrene affords the corresponding cyclopropanes in a 10:1 *cis*/*trans* ratio. The origin of diastereoselectivity has been investigated. The Cr participation that stabilises the (carbene)iron was expected to induce a *trans* selectivity. However, when aromatic alkenes are used, a π-stacking effect leads to *cis* selectivity.[59]

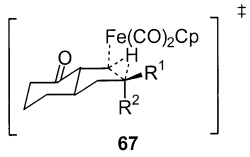


Scheme 34. Cyclopropanation of styrene by **63**

(Carbene)metal complexes are also known to insert into X–H bonds (X = Si, C). Examples of Si–H insertion reactions from alkylidene and benzylidene complexes [Fe(C_5H_5)(CO)(PR_3)(=CHR′)]$^+$ (R = Ph, Et) have been described.[60] With regards to the C–H bond, an intramolecular procedure from (carbene)iron complexes has been developed as a highly stereoselective route to cyclopentanes (Scheme 35).[61] The carbene complexes **65** are generated by *S*-methylation of thiophenyl derivatives **64** and loss of thioanisole. Intramolecular C–H insertion affords the fused cyclopentanes **66**. The main stereochemical features of the cyclisation have been investigated. In agreement with the observed diastereoselectivities, the reaction may proceed through a one-step, concerted insertion of a (carbene)iron complex into a properly situated C–H bond, namely via the chair-like cyclic transition state **67** (Scheme 36).



Scheme 35. Intramolecular C–H insertion reactions involving transient (carbene)iron complexes

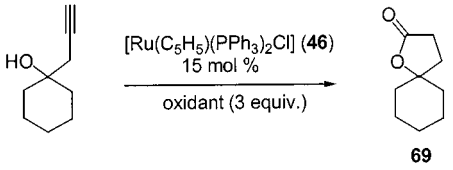


Scheme 36. Chair-like cyclic transition state

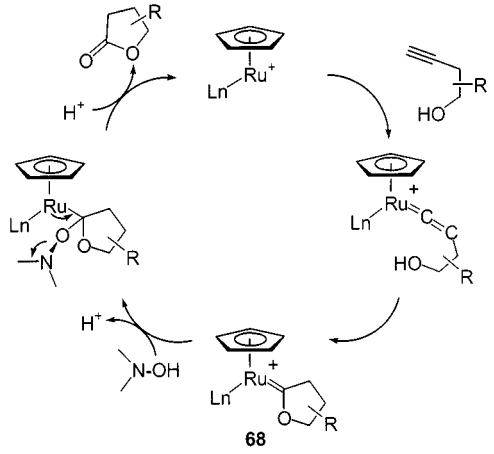
4. Carbene Complexes as Intermediates in Catalysis

4.1. Oxidative Cycloisomerisation of Homopropargyl Alcohols

Homopropargyl alcohols react with Ru complexes to form oxycarbene species via hydroxyvinylidenes.[28] This approach was used to convert homopropargyl alcohols into γ-butyrolactones through a mild oxidative cycloisomerisation process catalysed by **46** (Scheme 37).[62] *N*-Hydroxyimides are used as oxidants which do not affect the catalytic activity. The proposed mechanism involves initial formation of the (oxycarbene)metal intermediate **68** followed by nucleophilic attack of *N*-hydroxyimide (Scheme 38). Eventually, the lactone **69** is released along with the imide.



Scheme 37. Ru-catalysed synthesis of γ-butyrolactones **69**

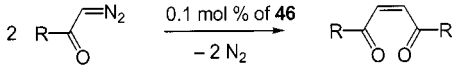


Scheme 38. Proposed catalytic cycle for oxidative cycloisomerisation of homopropargyl alcohols

4.2. Reactions Involving Diazo Compounds

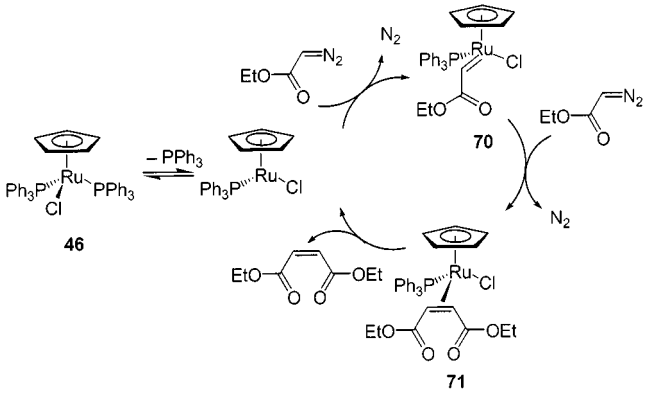
It is generally agreed that carbene species are key intermediates in transition-metal-catalysed C−C bond-forming reactions involving diazo compounds. However, the catalytically active (carbene)Ru species have rarely been isolated or detected during these processes.[3,63] Complex **46** was found to be a catalyst for carbene−carbene coupling, insertion reactions into X−H bonds (X = N, S), cyclopropanation of olefins, and carbene transfer reactions. The formation of neutral carbene intermediates from the 16-electron species $[Ru(C_5H_5)(PR_3)(Cl)]$ is a key step in all these catalytic reactions involving diazo compounds and **46** as a catalyst.

Stereoselective decomposition of α-diazo carbonyl compounds N_2CHCOR [R= Me, *n*Pr, *i*Pr, $(CH_2)_{10}CH_3$] catalysed by **46** affords the corresponding ene-diones RCOCH=CHCOR, the *cis* isomers being formed in 95−97% yield (Scheme 39).[64]

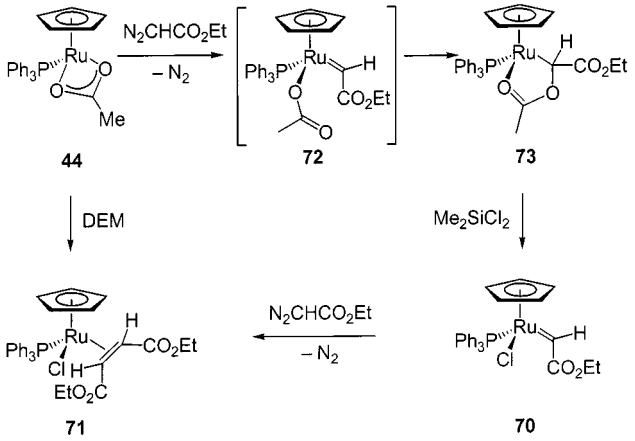


Scheme 39. Formation of *cis*-enediones from α-diazo carbonyl compounds

Under the same conditions, ethyl diazoacetate (EDA) is converted into diethyl maleate (DEM). The observed stereoselectivity (95−99%) may be due to steric factors. A detailed study suggests that the less crowded (*cis*-π-olefin)metal intermediate **71** is formed (Scheme 40). The proposed mechanism involves the carbene complex $[Ru(C_5H_5)(PR_3)(Cl)\{=CHCO_2Et\}]$ (**70**) (Scheme 39). The latter would be formed by dissociation of a PPh_3 ligand from **46**, a key step of the catalytic process. The highly reactive species **70** was spectroscopically not detected in the reaction mixture but has been independently prepared from the Ru acetate precursor **44** and characterised in solution (Scheme 41). Addition of equimolar amounts of EDA to **44** gives the metallacycle derivative **73**. Its formation arises from nucleophilic addition of the κ^1-acetate group at the electrophilic carbene carbon atom. Complex **73** is then converted at −40 °C to the expected carbene derivative **70** by displacement of the acetato group using Me_2SiCl_2. Finally, the DEM complex **71** is formed upon addition of another equivalent of EDA. The reactions have been monitored by NMR spectroscopy allowing all of the intermediates to be characterised.



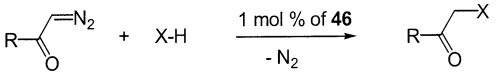
Scheme 40. Proposed mechanism for EDA dimerisation



Scheme 41. Independent synthesis of the carbene intermediate **70** and the DEM complex **71**

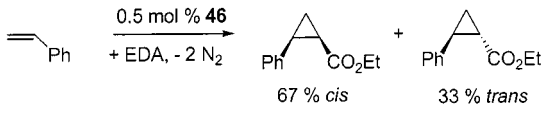
Complex **46** also catalyses chemoselective insertion reactions of α-diazo carbonyl compounds $N_2CHC(O)R$ [R = CH_3, *n*Pr, *i*Pr, $(CH_2)_{10}CH_3$, $(CH_2)_{14}CH_3$, Ph] into N−H and S−H bonds.[65] This procedure affords α-oxo amines and α-oxo thioethers in very good yields (Scheme 42). As proposed for the synthesis of *cis*-enediones, a (carbene)ruthenium complex $[Ru(C_5H_5)(PR_3)(Cl)\{=CHC(O)R\}]$ is in-

volved in the catalytic process. Nucleophilic attack by amine or thiol (X−H) gives the product $RC(O)CH_2X$.

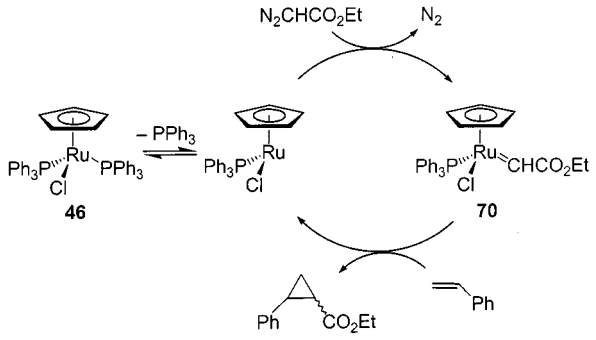


Scheme 42. Insertion reactions of diazo carbonyl compounds into X−H (X = N, S) bonds catalysed by **46**

Selective catalytic carbene transfer reactions from diazo compounds to terminal alkenes have been reported. Complex **46** is an efficient catalyst for cyclopropanation of styrene with EDA (Scheme 43).[38] The catalytic activity of Ru derivatives of general formula $[Ru(\eta^5\text{-ligand})(PR_3)_2(X)]$ have also been investigated. The reaction is performed in pure alkene solvent, in order to avoid dimerisation of EDA. The cyclopropane products are readily obtained in high yields and with significant *cis* stereoselectivity. For instance, in the case of **46**, optimum conditions gave rise to a 95% yield of ethyl 2-phenylcyclopropanecarboxylate with a stereoselectivity of 67% *cis* versus 33% *trans*. As above, the reaction is likely to proceed via the carbene derivative **70** that would account for the observed stereoselectivity (Scheme 44). However, no spectroscopic evidence for the formation of this intermediate in the reaction mixture was obtained.

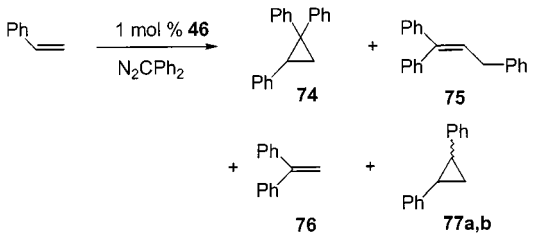


Scheme 43. Ru-catalysed cyclopropanation of styrene with EDA



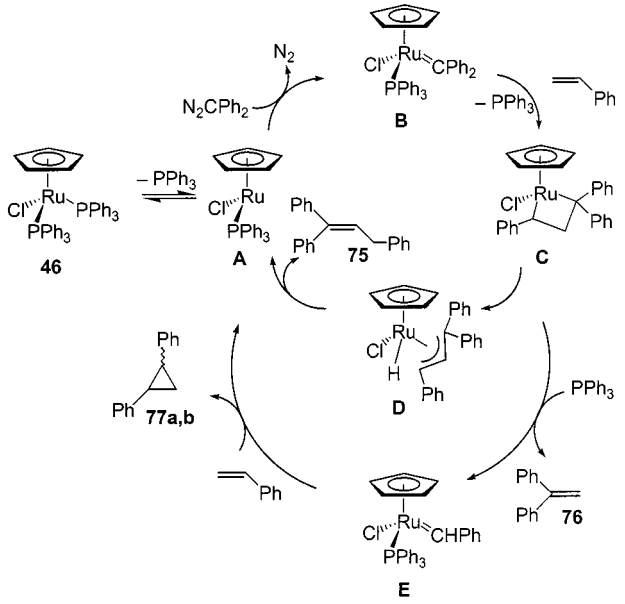
Scheme 44. Proposed mechanism of cyclopropanation of styrene with EDA catalysed by **46**

When diphenyldiazomethane is used, an unusual C−C coupling reaction takes place (Scheme 45).[38] The reaction with styrene in the presence of **46** (1 mol %), affords mainly 1,1,3-triphenylpropene (**75**) (58%), together with a 1:1 mixture of 1,1-diphenylethene (**76**) (17%), and 1,2-diphenylcyclopropanes **77a**,**b** (16%). Only 9% of the expected cyclopropyl derivative **74** is present, the product is actually formed in a thermal side reaction from styrene and diphenyldiazomethane without involvement of **46**. The carbene intermediate **45a** has been spectroscopically identified during catalysis. In a stoichiometric reaction, complex **45a** can transfer its carbene ligand to styrene to give the compounds **75**, **76**, and **77**, formed with a distribution comparable to that of the catalytic reaction.



Scheme 45. Ru-catalysed C−C bond-forming reactions from styrene and diphenyldiazomethane

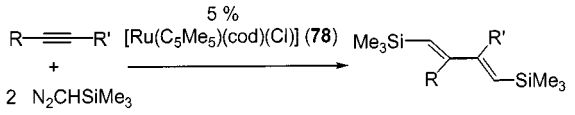
On the basis of the mechanism suggested for (sulfonato)rhodium complexes,[66] the formation of compound **75** results from a formal $:CPh_2$ and $:CHCH_2Ph$ coupling (Scheme 46). In the first stage, the carbene derivative **B** is generated from **A**. Coordination of styrene and coupling with the carbene ligand affords a metallacyclobutane intermediate **C**. Then, **C** rearranges into the π-allyl complex **D** by a β-H elimination. Reductive elimination affords the observed propene derivative **75**. Note that the metallacycle **C** is postulated in olefin metathesis reactions and can account for the formation, in a side reaction, of 1,1-diphenylethene (**76**). Thus, this second competitive reaction would lead to the formation of a benzylidene complex **E**. Carbene transfer to styrene provides the cyclopropanes **77** and regenerates **A**.



Scheme 46. Proposed mechanism for the formation of **75**, **76**, and **77**

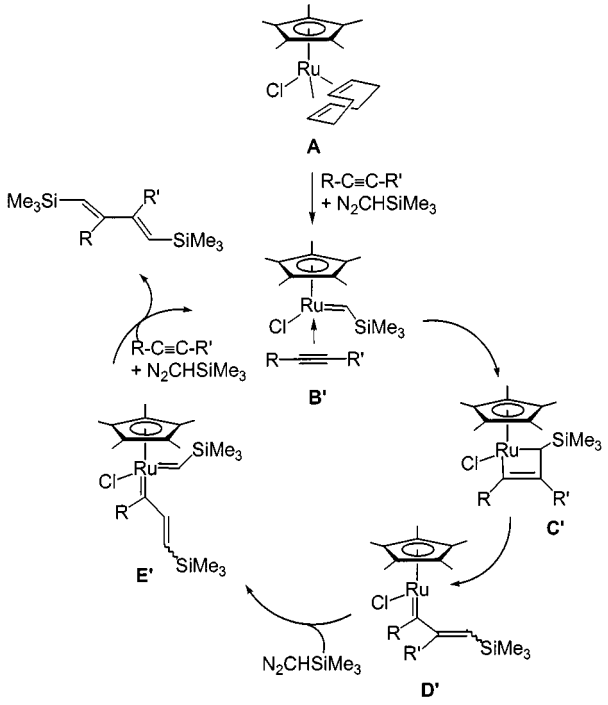
The above results suggest that complex **46** and related complexes constitute a promising class of catalysts for chemo-, regio-, and stereoselective processes involving diazo compounds. A wide range of synthetically useful trans-

formations have been developed. In another example, the ruthenium-catalysed addition of diazo compounds to alkynes has been reported.[67] This double addition is catalysed by [Ru(C_5Me_5)(cod)(Cl)] (**78**) allowing, for example, the access to 1,4-bis(trimethylsilyl)buta-1,3-dienes, by combination of two molecules of trimethylsilyldiazomethane and one of alkyne (Scheme 47).



Scheme 47. Synthesis of 1,4-bis(trimethylsilyl)butadiene catalysed by **78**

A plausible mechanism for this selective process has been proposed (Scheme 48). Displacement of the cod ligand by one molecule of alkyne and trimethyldiazomethane to the ruthenium centre provides the (carbene)ruthenium intermediate **B′**. The intramolecular C−C coupling leads to **C′** which then rearranges into the unsaturated vinylcarbene derivative **D′**. Addition of a second molecule of diazomethane leads to the bis(carbene) **E′**. Finally, coupling of the two carbene ligands affords the observed diene. This reaction constitutes an unusual 2:1 coupling between diazoalkanes and a wide range of alkynes, demonstrating that it is possible to selectively create two C=C double bonds.



Scheme 48. Proposed mechanism for the catalytic formation of functional conjugated dienes

5. Concluding Remarks

The importance of the carbene complexes is reflected by their widespread use in synthesis. In stoichiometric reactions, electrophilic iron complexes are involved in diastereoselective syntheses of fused cyclopentanes. The development of enantioselective methodologies is an important challenge in organic synthesis. In catalysis, most of the (carbene)ruthenium complexes are generated from diazo compounds. An alternative pathway is via vinylidene complexes. The intermediary of allenylidene complexes is still rare. Condensation of the Ru=C double bond with unsaturated substrates appears to be a promising new field. The search for new catalysts is highly desirable, and then carbene complexes could become standard tools in synthesis provided that these species are readily accessible and easily handled.

Acknowledgments

I would like to thank my co-workers who have contributed to this project. Their names are mentioned in the references. I am indebted to the CNRS and the University of Rennes 1 for generous support of this work.

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