The Chemistry of Metallacyclic Alkenylcarbene Complexes, 4[◇]

Unsaturated Metallacyclic Carbene Complexes as Flexible Tools in Organic Synthesis. Novel Rearrangement and Cascade Pathways to Functionalized Alkadienes, Carbo-, and Heterocycles

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Cationic metallacyclic carbene complexes of iron and cobalt bearing a terminal η^3-allyl ligand are susceptible to nucleophilic attack at different sites depending on the particular set of substituents, the central metal fragment, and the nucleophile. Attack of enolates, cuprates, acetylides, or heteroatom nucleophiles like phosphanes at the metallacyclic perimeter of the iron complexes **18** provides an easy access to unsaturated organic products like 1,2- or 1,3-dienes, δ-lactones, and functionalized cyclopentenones through novel rearrangement or cascade pathways. Synthetic applications are described; factors governing reactivity/selectivity are discussed; X-ray analytical structures of novel metallacycles are provided.

The usefulness of "Fischer-type" transition metal carbene complexes[1] for organic synthesis has been amply demonstrated over the last decades. They opened up novel reaction pathways that have been exploited in a host of shortcut procedures for the controlled and very often regio-/stereoselective formation of C−C and C−heteroatom bonds. Excellent reviews and papers have been published covering both their thermal[2] and photochemical[3] reactions with an impressive array of various organic functional groups. Of particular interest to synthetic application as well as to mechanistic studies are unsaturated carbene complexes. Derivatives of type **1** featuring an η^2-coordinated olefin ligand are supposed to be − together with the corresponding metallacyclobutanes **2** − pivotal intermediates in the cyclopropanation[4,5], metathesis[6], and the Ziegler-Natta polymerization[7] of alkenes (Scheme 1). Isolation of stable examples of **1** was achieved for group V[8a], VI[8b], and VIII[8c] central metals. In α,β-unsaturated carbene complexes **3**[9] the adjoining functional groups "carbene" and "olefin/acetylene" mutually influence each others reactivity, or by combined participation they can even give rise to entirely novel reactions (Scheme 2).

For instance, the metal carbene functionality in **3** was shown to enhance the susceptibility of the C=C bond towards "Michael-type" additions of nucleophiles[10] or cycloadditions of alkenes or alkadienes[11]. With substituted alkynes, compounds **3** can undergo different types of multistep annulation processes either with or without concomitant incorporation of carbon monoxide. Typical products of

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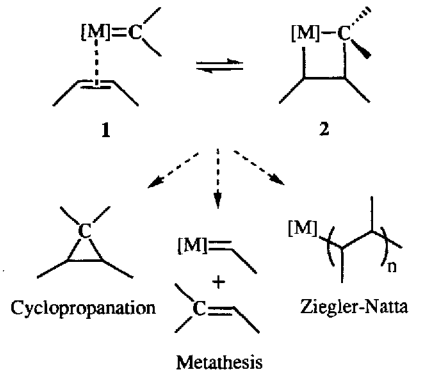
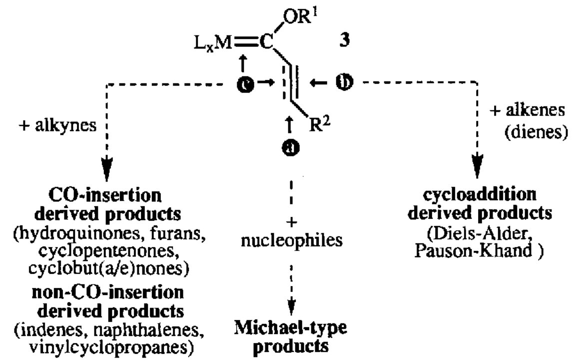
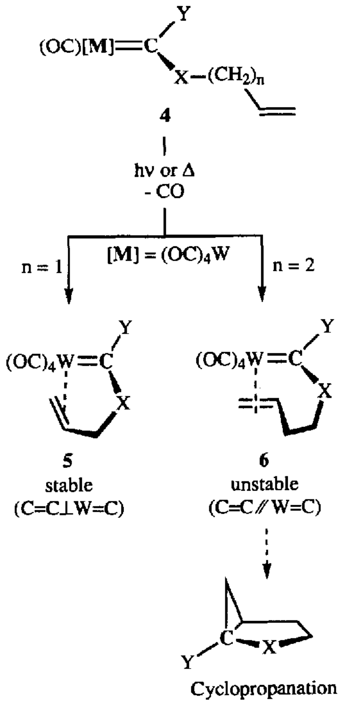
Scheme 1



Scheme 2



Scheme 3



the first pathway are hydroquinones (the Dötz reaction)[12], furans[13], cyclopentenones[14], and cyclobutenones[13a]. Without insertion of carbon monoxide, indenes[13a,15,16], cyclopentadienes[17], or vinylcyclopropanes[18] may result. Several mechanistic proposals[15,19–21] were put forward to account for the observed influence of crucial parameters like solvent, stoichiometry, central metal fragment, and substituents at the carbene carbon atom or at the vinyl residue on the formation of each of these products through different reaction channels. "Fischer-type" carbene complexes **4**, which contain an olefin function that is farther away from the carbene carbon than the olefin function in **3** have been thoroughly investigated as well (Scheme 3).

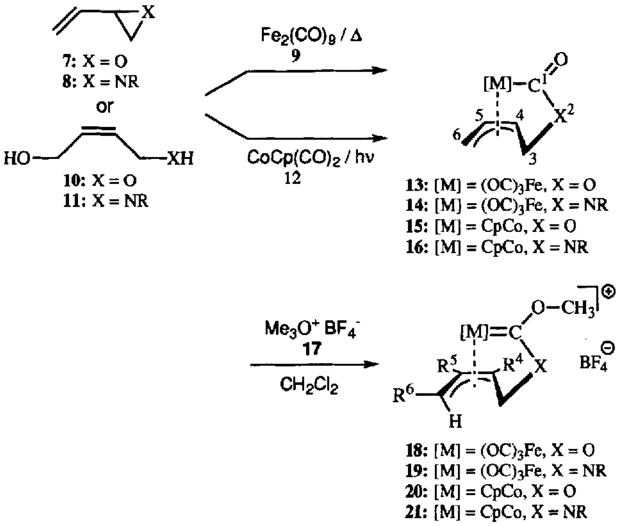
When the "tether" [i.e. the spacer$-X-(CH_2)_n-$ between the carbene carbon and the olefin] is of an appropriate length, η^2-coordination of the alkene with loss of a ligand such as CO may occur upon heating or irradiating. Sometimes this event can cause an acceleration of "normal" *inter*molecular carbene reactions that depend heavily on such an initial CO loss, for example the Dötz synthesis[11b,21]. More interesting though is the formation of isolable metallacyclic olefin-carbene complexes like **5** and **6**[22–24], which have shown to be excellent model systems for studying *intra*molecular variants of metathesis, cyclopropanation, or annulation reactions such as the ones mentioned above. As a general rule, the reactivity/stability of such complexes chiefly depends on the ring size (the "tether" length), which in turn governs the ring geometry and thus the spatial arrangement of the [M]=C and the C=C bonds relative to each other. Apparently, chelate systems, such as **5** with two atoms (irregardless of their identity as carbon- or heteroatoms) that join the carbene and alkene ligands are particularly stable having both functional groups oriented in an unfavourable "perpendicular" arrangement[25]. When the ring size is increased by one atom as in **6**, the [M]=C carbene and C=C olefin units can easily adopt a parallel alignment, which is appropriate for intermediate metallacyclobutane formation. Whether cyclopropanation (as with **6**) or metathesis occurs is determined by the nature of the central metal fragment, the carbene substituents, and the solvent.

Objective and Outset

Our intention was to introduce more flexibility into the use of unsaturated metallacyclic carbene complexes to provide a contrast to the rigid "either-or" behaviour of olefin-carbene systems that, for example, **5** or **6** offer. We looked for stable unsaturated complexes with variable (or even controllable) "tether" length/ring geometry and thus with variable reactivity. Complexes with an *allyl* instead of the *olefin* terminus in the metallacycle should allow such reactivity changes; nucleophilic attack at an η^3-ligand would lead to an olefin-terminated ring with the new π-donor ligand in a shifted location.

We started from metallacyclic ferralactones **13** or -lactams **14**, which have been investigated by Murdoch[26], Heck[27], Aumann[28], and Ley[29], and prepared the cationic carbene complexes **18** and **19** as air-stable crystalline compounds by alkylation of **13** and **14** with $(CH_3)_3O^+BF_4^-$ **17**[30]. 10 g batches (>80% yield) are obtainable from reactions of vinyloxiranes **7**, vinylaziridines **8**, substituted butene-1,4-diols **10**, or 4-hydroxyallylamines **11** with diironenneacarbonyl **9** under various conditions[28,29]. Analogous cobalt metallacycles **20**, **21** are likewise accessible[31] by irradiating mixtures of **7** or **8**, respectively and cyclopentadienyldicarbonyl cobalt **12** in THF with subsequent alkylation of the acyl complexes **15** or **16** (Scheme 4).

Scheme 4

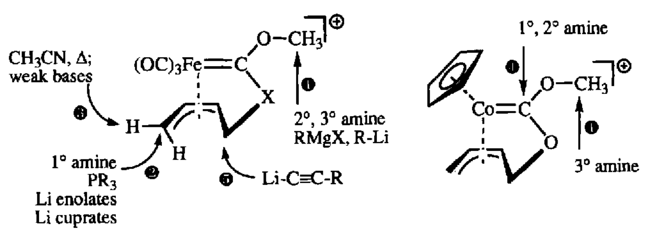


Most derivatives of **18**, **19**, **20**, and **21** can be easily purified by column chromatography (silica; $MeCN/CH_2Cl_2$ 1:1) and stored for months. These general procedures are quite flexible. In addition to swapping the central metal fragment and the endocyclic carbene substituent X, the introduction of various substituents (R^{2-6}) at the metallacyclic perimeter is a way of "fine-tuning" the reactivity and selectivity of these complexes towards different nucleophiles.

Modes of Reaction with Nucleophiles: An Overview

Cationic metallacyclic (ω-alkenyl)carbene complexes such as **18**, **19**, **20**, and **21** should in principle be susceptible to nucleophilic or basic attack at five different sites: the methyl group of the alkoxy substituent (path 1)[32], the terminus C-6 of the allyl ligand (path 2), the protons at C-6 (path 3), the carbene carbon C-1 (path 4), and the homoallylic carbon atom C-3 (path 5). We have observed each of these conceivable reaction pathways with different nucleophiles, although there are remarkable differences between the iron and the cobalt complexes both in terms of overall reactivity and of the sites preferred by a particular nucleophile (Scheme 5).

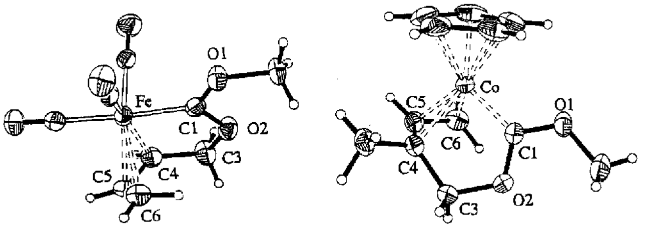
Scheme 5



The iron complexes **18** and **19** are distinctly more reactive than **20** and **21** and show a broader range of possible reactions with bases and nucleophiles; this higher reactivity renders minor structural alterations (for instance in the nature of X or the residues R^{2-6}) more effective and influential. Although path 1 reactions, which involve methyl transfer to the base or nucleophile with reformation of the starting lactones **13**, **15** or lactams **14**, **16**, are of little synthetical use, the ease and readiness with which even sterically hindered tertiary amines like diisopropylethylamine get methylated is worth mentioning. While the cobalt carbene complexes **20** and **21** methylate only tertiary amines, the corresponding iron analogues transfer their methyl group to secondary amines, and Grignard, and alkyllithium compounds as well. According to plan lithium enolates, lithium cuprates (as carbon nucleophiles) and heteroatom nucleophiles, such as phosphanes or primary amines, attack the iron complexes **18** and **19** at the allyl terminus C-6 (path 2 reaction). However, the cobalt counterparts are inert to all carbon nucleophiles and phosphanes but undergo aminolysis at the carbene carbon (path 4 reaction) with primary amines, which is typical of "Fischer-type" systems. The iron complexes **18** and **19** on the other hand are totally lacking any comparable carbene activity. By path 3 weak bases or even donor solvents like acetonitrile, at elevated temperature, can abstract a proton from the terminal position C-6 (path 3 reaction), which leads to highly reactive neutral intermediates. With lithium acetylides the iron complexes **18** give rise to the formation of substituted cyclopentenones; this reaction probably commences by nucleophilic attack at the homoallylic carbon atom C-3 (path 5 reaction).

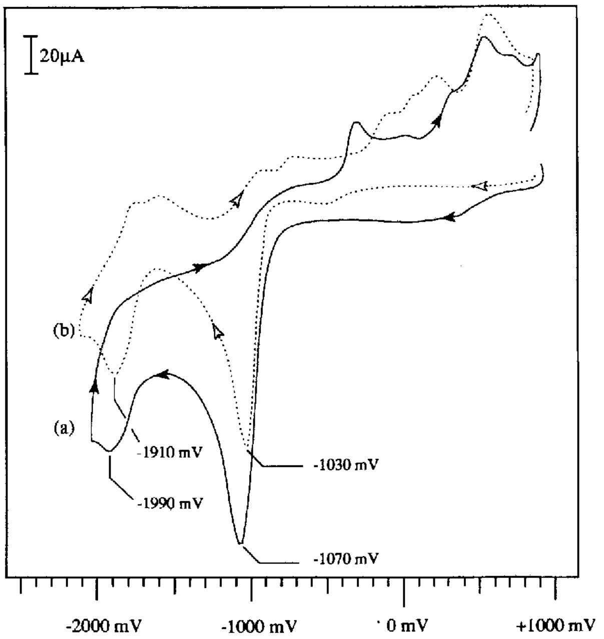
In summary, the iron complexes show a more varied reactivity pattern towards nucleophiles and bases with an emphasis on reactions at the metallacyclic perimeter, whereas the cobalt analogues are significantly less reactive with a preference for attack at the carbene carbon atom. How may this phenomena be explained? As both types of complexes possess quite similar structural features, sterical factors are not likely significant. Figure 1 depicts molecular structures as obtained from X-ray analyses of the cations of the iron complex **18a** (R^{3-6} = H) and the cobalt complex **20b** ($R^{3,5,6}$ = H, R^4 = Me). Most of the relevant bond distances and angles match each other well. Comparable bond lengths, for instance, differ by less than 0.1 Å. In both cases the allylic moieties are *syn*-configurated and have similar angles C4–C5–C6 [**18a** 122.0°, **20b** 119.3°]; they occupy positions at identical distances from their respective metal centers. As only complexes with an *E*-configurated C1–O1 bond are formed, all relevant sites (methoxy residue, C-1, and C-6) appear to be sterically accessible to nucleophiles with equal ease in both bases. Furthermore, the electron transfer behaviour of **18a** and **20b** as inferred from cyclic voltammetry (Figure 2) provides no explanation for their different reactivities. In the cathodic direction, both compounds give rise to two irreversible reductive waves at very similar peak potentials (−1070 mV and −1990 mV for **18a**; −1030 mV and −1910 mV for **20b**) without any noticeable influence by the central metal[31].

Figure 1. Molecular structures of the cations of **18a** (R^{3-6} = H; left) and **20b** ($R^{3,5,6}$ = H, R^4 = CH_3; right)[a]



[a] Selected bond lengths [Å] and angles [°]: **18a**: Fe−C1 1.921, Fe−C4 2.119, Fe−C5 2.081, Fe−C6 2.170, C1−O1 1.294, C1−O2 1.293, C3−O2 1.473, C3−C4 1.499, C4−C5 1.424, C5−C6 1.408, O1−C1−O2 114.4, C4−C5−C6 122.0; **20b**: Co−C1 1.853, Co−C4 2.070, Co−C5 1.993, Co−C6 2.091, C1−O1 1.300, C1−O2 1.312, C3−O2 1.445, C3−C4 1.526, C4−C5 1.427, C5−C6 1.415, O1−C1−O2 112.8, C4−C5−C6 119.3.

Figure 2. Cyclic voltammograms of **18a** (a) and **20b** (b)[a]



[a] As 10^{-3} M solutions in acetonitrile with 0.1 M NBu_4BF_4; scan cycle +950 mV → −2100 mV → +950 mV at a rate of 200 mVs^{-1}; working electrode: carbon disk, counter electrode: platinum wire, reference electrode: tungsten wire; ferrocene as internal standard.

Semiempirical calculations, starting from the X-ray analytical geometries can provide a suitable explanation for the observed differences in reactivity. We employed various computational programs and methods. Although furnishing slightly different values for charge densities and orbital coefficients for given atoms, AMPAC5.0 (SAM1)[33], SINDO1 (ROHF),[31,34], and ZINDO (UHF)[35] agree on the following trend: there are no significant orbital coefficients at the carbene carbon C-1 in the LUMO of either complex, but unlike **20b**, complex **18a** has relatively large coefficients at the allylic terminus C-6. As to the calculated charge densities, quite the reverse picture emerges: the entire organic ligand (carbene-allyl) bears only a small positive charge in **18a**, whereas in **20b** the carbene carbon especially bears a distinct positive partial charge. Therefore, iron metallacycles **18** should be prone to orbital-controlled reactions at the allylic end C-6, especially with "soft" or neutral nucleophiles; cobalt complexes **20** should be amenable only to charge controlled attack of "hard" nucleophiles at the carbene carbon C-1. This corresponds fairly well with the observed reactivity.

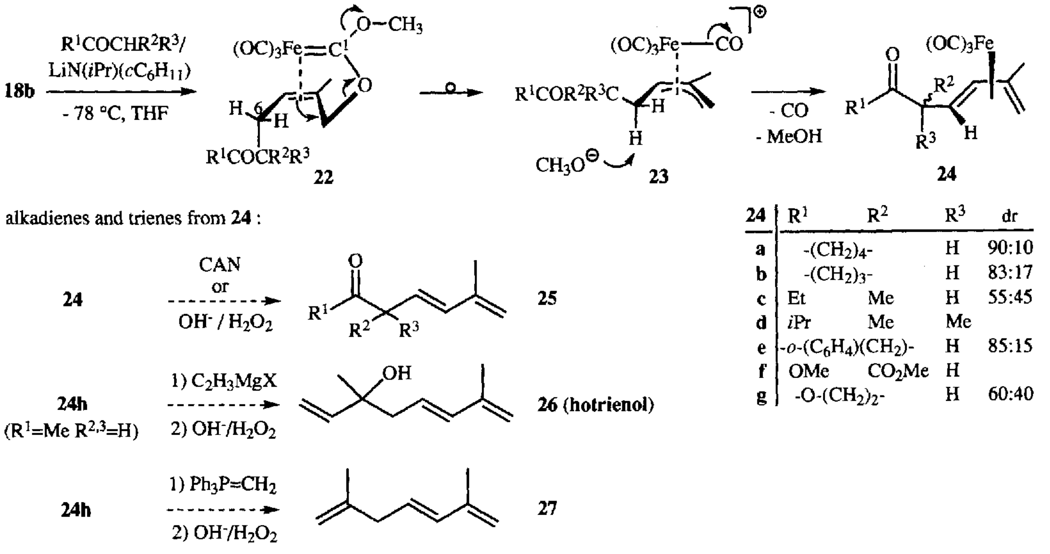
Applications of Path 2 Reactions: Syntheses of Functionalized Dienes and Trienes

The ironcarbene complexes **18** readily react with lithium enolates of ketones or esters in THF at −78 °C to give the corresponding 4-substituted (3*E*)-1,3-diene complexes **24** in 70−80% yield without other isomers. As depicted in Scheme 6 the reaction is likely to start with an attack of the enolate at the C-6 terminus of **18** to give a neutral, fairly unstable (η^2-alkene) ironcarbene complex **22**.

Due to its geometrical and electronic properties, **22** does not undergo cyclopropanation but − as a formal ferravinyl allyl ether − an intramolecular "Claisen-type" rearrangement to the cationic allyltetracarbonyliron compound **23**. Deprotonation by the methoxide anion from the opposite side of the central metal atom, loss of carbon monoxide, and recomplexation yields the η^4-(3*E*)-1,3-diene complex **24**. Because the starting metallacycles **18** are chiral, products **24** derived from (pro)chiral enolates are formed as mixtures of diastereoisomers in a ratio that depends chiefly on the bulkiness of the nucleophile. Ratios of up to 90:10, in the case of the enolates derived from indanone or cyclohexanone, reveal a distinct inductive ability of the chiral metallacyclic plane in **18**[36]. The corresponding (3*E*)-6-oxo-1,3-dienes **25** can be easily obtained by demetalation either with CAN or with H_2O_2/KOH. Making use of the protective properties of the tricarbonyliron fragment, the carbonyl group in **24** can be further modified under basic conditions prior to decomplexation[37]. For instance, hotrienol **26**, an (3*E*)-1,3,7-triene-6-ol, which occurs naturally in the leaf oil of the japanese *Ho* tree[38], can be prepared from 1-methyl-1-vinyl oxirane **7b** in 5 steps in 45% overall yield by reaction of the diene complex **24h** (R^1 = Me, $R^{2,3}$ = H) with vinylmagnesiumchloride and subsequent demetalation. Alternatively, the keto function in **24** can be transformed with phosphorous ylides to give (3*E*)-1,3,6-trienes such as **27** with a tris(unsaturated) backbone, which is possessed by a number of natural terpenes. (Acetone does not give stable lithium enolates, therefore the corresponding potassium enoxyborates, $K^+[R_3BOCR^1{=}CR^2H]^-$, should be used instead to prepare diene complexes like **24h**).

Diene complexes bearing a saturated side chain in the 4-position or an additional olefin function in conjugation with the 1,3-dienyl system are accessible by reaction of the metallacycles **18** with the respective lithium organocuprate. This reaction proceeds presumably by the same general

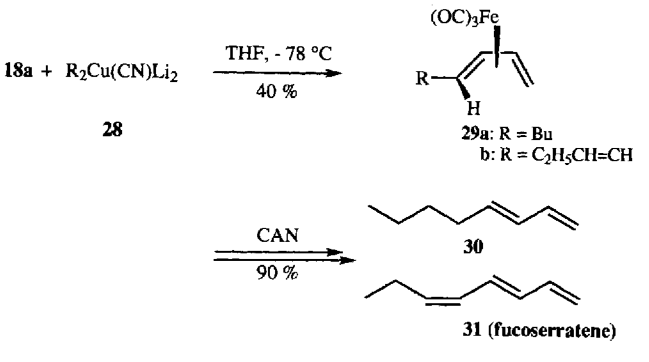
Scheme 6



24	R¹	R²	R³	dr
a	-(CH₂)₄-		H	90:10
b	-(CH₂)₃-		H	83:17
c	Et	Me	H	55:45
d	iPr	Me	Me	
e	-o-(C₆H₄)(CH₂)-		H	85:15
f	OMe	CO₂Me	H	
g	-O-(CH₂)₂-		H	60:40

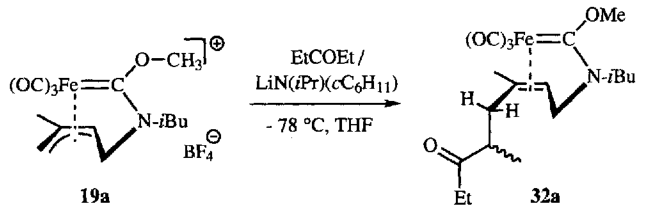
mechanistic pathway outlined for the enolates[36]. Fucoserratene **31**, a natural pheromone component of the alga *fucus serratus*[37,39], can be prepared from the iron complex **18a** and *Z*-butenyl cuprate **28b** in ca. 40% yield (Scheme 7).

Scheme 7



Interestingly, the aminooxocarbene complexes **19** do react with lithium enolates also. But here the resulting neutral (η^2-alkene)carbene complexes **32** are sufficiently stable to be isolated and characterized for two reasons. First, any rearrangement resembling **22** → **23** would create an isonitrile ligand at a zero-valent transition metal centre, which is less favourable. As an X-ray structural analysis of **32a** (Figure 3) reveals, it is unlikely that a subsequent cyclopropanation will occur either: the alkene ligand is oriented skew to the Fe=C bond. To our knowledge this is the first example of a neutral metallacyclic (η^2-alkene)carbene complex with $Fe(CO)_3$ as the central metal fragment.

Scheme 8



The isolation of complexes **32** strongly supports the general mechanism of path 2 outlined above. Heteroatom nucleophiles like phosphanes appear to react in a similar way giving rise to the formation of stable (3*E*)-4-phosphonio-1,3-diene tricarbonyliron complexes **34**. These can be deprotonated at −78 °C with strong bases like sodium hexamethyldisilylamide (NaHMDS) at the 4-position to give the corresponding highly reactive cumulated ylides **35** as deep red solutions in THF. Although not isolable, **35** undergo Wittig olefination reactions with aldehydes furnishing – after demetalation with CAN – vinylallenes (i.e. 1,2,4-trienes) **36** in moderate to good yields. The whole sequence can be conveniently performed in "one pot" as is depicted in scheme 9 for the synthesis of the pheromone **36a** of the beetle *Acanthoscelides obtectus* from the glycidic ester **33** (available itself by Darzens condensation of methylbromoacetate and acroleine) in 45% overall yield.

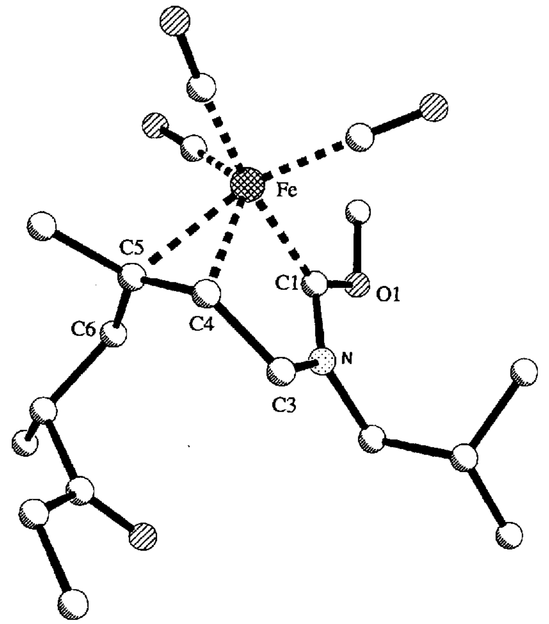
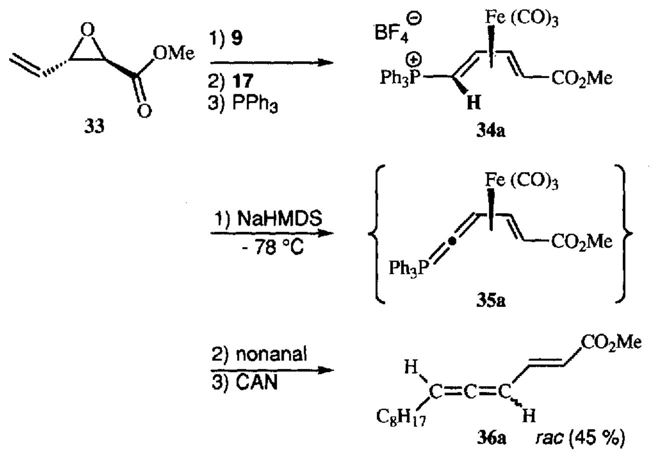


Figure 3. Molecular structure of **32a**[a]

[a] Selected bond lengths [Å] and angles [°]: Fe–C1 1.964, Fe–C4 2.083, Fe–C5 2.158, C1–O1 1.338, C1–N 1.305, C3–N 1.441, C3–C4 1.520, C4–C5 1.407, C3–C4–C5 125.4, C4–C5–C6 125.1, C1–Fe–C4 80.4, C4–Fe–C5 67.8, C1–Fe–C5 89.9.

Scheme 9



Applications of Path 3 Reactions: Syntheses of 2*H*-Pyrans and δ-Lactones by Intramolecular Carbene Transfer

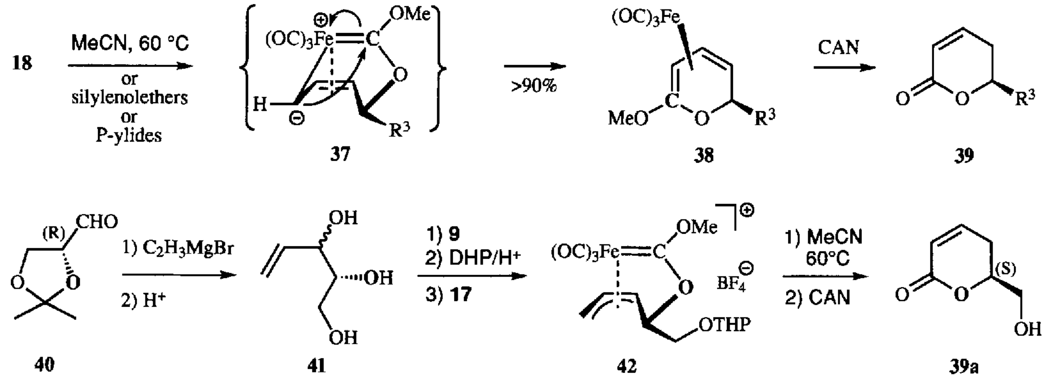
In contrast to lithium enolates and enoxy borates, silyl enol ethers do not undergo C–C coupling reactions with the ironcarbene complexes **18** but act as bases and formally abstract a proton from the allyl terminus C-6 (path 3 reaction), presumably with initial formation of a highly reactive neutral complex **37**, which we have not yet been able to isolate. It takes only minor structural reorganizations in terms of an intramolecular carbene transfer from the iron atom to C-6 to arrive at the novel 6-methoxy-2*H*-pyran tricarbonyliron complexes **38**, which form as stable compounds in over 90% yield[30]. We first considered the "desilylating" counterion BF_4^- to be of pivotal importance to this reaction, but other bases like phosphorous ylides or even the donor solvent acetonitrile at ca. 60 °C emerged as effective in producing high yields of **38**. Treatment of **38** with CAN leads to demetalation and cleavage of the methoxy group in one step thus furnishing the corresponding α,β-unsaturated δ-lactones **39** under mild conditions. As a concrete application, we submit the synthesis of 2-hydroxymethyl pyranone **39a** shown in Scheme 10. This compound is a key intermediate in syntheses leading to a number of natural products bearing unsaturated side chains at the 2-position of the parent lactone[40]. Grignardation of the protected D-glyceric aldehyde **40** (which is readily available by oxidative cleavage of mannitol bisacetonide) with vinylmagnesiumbromide gives the triol **41** as a mixture of diastereoisomers, which can be transferred into the corresponding diastereomeric mixture of the THP-protected carbene complexes **42**; only the major diastereomer of the two formed is depicted, because both eventually give the same product **39a**. Heating solutions of **42** in acetonitrile for an hour and subsequent treatment with CAN at room temperature furnishes the target lactone **39a** in ca. 45% overall yield. The configuration at C-2 is completely retained. This sequence has some advantage over Aumann's and Ley's original shortcut syntheses of δ-lactones by high-pressure carbonylation at elevated temperatures of the ferralactones **13**[28,29].

Path 5 Reactions with Lithium Acetylides: Cascade Synthesis of Highly Substituted Cyclopentenones

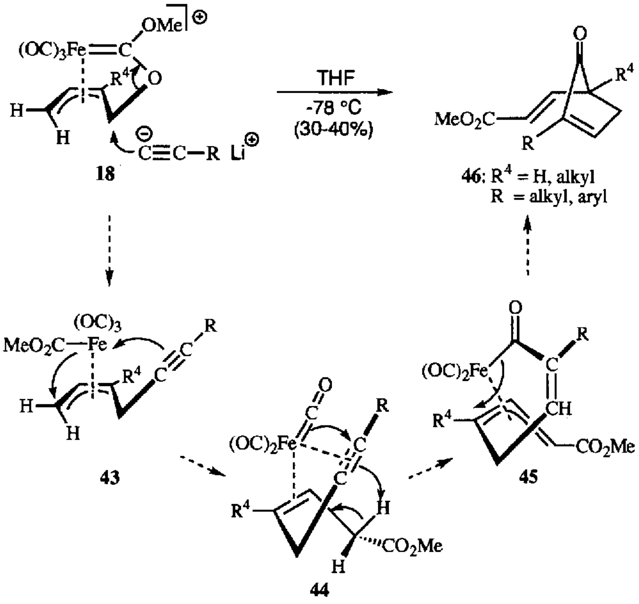
When THF solutions of lithium acetylides (freshly prepared by reaction of the corresponding terminal alkyl- or arylalkynes with *n*-BuLi at −78 °C) are added to **18** in THF at −78 °C, an instantaneous reaction takes place that gives after aqueous workup the 2,5-disubstituted cyclopentenones **46** in as yet unoptimized 30–40% yield. This cascade process furnishes four new C–C bonds with concomitant insertion of one CO unit and a formal transfer of the carbene function as a methoxycarbonyl group to the former allyl terminus C-6. **46** is predominantly (GC > 95%) formed as the isomer with *E* configuration of the exocyclic double bond and with the alkyl residue of the starting acetylene next to the carbonyl group of the cyclopentenone ring. The mechanistic details of this unprecedented reaction have not yet been elucidated, but we can provide a proposal (Scheme 11) featuring reasonable intermediates from the aforementioned semiempirical calculation methods.

Unusual attack of the acetylide anion at the homoallylic carbon atom C-3 (path 5 reaction) could yield the neutral (methoxycarbonyl)allyliron complex **43**. This species could immediately rearrange by transfer of the ester group to the allyl terminus C-6 with formation of complexes like **44**; this process is facilitated by coordination of the alkyne unit to the iron atom. Calculations show a low-energy trajectory leading from **44** to the metallacyclic acylallyliron complex **45** through simultaneous CO insertion and proton transfer from the former C-6 to the acetylene ligand, which restores the η^3-allyl system. We were able to rule out alternative pathways to **46**, for example initial base-induced formation

Scheme 10



Scheme 11



of a corresponding 2*H*-pyran-tricarbonyliron complex **38** followed by ring opening and subsequent cyclocarbonylation[41] of the diene complex thus formed, because **38** proved unreactive towards 1-alkynes or acetylides. Path 5 reactions still require optimization and improvement in the yields. However, they appear quite promising for application to natural cyclopentenone synthesis if one considers the value of prominent transition metal mediated sequences with similar cascades of C–C bond formation and CO insertion reactions with the same regiochemistry of the acetylene addition such as those of Pauson and Khand[42] or Dötz[2b,12].

Conclusions and Perspectives

Allyl-terminated metallacyclic carbene complexes show a more flexible behaviour towards carbon and heteroatom nucleophiles and bases than those terminated by an η^2-alkene ligand. At least five different modes of reaction were elucidated; three of them open shortcut and selective rearrangement and cascade pathways to oligo-functionalized unsaturated products like 1,2-dienes, 1,3-dienes, cyclopentenones, and 2*H*-pyran derivatives. It is exclusively the interplay of the carbene and allyl moieties, which are located at a particular distance from each other in the iron complexes **18** and **19**, that renders such novel sequences untypical of the individual functional groups feasible. The reactivity of our metallacyclic carbene complexes is distinctly dependent on the structural and electronic parameters both of the complexes themselves (central metal fragment, carbene substituents, residues at the perimeter, counter anion etc.) and of the reaction partners ("softness" and charge density of nucleophiles, counter cation, solvent). Therefore there should be ample chance for "fine-tuning". We are currently probing the chemistry of analogous carbene complexes featuring different central metal moieties, such as $(C_5H_5)(OC)Mn$ or an allyl ligand tethered to the carbene carbon not linearly (i.e. terminally) but angularly (i.e. to the central allylic carbon atom). There is also considerable potential for future developments in the exploitation of the inherent chirality of most of our metallacycles and of the respective asymmetric aspects of their reactions outlined above.

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