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Chelated η^2-alkene- and η^3-allyl-carbene complexes of late transition metals: structure–reactivity relations and preparative use[☆]

Part 10. The chemistry of metallacyclic alkenylcarbene complexes

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Abstract

Chelated alkene–carbene complexes of Group VI metals typically undergo intramolecular [2 + 2]-cycloaddition reactions, whereas the iron analogues and related (η^3-allyl)–ironcarbene complexes show a more diverse behaviour. They are amenable to reactions at the carbene carbon atom, at the terminus of the π-ligand and even at the tether depending on intrinsic stereoelectronic parameters as well as external factors like solvent polarity and 'softness' of attacking nucleophiles. Cascades with extensive reorganization of the organic ligand leading to oligo-enynes, δ-lactones and cyclopentenones may ensue. They are discussed together with some new findings allowing a generalized mechanistic description. The chemical and configurational stabilities of planar-chiral alkene–carbene and allyl–carbene complexes of iron, chromium, manganese and cobalt are compared. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbene complexes; Alkene complexes; Allyl complexes; Metallacycles; Fe

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1. Introduction

Within the vast field of synthetic applications of 'Fischer type' transition metal alkylidene (i.e. carbene) complexes, reactions with alkenes and alkynes occupy an eminent position [2]. Processes like the cyclopropanation [3] and the metathesis or polymerization of olefins/acetylenes [4] are of equal industrial importance and academic fascination due to their mechanistic implications. Pivotal intermediates in these and related modern laboratory-scale reactions are carbene–(η^2-alkene) complexes **1** or the alkyne analogues **2**. They are not usually stable and could be isolated only in exceptional cases [5]. Readily formed upon displacement of common ancillary ligands such as CO by the respective unsaturated π-donor, their further fate is governed by a delicate interplay of various factors. The nature of the central metal fragment and the substituents both at the carbene carbon atom and at the olefin/acetylene ligand are no less important than external parameters such as temperature, solvent polarity and the CO pressure applied. Even more complicated are reactions of an alkene and an alkyne (or an enyne) with a carbene complex as is the case in the Dötz synthesis of naphthols from chromium arylmethoxycarbene complexes and acetylenes. For such multi-component sequences the order of the elementary reaction steps is also essential to the outcome [2h]. The overall picture of possible reaction channels for **1** and **2** is thus rather diverse and more stable derivatives of these types were employed in model studies to pinpoint the influence of the individual parameters. Most, but not all [6] of the follow-up chemistry of **1**/**2** appears to proceed via metallacyclobutane/-ene species **3**, which can only form for a collinear spatial arrangement of the alkene/alkyne multiple bond with respect to the M=C carbene bond. Consequently, a simple way to block undesired reaction channels and to obtain olefin–carbene complexes stable enough to allow structure–reactivity stud-

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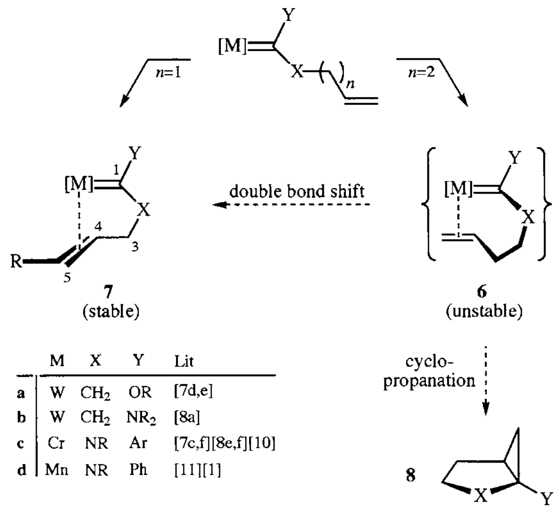
ies is the use of chelated congeners of type **4**. By tethering the η^2-alkene ligand to the carbene carbon atom, stabilizing or activating geometry and entropy constraints can be imposed on carbene–alkene(–alkyne) reactions, thus favouring or suppressing one or some of all possible pathways.

The purpose of this paper is twofold. First, it adds some recent results like the isolation of 'missing links' in the various series of title complexes, an X-ray structure of a derivative with extended π-ligands and new mechanistic insights into multistep rearrangement processes involving the entire organic ligand of allyl–iron-carbene complexes. Secondly, it is to provide a general, though not comprehensive, overview of structure–reactivity relations and preparative applications of both classes of chelated η^2-alkene- and η^3-allylcarbene complexes **4** and **5** of late transition metals, especially iron (Fig. 1).



	M	X	Y	Lit
a	W	CH_2	OR	[7d,e]
b	W	CH_2	NR_2	[8a]
c	Cr	NR	Ar	[7c,f][8e,f][10]
d	Mn	NR	Ph	[11][1]

Scheme 1.

2. Results and discussion

2.1. Syntheses and stabilities of (η^2-alkene)–carbene complexes

Various successful approaches towards the synthesis of isolable complexes **4** have been reported. They differ mainly in the order in which the two η^2-ligands are attached to the central metal and in the precursor functional groups these ligands are prepared from. Depending on the particular complex, on the availability of starting compounds and on the stability of intermediates, in some cases only one, in others even several alternative synthetic routes to the target systems may be followed. The individual intrinsic stability of (η^2-alkene)–carbene complexes **4** thus obtained is then very much influenced by the factors mentioned in the Section 1.

2.1.1. Synthesis by direct coordination of an alkene

Fischer carbene complexes with alkenyl groups tethered to the carbene carbon atom are well known for almost every late transition metal. Intramolecular coordination of the distal olefin in the side-chain with loss of a ligand such as CO produces complexes **4**. This can occur upon heating or irradiation when the double bond is located at an appropriate distance from the carbene carbon atom. Rudler et al. [7] and Casey et al. [8] prepared various chelated tungsten and chromium carbene–olefin complexes with tether lengths of $n = 1$ and $n = 2$. Some general trends are obvious from their work. Whereas complexes **6** with a three-atom spacer between the double bonds are unstable and prone to intramolecular cyclopropanation to bicyclic products, complexes **7** with a two-atom tether are rather stable due to a skew orientation of the two double bonds. Only when treated with an alkyne these complexes undergo carbocyclization reactions following a domino insertion-cyclopropanation pathway. Aminocarbene complexes (X/Y = NR) are more stable than the alkoxy analogues. In fact, chromium and manganese do not form any stable oxosubstituted (η^2-alkene)–carbene complexes at all. Complexes of either type are of equal stability when having the heteroatom in an *exo*- (Y = O, NR) or an *endo*-cyclic (X = O, NR) position. Intermediate tungsten complexes of type **6** could be indentified in the course of cyclopropanation reactions, but the congenerous chromium complexes have not been isolated and characterized yet, although there is some evidence for their involvement in reactions of the corresponding acyclic alkoxycarbene complexes [9]. Apart from undergoing cyclopropanation, tungsten and chromium complexes of type **6** can rearrange to the more stable chelates **7** by sequences of [H]-shifts (i. e. double bond isomerization). Formal migration of the double bond over a distance of up to five carbon bonds has been observed [7d,e,8b,e] (Scheme 1).

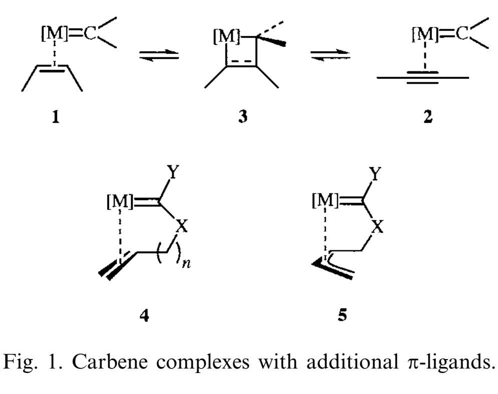
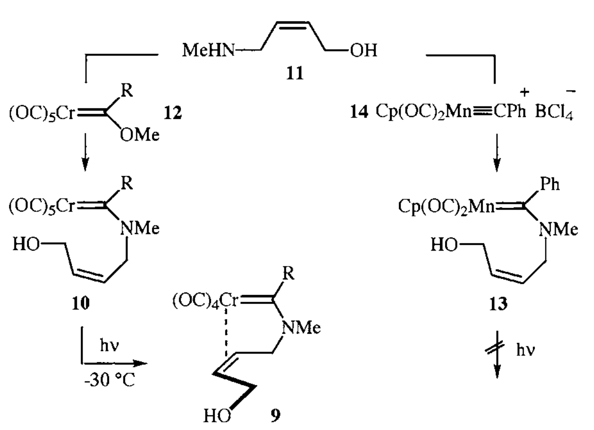
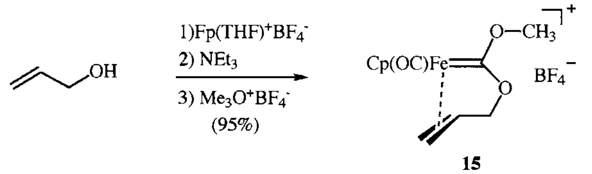


Fig. 1. Carbene complexes with additional π-ligands.



Scheme 2.



Scheme 3.

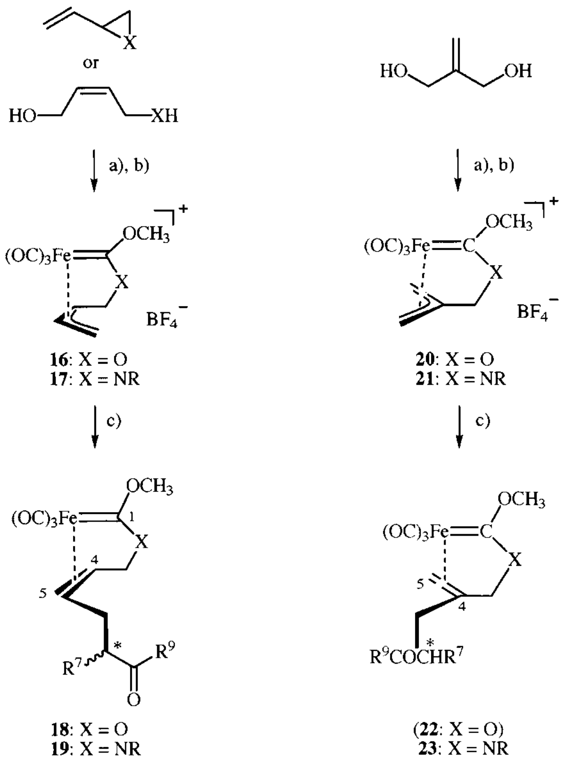
Most of the known complexes of type **7** feature terminal alkene groups or at best an alkyl residue R at C-5. Little is known about the effect of other functional groups on the coordination tendency of the adjacent π-ligand. Our group prepared chelated amino chromiumcarbene complexes **9** with a hydroxymethylene group attached to the olefin by way of the 'uncoordinated' precursor complexes **10**. These are available by a normal aminolysis reaction of 4-amino-2-buten-1-ols such as **11** and the respective methoxycarbene complexes **12**. Whereas π-coordination of olefins and acetylenes is quite often achieved by thermally induced displacement of CO, warming of **10** only leads to its decomposition. However, its irradiation at − 30°C furnishes **9** in excellent yields [1]. Apart from the chemical stability their configurational (optical) stability bears much importance for conceivable applications as stereoinducing scaffolds in intramolecular alkene–carbene–alkyne or related reactions. Diastereoisomers of esters of **9** with enantiopure carboxylic acids can be separated by column chromatography and are configurationally stable at room temperature. Dötz, Moreto et al. [10b] found similar tungsten complexes to interconvert or racemize at room temperature in the majority of cases.

A similar relationship between ring size and reactivity/stability emerges for the few chelated Group VII alkene–carbene complexes published so far [11]. Only derivatives with ring size 4.5 (i.e. with a two-atom spacer), with an amino substituted carbene carbon atom and a terminal olefin ligand are known. Whereas the acyclic manganese complex **13** is readily accessible by addition of the amino group of **11** onto the carbyne complex **14**, its irradiation does not lead to the Mn-analogues of **9** but only to decomposition. As the corresponding complex lacking a terminal hydroxy group could be prepared in this way, it is obviously the hydroxy group itself that prevents ligation of the adjacent olefin moiety [1] (Scheme 2).

Iron is the Group VIII metal that most readily forms stable chelated alkene–carbene complexes of the general type **4**, although not many were reported until lately [12]. A variant of the direct complexation of a pendent alkene onto an existing carbene-bonded Cp(OC)Fe fragment has been recently worked up by Guerchais et al. [13]. Our group prepared a similar cationic bisalkoxycarbene complex **15** [14] by Meerwein alkylation of the corresponding ferralactone, which in turn is available from allylalcohol and $\mathrm{Fp(THF)^+BF_4^-}$ in two steps (coordination of the olefin and subsequent base-induced lactonization) [15]. This is one of the rare cases where olefin ligation is the first step and carbene formation is the last step in the synthesis of an alkene–carbene chelate complex. The approach of direct coordination of a preformed alkene seems to be restricted to terminal alkenes or to alkenes with one small substituent which does not interfere with ligation. In addition, the alkene–carbene complexes must then be sufficiently stable to survive the conditions of their preparation, i.e. the photolysis or thermolysis of an ancillary ligand such as CO (Scheme 3).

2.1.2. Synthesis from chelated (η^3-allyl)–carbene complexes

Tricarbonyliron complexes of type **4** are less stable than their Cp(CO)Fe congeners, direct coordination of a preformed alkene ligand does not provide a general access to them. We found the reaction of the electrophilic cationic (η^3-allyl)–carbene complexes **16**/**17** [16] with certain carbon and heteroatom nucleophiles more effective and flexible. These air-stable starting complexes are easily accessible in two steps from the reaction of ironcarbonyls with vinylepoxides, butene-1,4-diols (for **16**), or with vinyl aziridines (for **17**), respectively, followed by Meerwein-alkylation of the intermediate ferralactones/-lactams [17]. 'Soft' carbon nucleophiles like lithium enolates, potassium enoxyborates and organocuprates all attack in orbital-controlled reactions on the allyl terminus (C-6) of the metallacycle. This forms neutral 5-substituted alkene–carbene complexes **18**/**19** [18]. The analogy with complexes **7** is obvious, but now additional functional groups and stereogenic centres may be incorporated in the side-chain at C-5. The reaction is quite selective in several respects. The complexes **18**/**19** in every case have a *cis*-configured C=C double bond and like **16**/**17** are planar-chiral and configurationally stable. There-



Scheme 4. Reagents and conditions: (a) $Fe_2(CO)_9$ in THF or PhH/ultrasound, r.t., 40–85%; (b) $Me_3O^+BF_4^-$, CH_2Cl_2, 70–95%; (c) $R^9COCH_2R^7$ and KH/BEt_3 at r.t. or LDA (or LICA) at −78 °C, 2 h, 85–95%.

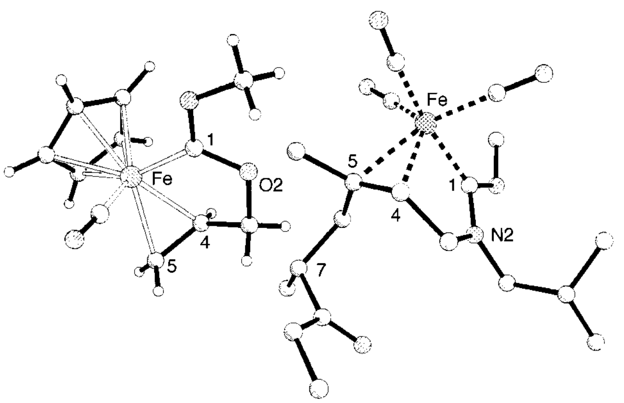


Fig. 2. Molecular structures of **15** (cation), left and of **19a** (R^2 = *i*-butyl, $R^5 = R^7 = CH_3$, $R^9 = C_2H_5$), right. Selected bond lengths (Å) and Casey's angles (°): **15**/**19a**: Fe–C1 1.88(9)/1.964, Fe–C4 2.108(9)/2.083, Fe–C5 2.143(9)/2.158, C1–O2/N2 1.316(9)/1.305, C1–OMe 1.288(9)/1.338, C4–C5 1.401(12)/1.407, α 91/85.5°, β 45.0/74.6°, γ 4.5/31.9°.

fore they can act as stereoinductors for the selective establishment of new stereocentres. Regiochemically ('kinetic' versus 'thermodynamic') and configurationally (*cis*- versus *trans*-) well-defined prochiral potassium enoxyborates were found to lead to complexes **18**/**19**, with a new stereogenic centre at C-7 regio- and diastereoselectively with *de* values up to 95 [18b] (vide infra). Even in cases of lesser selectivity, only two easy to separate diastereoisomers are formed. Additional isomerism due to the $C1–OCH_3$ bond does not occur. All aminooxocarbene complexes **17**/**19** are *Z*-configured and all dioxocarbene complexes **16** are *E*-configured with respect to this bond, most likely because of steric restraints. Pure diastereoisomers of **19** do not equilibrate at room temperature. Enantiomerically pure allyl–carbene complexes **16** and **17** are likewise optically stable and could be obtained by alkylation of the respective ferralactones/-lactams. These were resolved by preparative-scale HPLC on cellulose tris(3,5-dimethylphenyl)carbamate/silica gel RP-8 [19]. Whereas the aminooxocarbene complexes **19** are chemically and configurationally stable and in most cases can be handled at room temperature, the dioxo analogues **18** are often too labile to allow isolation. Their follow-up chemistry has however proved exceedingly useful in the construction of functionalized dienes (vide infra). Only recently were we able to isolate and characterize the first such complex **18b** ($R^4 = R^7$ = Me, R^9 = Et) by a quick flash chromatography at 0°C. Its life span is in the range of a few hours at this temperature.

By reaction of nucleophiles with cationic allyl–carbene complexes **20**/**21** featuring a centrally tethered π-ligand, the analogous neutral 4-substituted alkene–carbene complexes **22**/**23** [20] could be obtained. Once more, the starting complexes are available by alkylation of the underlying ferralactones as prepared from ironcarbonyls and either isobutenediol or unsaturated carbamates [21]. The 4-substituted alkene–carbene systems appear to be slightly less stable than the 5-substituted complexes. The dioxo derivatives **22** could not be isolated in substance but instead would undergo a quick rearrangement to trimethylenemethane complexes. Little difference was found in terms of the stereoinductive effect of the planar-chiral metallacycle in the two complex series, for a given type of enolate with identical residues R^7 and R^9. Still, regioselectivities and chemical yields are significantly better for potassium enoxyborates than for lithium enolates, whereas diastereoselectivities are comparable. No isomerism as to the $C1–OCH_3$ bond occurs for the complexes **20**–**23** either (Scheme 4).

Fig. 2 shows the molecular structures of the cation of the dioxocarbene complex **15** and of a derivative of the neutral aminooxocarbene complexes **19** as obtained by X-ray single crystal analyses. As pointed out in the beginning, the spatial orientation of alkene and carbene double bonds relative to each other is of pivotal importance to any cycloaddition-related reactivity of (η^2-olefin)–carbene complexes. Casey defined several angles to unambiguously describe this orientation [8e]. β is the dihedral angle between the plane containing the carbene carbon, the metal and the olefin midpoint and the plane defined by the metal and the two alkene atoms. β is 0° for parallel [M=C] and [C=C] units and it is 90° for a perpendicular arrangement of these groups. The angle γ is independent of olefin rotation and defines the twist between the plane of the carbene carbon, the metal, and the alkene midpoint and the plane of the carbene group [CXY]. Apart from certain electronic requirements cyclopropanation and metathesis reactions normally require β to be near 0° and γ not to be, which is the case for most Group VI metal complexes of type **6**. Although having the same tether length, central metal and bisdonor substitution of the carbene carbon atoms, the iron complexes **15** and **19a** have distinctly different structures. Typical of dioxocarbene complexes, **15** has an *E*-configured C1–OMe bond whereas this bond has a *Z*-configuration in **19a**. In **15** ($\beta = 45°$) the axes of the M=C1 and the C=C bonds are less deviating from a parallel alignment than in **19a** ($\beta = 74.6°$), but for the planes containing the olefin (C3, C4, C5) and the carbene (Fe, C1, O/N) moieties the opposite is true. **15** has a very small angle γ (4.5°) compared to **19a** ($\gamma = 32°$). This is probably due to unrestricted rotation about the M–C1 bond in complexes of the type $CpL_2M{=}CR_2$ (M = Fe, Mn) for electronic reasons and thus to a possible optimization of the conformational requirements of the chelate ring. The ‘flatness’ of tricarbonyliron complexes of type **19** seems to be a compromise midway between electronic and steric demands of the groups involved. Both iron complexes **15** and **19a** are rather far removed from optimum cyclopropanation/metathesis geometry. As ironcarbene complexes are known to normally undergo such reactions only under drastic conditions anyway, their relatively high stability is reasonable. More elusive derivatives like the dioxo complexes **18** and **22** owe their instability to the availability of reaction pathways quite different from cyclopropanation and metathesis, such as irreversible intramolecular rearrangements (vide infra).

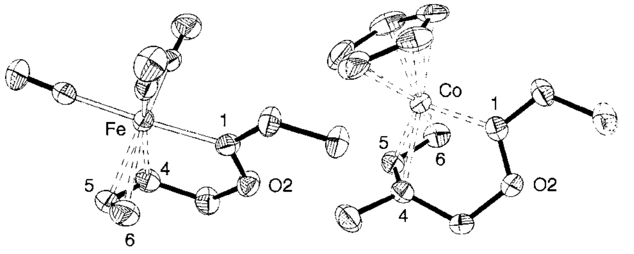
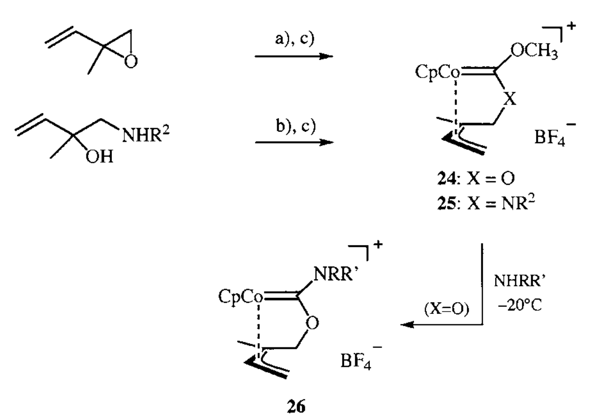


Fig. 3. Molecular structures of the cations of **16a**, left and of **24**, right (ORTEP representations, 50% probability ellipsoids). Selected bond lengths (Å): **16a**/**24**: [M]–C1 1.921(4)/1.853, [M]–C4 2.119(4)/2.070, [M]–C5 2.081(4)/1.993, [M]–C6 2.170(5)/2.091, C4–C5 1.424(6)/1.427, C5–C6 1.4087/1.415; γ 33.3°/28.8°.

2.2. Synthesis of other chelated (η^3-allyl)–carbene complexes

2.2.1. (η^3-Allyl)–cobaltcarbene complexes

(η^3-Allyl)–cobaltcarbene complexes **24**/**25** which are isoelectronic to the iron analogues **16**/**17** are also readily available by Meerwein-alkylation of the corresponding cobaltalactones/-lactames [1] [22]. The latter can be obtained by UV-irradiation of mixtures of (η^5-cyclopentadienyl)dicarbonylcobalt and either vinylepoxides or 1-amino-3-buten-2-ols in THF or benzene at elevated temperature. Whereas the iron complexes normally react with ‘soft’ nucleophiles at their allyl ligand, the cobalt congeners behave more like typical Fischer carbene systems. Primary amines — including functionalized ones like α-aminoesters — aminolyse the dioxo complexes **24** by attack on the carbene atom C-1 and displacement of the methoxy group to give the (*exo*-amino)oxocarbene complexes **26**. The (*endo*-amino)oxocarbene complexes **25** do not react with any types of amines due to a stereoelectronic shielding of their carbene carbon atoms by the ring nitrogen atom and its substituent. Carbon nucleophiles like enolates do not attack on the terminal C-5 of **24**/**25** to produce substituted alkene–carbene complexes analogous to **18**/**19** which are hitherto unknown, but merely demethylate to give back the cobaltalactones/-lactams. All of the above cobaltcarbene complexes are bright yellow, air-stable crystalline compounds which can be easily purified by open-air column chromatography over silica gel ($MeCN–CH_2Cl_2$, 1 + 1). Although of different reactivity towards nucleophiles, the iron complexes **16**/**17** and the cobalt congeners **24**/**25** are quite similar in terms of structure and electron transfer behaviour (as inferred from cyclic voltammetry [22]). Again, certain angles can be defined to describe the orientation of the functional groups. The angle γ between the mean plane of the carbene group [M=CXY] and the plane containing the carbene carbon atom, the metal, and the centre of the allylic triangle, is of considerable diagnostic value as it describes the gap between the ends C-1 and C-6 of the organic ligand. The larger γ, the flatter the metallacycle, i.e. the closer these ends get to each other. This is important for the discussion of intramolecular cyclization reactions of these complexes (vide infra). Fig. 3 depicts molecular structures as obtained from X-ray analyses of the cations of the iron complex **16a** ($R^4 = H$) and the cobalt complex **24**. The latter is less flat ($\gamma = 28.8°$) than the iron complex ($\gamma = 33.3°$), but most of the other relevant bond distances and angles match each other well. In both cases the allylic moieties are *syn*-configured and have similar angles C4–C5–C6 (**16a** 122.0°; **24** 119.3°); the C1–O1 bonds are both *E*-configured (Scheme 5).



Scheme 5. Reagents and conditions: (a) $CoCp(CO)_2$, *hν*, PhH, 40°C, 3 h, 50%; (b) $CoCp(CO)_2$, *hν*, THF, 70°C, 3 h, 35%; (c) $Me_3O^+BF_4^-$, CH_2Cl_2, 80%.

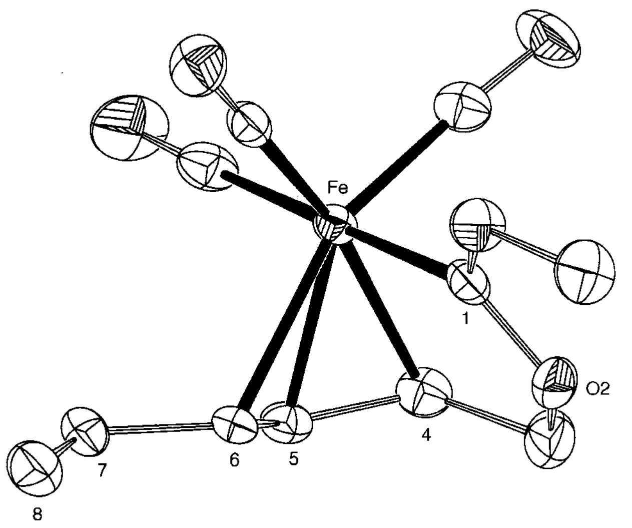


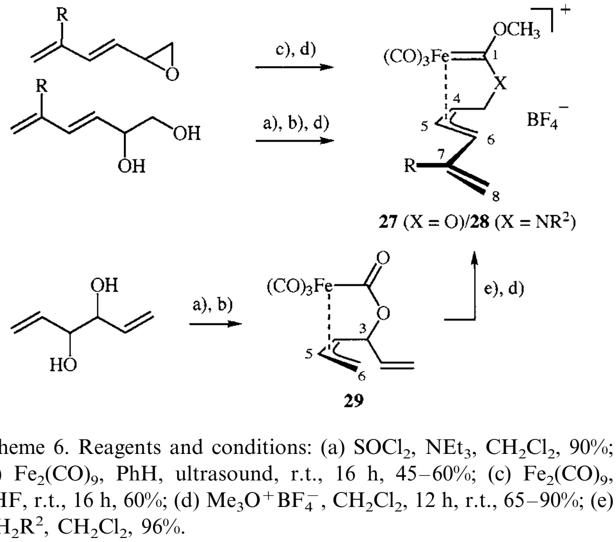
Fig. 4. Molecular structure of the cation of **27a** ($R^7 = H$) (ORTEP representation, 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Fe–C1 1.927(2), Fe–C4 2.089(3), Fe–C5 2.090(3), Fe–C6 2.267(3), C4–C5 1.397(4), C5–C6 1.401(4), C6–C7 1.471(4), C7–C8 1.319(4), C4–C5–C6–C7 −168.4°, C5–C6–C7–C8 −162.6°, γ 38.9°.

2.2.2. *(η^3-Pentadienyl)–ironcarbene complexes*

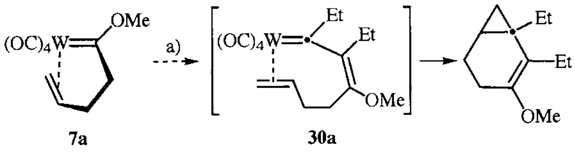
Chelated [η^n-oligo-ene(yl)]–carbene complexes are virtually unknown for hapticities greater than $n = 4$. Only derivatives bearing the exceptionally stable, aromatic η^5-cyclopentadienyl ligand were published [23]. Our group was more interested in structural analogues of complexes of types **16** and **17** with an additional vinyl residue at either end of the η^3-allyl ligand, i.e. at C-4 or C-6. They could in principle undergo ring enlargement to a different η^3-pentadienyl complex, or could furnish a proper η^5-pentadienyl complex by loss of CO. The reaction of butadienyl-substituted epoxides or cyclic sulfites derived from respective vicinal diols with diironnonacarbonyl leads to 6-vinyl-substituted (η^3-allyl)ferralactones which can be methylated with trimethyloxonium tetrafluoroborate to give the corresponding dioxocarbene complexes **27** [24]. An X-ray single crystal structure could be recently obtained of derivative **27a** ($R^7 = H$; Fig. 4). The entire π-system is almost planar with only a slight twist between the allyl moiety and the vinyl residue. However, these groups are no longer electronically coupled as the corresponding bond lengths are characteristic of an η^3-allyl (ca. 1.40 Å) and an isolated vinyl group (ca. 1.32 Å). The length of bond C6–C7 separating them is ca. 1.47 Å and so lies in the typical range of sp^2-C–sp^2-C single bonds. Although the allylic 'triangle' is rather symmetric in terms of bond lengths, its three carbon atoms are not equally tightly coordinated to the central metal which seems to be shifted towards the inner end of the pentadienyl system. The bond between iron and the 'terminal' allylic carbon atom (C-6) is unusually long (ca. 2.27 Å) and the [Fe=COO] plane is more strongly inclined ($\gamma = 38.9°$) with respect to the plane of the allyl ligand than in other allylironcarbene complexes lacking a vinyl substituent. Aminooxocarbene complexes **28** are best prepared indirectly from 4-vinyl-substituted (η^3-allyl)ferralactones such as **29**, available by the standard route from vicinal bisallylalcohols. They react with amines by formation of the corresponding 6-vinylferralactams (i.e. by attack of the base on C-6, chelate opening and finally recyclization) [25] which can then be methylated using $Me_3O^+BF_4^-$. Complexes **27** and **28** show no tendency towards ring enlargement or opening or increase of hapticity to form an η^5-π-ligand (Scheme 6).

2.3. *Reactions and applications of (η^2-alkene)- and (η^3-allyl)–carbene complexes*

The reactivity of the title complexes is dependent on various internal and external parameters. Important



Scheme 6. Reagents and conditions: (a) $SOCl_2$, NEt_3, CH_2Cl_2, 90%; (b) $Fe_2(CO)_9$, PhH, ultrasound, r.t., 16 h, 45–60%; (c) $Fe_2(CO)_9$, THF, r.t., 16 h, 60%; (d) $Me_3O^+BF_4^-$, CH_2Cl_2, 12 h, r.t., 65–90%; (e) NH_2R^2, CH_2Cl_2, 96%.



Scheme 7. Reagents and conditions: (a) C_2H_5–C≡C–C_2H_5, r.t., 12 h.

intrinsic factors are the bulkiness and electron-richness of the central metal fragment and of the substituents at the carbene carbon and carbon atoms C-3 and C-5/C-6 of the organic ligand. Of equal importance are the overall charge and the spatial orientation of the [M=CXY] and the olefin/allyl moieties relative to each other. Crucial external parameters are the 'softness' of attacking nucleophiles and the polarity (donor quality) of the solvent. So far, four major types of reactions have been observed. Intramolecular reactions with participation of both π-ligands (such as cyclopropanation), reactions initiated by nucleophilic attack on the carbene carbon atom (such as Fischer aminolysis), and transformations commencing with reactions at the π-ligand or at the spacer between this and the carbene carbon. Combinations of such processes are possible. The planar chirality of the complexes occassionally has been used in diastereoselective variants.

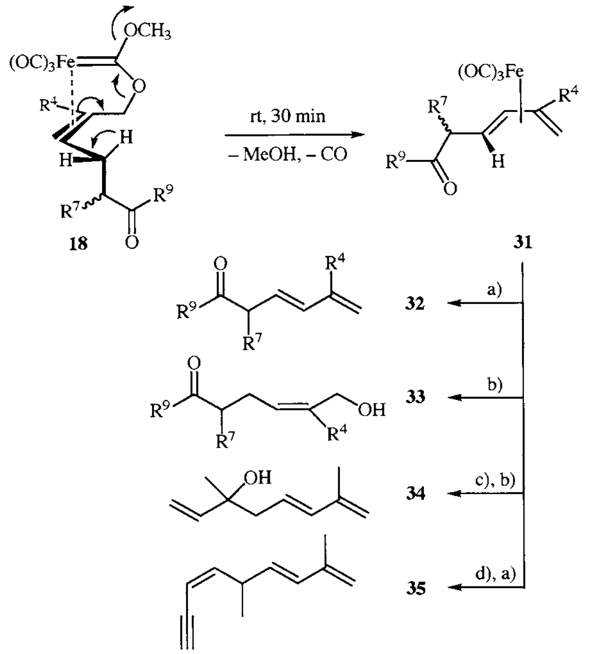
2.3.1. Intramolecular cyclopropanation reactions of Group VI metal complexes

Alkene–carbene complexes were initially prepared to study cyclopropanation and metathesis processes. Intramolecular variants of these require a Group VI central metal and at least a three-atom spacer between the functional groups, i.e. a complex of type **6**. Rudler et al. developed an alternative concept for the activation of stable complexes of type **7** by insertion of an alkyne to give a larger metallacycle **30** with a four-atom spacer capable of adopting the proper 'cyclopropanation geometry' and of formation of bicycles in a domino-type fashion (Scheme 7) [26]. It remained unclear whether and at what stage the olefin dissociates from and recoordinates to the metal. Several groups reported multi-component domino carbene–alkene–alkyne reactions purportedly proceeding via complexes of types **6** or **30** and yielding oligo(hetero)cyclic organic products [2h] [27]. Neither stable Group VII and Group VIII metal alkene–carbene complexes (e.g. **7d**, **15**, **18**, **19**, **23**) nor allyl–carbene and (η^n-pentadienyl)–carbene complexes (e.g. **16**–**17**, **20**–**21**, **24**–**28**) undergo such domino alkyne insertion-cyclopropanation reactions due to the inavailability of vacant coordination sites. Dissociation of ligated alkenes or allyl moieties, or of ancillary CO ligands in these complexes normally requires more drastic conditions (e.g. heat or oxidants) than for similar Group IV–VI π-complexes.

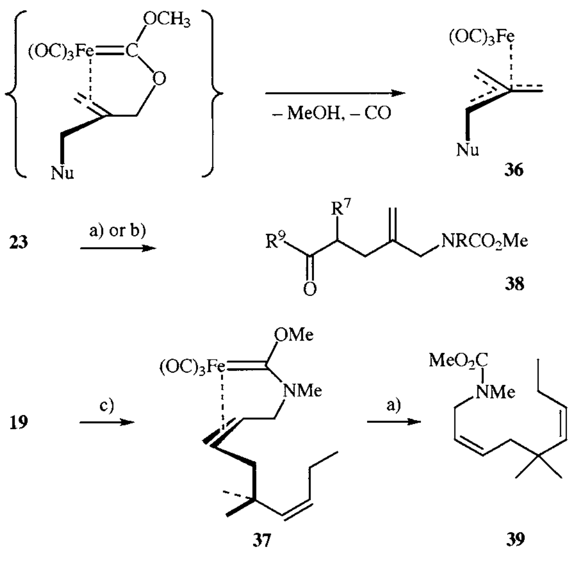
2.3.2. Fragmentation of alkene–irondioxocarbene complexes

Alkene–irondioxocarbene complexes **18** are rather unstable, prone not to cyclopropanation but to a fragmentation reaction which encompasses both η^2-ligands. This could be regarded as a formal metalla-Claisen rearrangement of their ferravinyl–allyl ether unit. It proceeds rapidly at room temperature even in the absence of bases or acids. For preparative applications it is not normally necessary to isolate the intermediate complexes **18** prepared from the allyl–carbene complexes **16** and the respective enolate. The product 6-oxo-(1,3*E*)-diene complexes **31** are valuable intermediates and can be further functionalized in many ways. Oxidative demetalation with ceric ammonium nitrate (CAN) gives the free *E*-6-oxo-1,3-dienes **32**, whereas oxidation with H_2O_2–NaOH leads to substituted (*Z*)-allylalcohols **33** [28]. Prior to decomplexation of the diene ligand, various transformations of the carbonyl group of **31** can be performed, thus making use of the protective and/or stereodirecting properties of the tricarbonyliron moiety [18b,c]. Grignardation of **31c** ($R^4 = R^9 =$ Me, $R^7 =$ H), obtained in three steps from 1-methyl-1-vinylepoxide, with vinylmagnesiumbromide gives the corresponding chain-lengthened diene complex as a 1:1 mixture of diastereoisomers. Its oxidation with H_2O_2–NaOH furnishes hotrienol **34**, naturally occurring in the leaf oil of the Japanese *Ho* tree and other plant sources. The carbonyl group in **31** can also be olefinated by phosphoranes or phosphonates with *E*/*Z*-selectivities greater than for analogous uncomplexed carbonyl compounds. In some cases such olefination reactions even proceed with complete inversion of the normal selectivity due to the bulky $Fe(CO)_3$ group sterically influencing the life span and the ability to rearrangement of intermediates. Potassium propargylic phosphonates, for instance, are known to usually yield *E*-configured alkenes but with **31** at −78°C produce predominantly ($Z/E = 6{:}1$) the corresponding diene complex with a *Z*-configured alkene. The organic trienyne ligand **35** can be liberated by oxidation with CAN (Scheme 8) [18c].

4-Substituted alkene–irondioxocarbene complexes **22** could not been isolated, yet. They are putative intermediates in the reaction of complexes **20** with enolates to give labile trimethylenemethane complexes of the general type **36** via a similar fragmentation with concomitant loss of methanol and carbon monoxide. Both series of alkene–iron(aminooxo)carbene complexes **19** and **23** are far more stable than their dioxo congeners, presumably due to a more stable N–C3 bond. Formation of a nitrile ligand would not drive the reaction to completion as does the loss of a newly generated CO ligand in the case of the dioxocarbene complexes. Complexes **19** and **23** can be further functionalized at the distal carbonyl group without dissociation of the alkene

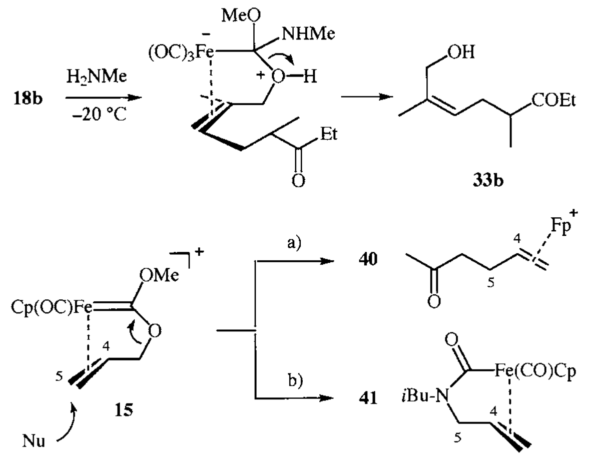


Scheme 8. Reagents and conditions: (a) CAN, MeOH, −20°C, 70–95%; (b) H_2O_2, NaOH, MeOH, 0°C, 60–85%; (c) $R^7 = H$, $R^4 = R^9 = Me$: $H_2C = CHMgBr$, THF, 0°C, 1 h, 60%; (d) $R^9 = H$, $R^4 = R^7 = Me$: $(EtO)_2POCHC{\equiv}CTMS^-$ K^+, THF, −78°C→r.t., 70%.



Scheme 9. Reagents and conditions: (a) four equivalents m-CPBA, $CHCl_3$, r.t.; (b) H_2O_2, NaOH, MeOH, 0°C, 2 h; c) X = NMe, $R^{7,7'} = Me$, $R^9 = H$: $Ph_3PCHC_2H_5$, THF, −78°C→r.t.

ligand or other cleavage of the chelate ring to give new stable alkene–carbene complexes such as **37**. The organic ligand may eventually be liberated oxidatively to yield various types of functionalized allylic carbamates such as **38** and **39** (Scheme 9) [18c,20a].



Scheme 10. Reagents and conditions: (a) Me_2CO–KH–BEt_3, THF, −78°C→r.t., 80%; (b) two equivalents $Me_2CHCH_2NH_2$, H_3CCN, r.t., 2 h, 84%.

2.3.3. Nucleophilic attack on either terminus C-1 or C-5/C-6 of the chelate ligand

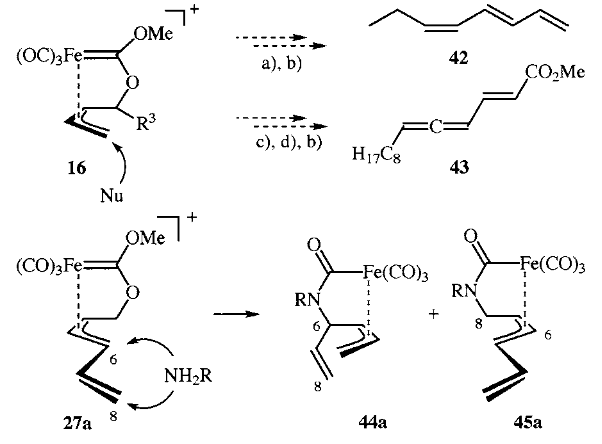
The instability of alkene–dioxocarbene complexes **18** is inherent and their rearrangement to diene complexes is not initiated by bases. The treatment of **18b** ($R^4 = R^7 = Me$, $R^9 = Et$) with methylamine at −20°C does not lead to deprotonation at C-6 and to formation of a diene complex, but to an aminolysis at the carbene carbon atom ('Fischer reaction'). However, deviating from the normal pattern, it is not the *exo*- but the *endo*-alkoxy substituent that gets displaced with formation of the free allylalcohol **33b**. It is unclear whether the chelate is initially opened by expulsion of the alkoxide or by dissociation of the η^2-alkene ligand, although the latter is rather unlikely. Fischer aminolysis is also a convenient way for the preparation of allyl–(*exo*amino)oxo cobaltcarbene complexes **26** from the dioxo congeners **24** (Scheme 5).

More typical of all types of chelated ironcarbene complexes is attack of nucleophiles on the terminus of the π-ligand. Contrary to the neutral alkene–dioxocarbene complex **18** the cationic complex **15** reacts with nucleophiles at its terminal carbon atom C-5. This might be due to the electron-releasing effect of the Cp ligand which renders the carbene C-1 less electrophilic and/or to the fact, that the terminal alkene ligand in the latter is sterically better accessible than the substituted olefin in **18**. Both carbon and heteroatom nucleophiles give rise to the formation of new (η^2-olefin) complexes by way of S_N2'-type processes. Upon reaction with **15** the potassium enoxyborate of acetone gets formally α-allylated to complex **40**, whereas an excess of isobutylamine furnishes the rearranged ferralactam **41** via a sequence of S_N2'-attack, relocation of the double bond, loss of the methoxy group and finally recyclization (Scheme 10) [14].

η^3-Allyl–ironcarbene complexes of types **16**–**17** and **20**–**21** all react with ‘soft’ nucleophiles in an orbital-controlled fashion at a terminal carbon atom of their unsaturated π-ligand. The reaction with enolates has already been highlighted as a valuable work-around for the synthesis of 4- and 5-substituted 8-oxoalkene–carbene complexes which are difficult to prepare otherwise (Scheme 4). In the case of the allyl–dioxocarbene complexes, the reaction also works well with various other types of nucleophiles like organocuprates and phosphines eventually leading to the corresponding terminally substituted diene complexes as products of the fragmentation process described in the previous section. With primary amines a quick recyclization step yields the respective ‘inverted’ ferralactams [16] [18a]. These approaches were used by our group to build up naturally occurring linear 1,3,5-trienes like the pheromone fucoserratene **42** and 1,2,4-trienes like the pheromone **43** of the dry-bean weevil [29]. Interestingly, the η^3-pentadienyl–dioxocarbene complexes **27**, despite the electronic decoupling between the 6-vinyl residue and the π-ligand and despite the weak Fe–C6 bond, are attacked by amines both at C-6 and C-8 to produce roughly 1:1 mixtures of the rearranged ferralactam complexes **44** and **45** (Scheme 11).

2.3.4. Rearrangement reactions following cleavage of the tether

Evidence for the tether carbon atom C-3 in allyl–irondioxocarbene complexes to be electron-deficient and the bond O2–C3 to be electronically ‘taut’ and prone to heterolytic cleavage to give elusive intermediates of type **46** has been amounting over the last few years. A good deal of reactions proceeding with extensive reorganization of the ligand framework were initially ill understood and appeared to be incoherent but can now be explained as proceeding via intermediates **46**. Reactions which hinge on the cleavage of bond O2–C3 are likely whenever an electron-releasing group (ERG) capable of stabilizing an adjacent carbenium ion is attached to C-3. This group can be either a built-in residue, a loosely coordinated external donor molecule or a ‘hard’ nucleophile attacking C-3 directly in a charge-controlled manner with formation of a covalent bond. The intermediate (σ-methoxycarbonyl)–(π-allyl)iron complex **46** can then undergo various follow-up reactions.



Scheme 11. Reagents and conditions: (a) $R^3 = H$: $(C_2H_5CH{=}CH)_2Cu(CN)Li_2$, THF, −78°C → r.t., 45%; (b) CAN, MeOH, 0°C, 90%; (c) $R^3 = CO_2Me$: PPh_3, CH_2Cl_2, r.t., 1 h; (d) NaHMDS, −78°C, 5 min then $C_8H_{17}CHO$ → r.t.

An old finding is that most ferralactones bearing two alkyl residues at C-3 such as the dimethyl derivative **47** cannot be converted into the corresponding allyl–carbene complexes but rather decarboxylate upon treatment with Meerwein salts or other Lewis acids such as BF_3 or $AlCl_3$. The C3–O2 bond is obviously very labile here and even a beginning interaction between the alkylating agent/Lewis acid and one of either oxygens of the lacton springs its cleavage. This reaction is not really catalytic in Me_3OBF_4 as decomposition products are formed alongside the diene complexes. Recently, we tried to prepare a 3-vinyl-substituted allyl–carbene complex by methylation of the ferralacton **29**. The product we obtained was wrongly assigned the expected carbene structure [24] but was now revealed by X-ray structural analysis to be a rearranged cationic methoxycarbonyl-(η^3-pentadienyl)tricarbonyliron complex **49**. We assume the formation of a cationic intermediate **46a** owing its stability to the adjoining vinyl group. A regioselective attack of the nucleophilic CO_2Me group on this cation and a 1,3-H shift complete the process which might also proceed in a more concerted manner not involving free carbocations. Despite a considerable reorganization of bonds, the shapes of product and starting complexes are strikingly similar. This together with the fact, that no (η^5-pentadienyl)tricarbonyliron complex is formed but instead the vacant coordination site at iron is occupied by the estercarbonyl oxygen atom support the assumption of a synchronous rearrangement. The molecular structure of the cation of **49** is depicted in Fig. 5. It is worth noting, that the congenerous 3-vinylferralactams **44a** can be methylated to the corresponding allyl–carbene complexes as expected and without cleavage of the N–C3 bond (Scheme 12).

When allylirondioxocarbene complexes **16** are treated with donor solvents like acetonitrile at 60°C or with weak bases like silyl enolethers in acetonitrile at room temperature, 6-methoxy-2*H*-pyran tricarbonyliron complexes **50** are formed in excellent yields [16]. This reaction is now believed to be not just an intramolecular carbene transfer with formation of a new bond between C1 and the allyl terminus C6 of an otherwise intact organic ligand but to involve an intermediate of type **46**. The role of the donor solvent would be to stabilize the cation at C-3 by donation of electron

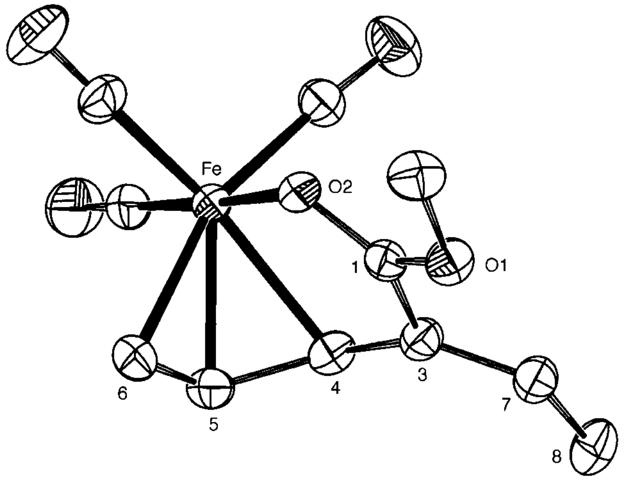
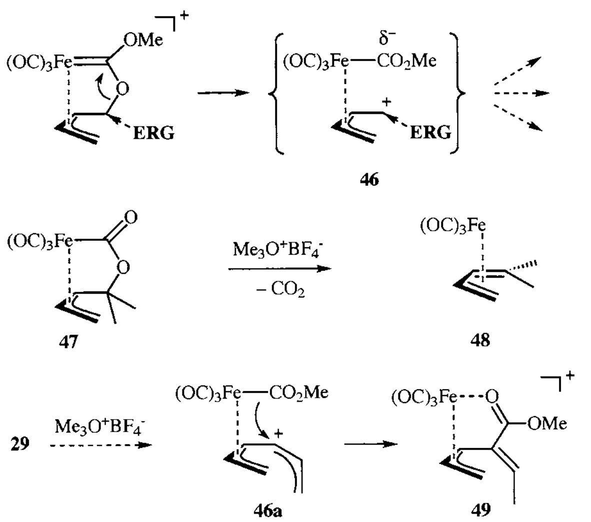


Fig. 5. Molecular structure of the cation of **49** (ORTEP representation, 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Fe–C6 2.145(3), Fe–C5 2.086(2), Fe–C4 2.170(2), Fe–O2 2.0095(18), C1–O2 1.242(3), C1–O1 1.304(3), C1–C3 1.470(4), C3–C4 1.485(4), C4–C5 1.421(4), C5–C6 1.403(2), C3–C7 1.348(4), C7–C8 1.493(4), C4–C3–C1 115.4(2)°, C4–C3–C7 118.2(3)°, C4–C3–C1–O1 167.50(19)°, C7–C3–C1–O2 156.2(2)°, C4–C3–C7–C8 −0.5(4)°, 'γ' 41.7°.

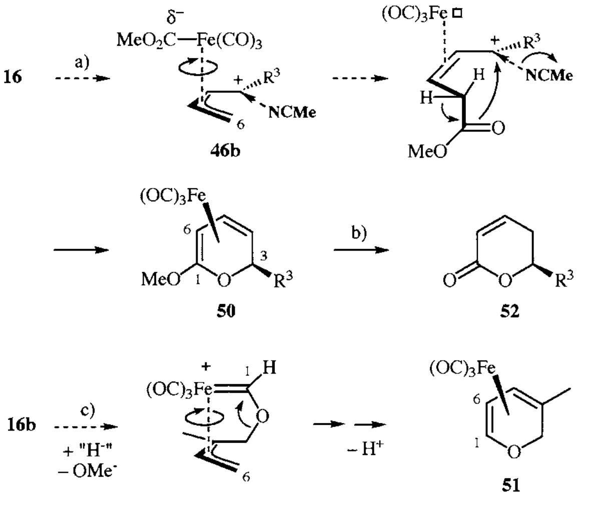


Scheme 12.

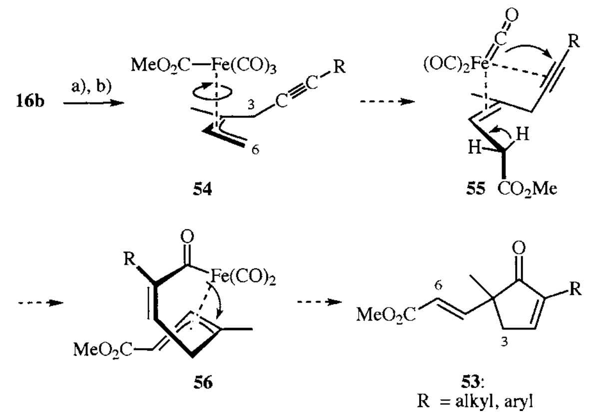
density and by steric shielding. Even in cases where $R^3 = H$, this intermediate is long-lived enough to allow rotation of the central metal fragment and bonding of the methoxycarbonyl group to the terminus C-6 of the allyl ligand. The final step is a ring-closing nucleophilic attack of the estercarbonyl oxygen on the cationic centre C-3 and removal of a proton at C-6 by any suitable mild base (either acetonitrile, BF_4^- or a silylenolether). The chirality at C-3 is preserved throughout the process. A similar rearrangement can be initiated by replacing the *exo*-methoxy substituent at C-1 by a less efficient donor such as hydrogen. Serendipitously we found certain lithium tetraalkylborates to be suitable sources of hydride. The formyl residue is then transferred to the allyl terminus C-6 and the ring closed by C–O bond formation to give pyran complexes like **51**. Rudler et al. described a comparable 'switching-on' of tungsten carbene complexes by hydride transfer from dihydropyridines with replacement of an alkoxy substituent [30] Scheme 13.

Aminooxoironcarbene complexes **17** do not undergo this reaction, nor do the cobalt allyl–carbene complexes **24**–**26**. They give only $Cp_2Co^+BF_4^-$ but no well-defined organic products under the same conditions. This is presumably due to the CpCo fragment being more electron-rich than $Fe(CO)_3$ thus rendering the O2–C3 less prone to cleavage. Maybe in addition, the wider gap between C1 and C6 as compared with the iron complexes (Fig. 3) is also of importance. Demetalation of **50** with CAN directly leads to the corresponding α,β-unsaturated δ-lactones **52**. This sequence was applied to the synthesis of (*S*)-2-hydroxymethyl pyranone **52b** ($R^3 = CH_2OH$) from D-glyceraldehyde in seven steps [29]. It is a key intermediate in the syntheses of numerous physiologically active derivatives of marine origin with unsaturated side chains R^3.

Another useful reaction of this type was found when allyl–dioxoironcarbene complexes **16** were treated with lithium acetylides. Contrary to 'softer' carbon nucleophiles such as enolates, enoxyborates and cuprates, these attack carbon atom C-3 in a charge-controlled reaction proceeding quickly even at −30°C. After aqueous work-up the 2,5-disubstituted cyclopentenones **53** are obtained in 40–50% yield [18a]. This remarkable one-pot, multi-step sequence furnishes four new C–C bonds (Scheme 14). Again, cleavage of the O2–C3 bond as initiated by nucleophilic attack of the acetylide is thought to be the first step of the cascade. The



Scheme 13. Reagents and conditions: (a) H_3CCN, 60°C, 6 h, or (1-trimethylsilyloxy) cyclopentene, H_3CCN, r.t., 12 h, >90%; (b) CAN, H_3CCN, 0°C, 1 h; (c) add to dihydrofuran-*t*-BuLi–BEt_3, −78°C, 1 h then→r.t., 85%.



Scheme 14. Reagents and conditions: (a) RC≡CLi, THF, −78°C → r.t.; (b) H_2O/air, 40–50%.

neutral (methoxycarbonyl)–allyliron intermediate **54** should then rearrange by transfer of the ester group to C-6 with formation of **55**. Simultaneous CO insertion and proton transfer from C-6 to the acetylene ligand restores the η^3-allyl system in **56**. A final cyclization/demetalation step then gives rise to metal-free products **53**. Due to its complexicity and selectivity, this domino procedure should see further application to the synthesis of natural products with cyclopentenone cores.

3. Conclusions and outlook

Electrophilic chelated alkene–carbene and allyl–carbene complexes of late transition metals allow access to a variety of functionalized unsaturated and cyclic organic target compounds. They are open to short-cut and selective rearrangement and cascade reactions triggered by attack of carbon and heteroatom nucleophiles on specific sites of the metallacycle. The outcome of these reactions is distinctly and predictably dependent on structural and electronic parameters both of the complexes themselves and of the reaction partners. Iron complexes were found to be particularly versatile and amenable to domino processes proceeding with extensive reorganization of the entire organic ligand. Their inherent planar chirality has been exploited for the construction of new stereogenic centres in *exo*-metallacyclic positions. Future progress in the field could arise from the fact that analogous alkene–carbene complexes of ‘earlier’ transition metals such as chromium are also of sufficient configurational stability to allow *enantioselective* variants of their typical reactions. Alkyne insertion-intramolecular cyclopropanation of enantiopure starting complexes could for instance lead to oligo(-hetero-)cyclic products with as many as three new stereogenic centres built up at once.

4. Experimental

4.1. General information

All reactions were carried out under an atmosphere of argon. All solvents were dried according to literature procedures and freshly distilled under argon prior to use. The starting complexes were prepared as published. Melting points are uncorrected. IR: Perkin–Elmer 1420. NMR: JEOL GNM GX 400 FT; TMS as internal standard. MS: Varian MAT-CH-4B (EFO-4B-source; 70 eV). MA: Heraeus Mikromat C-H-N.

*4.2. (4Z)-[(4–5-η^2)-4,7-dimethyl-1-methoxy-2-oxa-8-oxo-4-decen-1-ylidene]tricarbonyliron(0) (**18b**)*

To a solution of *N*-cyclohexyl-*N*-isopropylamine (0.20 ml; 1.20 mmol) in THF (4 ml) at 0°C was added a 1.75 M solution of *n*-butyllithium in *n*-hexane (0.48 ml; 1.20 mmol). After 30 min this solution was cooled to −78°C and then treated with 3-pentanone (0.13 ml; 1.20 mmol). The resulting solution was slowly transferred by means of a cannula to a stirred slurry of the racemic allyl–carbene complex **16b** ($R^4 = CH_3$) (353 mg; 1.00 mmol)) in THF (2 ml), kept at −78°C. After 1 h the reaction mixture was quenched with 0.10 ml of a saturated aqueous NH_4Cl solution and then warmed up to room temperature (r.t.). Any volatile components were evaporated under vacuum, the remaining crude product was redissolved in a little diethyl ether and then quickly filtered over a short plug of silica gel. The resulting filtrate was concentrated at 0°C and the yellow oily product thus obtained finally dried on an oil pump and then characterized. It is thermally unstable and the spontaneous rearrangement to the corresponding diene complex is complete after 30 h at +4°C. Yield: 246 mg (70%), mixture of diastereoisomers. ^{13}C-NMR (C_6D_6): $\delta = 15.3/17.9$ (C10), 23.8/26.6/27.0 (4-Me, 7-Me), 31.3/35.9 and 37.0/38.1 (C6, C9), 48.8/49.2 (C7), 55.7/55.9 (C5), 57.2/57.3 (OMe), 66.5/67.1 (C4), 73.8/79.6 (C3), 212.3/214.7 (C8), 215.4 (Fe=CO), 261.1 (C1). IR (film): $\nu = 2965$ cm^{-1}, 2935, 2855, 2025, 1935, 1710, 1460, 1290. MS (70eV): m/z (%) = 324 (10) [M^+–CO], 296 (10) [M^+–2CO], 268 (20) [M^+–3CO], 236 (20) [*268*–MeOH], 210 (100), 152 (85), 140 (90), 56 (55), 28 (85). Anal. Calc. for $C_{15}H_{20}FeO_6$ (352.2): C, 51.16; H, 5.72. Found: C, 51.30; H, 5.79%.

*4.3. Aminolysis of **18b** to give (Z)-1-hydroxy-2,5-dimethyl-6-oxo-2-octene **33b***

A solution of freshly prepared alkene–carbene complex **18b** (245 mg; 0.70 mmol) in ether (2 ml) was chilled to −20°C and treated with liquid methylamine (0.50 ml). After 1 h the resulting reaction mixture was warmed up to r.t., all volatile components were removed on a BÜCHI rotavapor and the residue thus obtained was purified by column chromatography (silica gel 60; diethyl ether–hexane, 1:2, v/v). Yield: 78 mg (0.46 mmol; 65%) as a colourless oil; $R_f = 0.35$ (diethyl ether–hexane, 1:2, v/v). ^{1}H-NMR ($CDCl_3$): $\delta = 1.02$ [t, ^3J(7-H/8-H) = 7.3 Hz, 3H, 8-H], 1.09 [d, ^3J(5-Me/5-H) = 7.2 Hz, 3H, 5-Me], 1.78 (s, 3H, 2-Me), 2.01–2.08 (m, 2H, 4-H), 2.34–2.56 (m, 3H, 7-H, OH), 2.58–2.65 (m, 1H, 5-H), 3.97 [dd, ^3J(1-H/OH) = 4.9, ^2J(1-H/1-H′) = 11.6 Hz, 1H, 1-H], 4.21 [d, ^2J(1-H/1-H′) = 11.6 Hz, 1H, 1-H′], 5.17 [t, ^3J(3-H/4-H) = 7.7 Hz, 1H, 3-H]. ^{13}C-NMR ($CDCl_3$): $\delta = 7.9$ (C8), 16.8 (2-Me), 21.6 (5-Me), 31.0 (C7), 35.0 (C4), 46.2 (C5), 61.3 (C1), 124.9 (C3), 136.6 (C2), 215.6 (C6). IR (film): $v = 3430$ cm^{-1}, 2970, 2935, 1710, 1460, 1375, 1010. MS (70eV): m/z (%) = 152 (15) [$M^+ - H_2O$], 95 (30), 57 (100), 43 (35), 29 (50). Anal. Calc. for $C_{10}H_{18}O_2$ (170.3): C, 70.55; H, 10.66. Found: C, 70.65; H, 10.68%.

4.3.1. (±)-[(4–6-η^3)-1-methoxy-2-oxa-5,7-octadien-4-yl-1-ylidene]tricarbonyliron(II) tetrafluoroborate (*27a*)

A solution of tricarbonyl[(4–6-η^3)-2-oxa-1-oxo-5,7-octadiene-1,4-diyl]iron(II) (0.58 g; 2.20 mmol) [24] in dichloromethane (30 ml) was treated with trimethyloxonium tetrafluoroborate (0.36 g; 2.42 mmol) and then stirred at r.t. for 16 h. The solvent was removed on a rotary evaporator and the remaining solid purified by column chromatography. Impurities were first eluted with diethyl ether and then with acetonitrile–dichloromethane, 1:10, v/v. Pure product complex **27a** was finally washed off the column with acetonitrile–dichloromethane, 1:1, v/v. Yield: 480 mg (1.05 mmol; 60%) as yellowish solid; R_f (CH_3CN–CH_2Cl_2, 1:1, v/v) = 0.57; m.p. 115°C. ^{1}H-NMR (CD_3CN): $\delta = 4.14$ (s, 3H, OCH_3), 4.63 [dd, ^3J(5-H/6-H) = 12.65, ^3J(6-H/7-H) = 9.90 Hz, 1H, 6-H], 4.78 [dd, ^2J(3-H^{exo}/3-H^{endo}) = 12.65, ^3J(4-H/3-H^{endo}) = 2.20 Hz, 1H, 3-H^{endo}], 4.90 [dd, ^2J(3-H^{endo}/3-H^{exo}) = 12.65, ^3J(4-H/3-H^{exo}) = 6.05 Hz, 1H, 3-H^{exo}], 5.06 [ddd, ^3J(4-H/3-H^{exo}) = 6.05, ^3J(4-H/5-H) = 7.70, ^3J(4-H/3-H^{endo}) = 2.20 Hz, 1H, 4-H], 5.45–5.55 [m, 2H, 5-H, 8-H^{trans}], 5.83 [dd, ^3J(7-H/8-H^{cis}) = 16.50, ^2J(8-H^{trans}/8-H^{cis}) = 0.8 Hz, 1H, 8-H^{cis}], 6.25 [ddd, ^3J(7-H/6-H) = 9.90, ^3J(7-H/8-H^{cis}) = 16.50, ^3J(7-H/8-H^{trans}) = 6.60 Hz, 1H, 7-H]. ^{13}C-NMR (CD_3CN): $\delta = 63.6$ (OCH_3), 70.1 (C6), 77.2 (C3), 85.5 (C4), 94.6 (C5), 123.8 (C8), 137.2 (C7), 201.7/204.4/205.1 (FeCO), 247.2 (C1). FAB-MS: m/z 279 (100) [cation], 251 (20) [*279*–CO], 223 (15) [*279*–2CO], 195 (18) [*279*–3CO]. Anal. Calc. for $C_{11}H_{11}BF_4FeO_5$: C, 36.11; H, 3.03. Found: C, 36.21; H, 3.09%.

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **27a**

Atom	x	y	z	U_{eq} [a]
Fe(1)	−4738(1)	−3112(1)	−2127(1)	18(1)
C(1)	−4739(2)	−4323(2)	−2351(6)	29(1)
O(1)	−4720(1)	−5071(1)	−2484(5)	50(1)
C(2)	−3618(2)	−3030(2)	−3434(4)	26(1)
O(2)	−2936(1)	−2942(2)	−4327(3)	40(1)
C(3)	−4322(2)	−3205(2)	355(4)	23(1)
O(3)	−4085(2)	−3224(1)	1914(3)	34(1)
C(10)	−4712(2)	−1842(2)	−1819(5)	21(1)
O(10)	−5116(1)	−1312(1)	−3051(3)	27(1)
C(11)	−5503(2)	−1758(2)	−4742(5)	33(1)
C(12)	−5572(2)	−2743(2)	−4500(4)	26(1)
C(13)	−6157(2)	−3182(2)	−3166(5)	22(1)
C(14)	−6306(2)	−2888(2)	−1281(4)	21(1)
C(15)	−6774(2)	−3452(2)	169(4)	27(1)
C(16)	−7142(2)	−3135(2)	1778(5)	34(1)
O(20)	−4309(1)	−1451(1)	−376(3)	28(1)
C(20)	−4295(2)	−473(2)	−255(6)	36(1)
B(1)	−7856(2)	−5271(2)	−4957(6)	39(1)
F(1)	−6975(2)	−5150(1)	−4132(6)	92(1)
F(2)	−8356(2)	−4486(1)	−5028(4)	63(1)
F(3)	−8406(2)	−5898(1)	−4003(4)	65(1)
F(4)	−7705(2)	−5570(2)	−6824(5)	96(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

4.3.2. X-ray crystal structure determination of (±)-[(4–6-η^3)-1-methoxy-2-oxa-5,7-octadien-4-yl-1-ylidene]tricarbonyliron(II) tetrafluoroborate (*27a*)

Clear, yellow single crystals were obtained by slowly cooling a solution of **27a** in diethyl ether–dichloromethane to 0°C; formula $C_{11}H_{11}BF_4FeO_5$, molar mass 365.86 g mol^{-1}, crystal size 0.35 × 0.35 × 0.35 mm, $a = 13.7951(2)$, $b = 15.0804(4)$, $c = 6.9617(4)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 1448.28(9)$ Å^3, $T = 173(2)$ K, $d_{calc} = 1.678$ g cm^{-3}, $\mu = 1.104$ mm^{-1}, $Z = 4$, orthorhombic, space group $Pna(1)$, Nonius Mach 3 diffractometer, $\lambda = 0.71073$ Å, Θ-range 2.00–25.04°; ω–Θ-scans, index ranges $-16 \leq h \leq 16$, $-17 \leq k \leq 17$, $-8 \leq l \leq 8$, 2461 collected reflections, 2381 independent reflections [$I > 2\sigma(I)$], 244 refined parameters, absorption correction by ψ-scans. Structure solution: direct methods (SHELXS-97), structure refinement: full-matrix least-squares on F^2 (SHELXL-97), H atoms calculated and not included into least-squares refinement, $R_1 = 0.0261$ [$w = 1/\sigma^2(F_0)$], $wR_2 = 0.0655$ (all data), largest difference peak and hole 0.309 and −0.309 e Å^{-3} (Table 1).

4.4. X-ray crystal structure determination of (±)-E-[(4–6-η^3)-3-methoxycarbonyl-2,5-hexadiene-4-yl]tricarbonyliron(II) tetrafluoroborate (*49*) [24]

Clear, yellow single crystals were obtained by slowly cooling a solution of **49** in dichloromethane to −18°C; formula $C_{11}H_{11}BF_4FeO_5$, molar mass 365.86 g mol^{-1}, crystal size 0.50 × 0.46 × 0.33 mm, $a = 7.9287(17)$, $b = 9.322(2)$, $c = 10.237(2)$ Å, $\alpha = 107.329(3)°$, $\beta =$

Table 2
Atomic coordinates ($\times 10^3$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **49**

Atom	x	y	z	U_{eq} [a]
F11	888.7(4)	80.5(3)	301.7(3)	105.0(11)
F12	808.3(4)	306.2(3)	410.5(2)	76.3(9)
F13	875.6(4)	266.1(5)	197.6(3)	124.7(16)
F14	644.0(3)	154.5(3)	229.2(3)	63.4(8)
B1	806.1(4)	201.3(4)	283.8(3)	36.9(9)
Fe1	707.41(4)	188.43(3)	−162.74(3)	23.2(1)
O6	735.1(2)	369.53(18)	−228.59(16)	24.4(5)
O7	616.8(2)	510.40(19)	−349.10(17)	27.8(5)
O11	525.5(3)	373.9(2)	68.6(2)	44.5(7)
O12	687.1(3)	−70.0(2)	−56.6(2)	46.2(7)
O13	068.9(3)	246.7(3)	−58.7(2)	50.5(8)
C1	759.7(3)	70.4(3)	−369.3(3)	31.2(7)
C2	591.9(3)	43.8(3)	−344.4(2)	29.6(7)
C3	474.3(3)	156.6(3)	−293.6(2)	27.1(7)
C4	458.1(3)	301.4(3)	−325.3(2)	24.9(6)
C5	614.0(3)	396.3(3)	−300.2(2)	23.3(6)
C8	768.7(4)	608.3(3)	−312.6(3)	34.8(8)
C9	312.2(3)	359.6(3)	−357.4(2)	27.9(7)
C10	139.1(3)	289.4(3)	−368.4(3)	34.6(8)
C11	598.9(3)	303.3(3)	−16.0(2)	29.5(7)
C12	693.4(3)	29.6(3)	−98.2(3)	31.3(7)
C13	931.4(3)	222.1(3)	−97.7(3)	33.5(8)
H1A	826(4)	−16(4)	−394(3)	34(8)
H1B	793(4)	150(4)	−401(3)	30(7)
H2	559(4)	−56(4)	−337(4)	42(9)
H3	375(4)	123(4)	−260(3)	36(8)
H8A	861(5)	556(4)	−362(4)	47(10)
H8B	802(5)	635(4)	−211(4)	53(10)
H8C	742(5)	696(4)	−341(4)	47(9)
H9	317(4)	458(4)	−370(3)	33(8)
H10A	138(4)	193(4)	−351(3)	38(8)
H10B	75(5)	290(5)	−465(4)	61(11)
H10C	72(5)	358(4)	−304(4)	48(10)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

93.870(3)°, $\gamma = 90.963(4)°$, $V = 720.1(3)$ Å^3, $T = 153(2)$ K, $d_{calc} = 1.687$ g cm^{-3}, $\mu = 1.111$ mm^{-1}, $Z = 2$, triclinic, space group $P\bar{1}(2)$, Nonius Mach 4 diffractometer, $\lambda = 0.71073$ Å, Θ-range 2.09–28.06°; ω–Θ-scans, index ranges $-10 \leq h \leq 10$, $-12 \leq k \leq 11$, $-13 \leq l \leq 12$, 3120 collected reflections, 2938 independent reflections [$I > 2\sigma(I)$], 243 refined parameters, absorption correction by ψ-scans. Structure solution: direct methods (SHELXS-97), structure refinement: full-matrix least-squares on F^2 (SHELXL-97), mixed H treatment, $R = 0.0448$ [$w = 1/\sigma^2(F_0)$], $wR = 0.1228$, largest difference peak and hole 0.89 and -0.69 e Å^{-3} (Table 2).

*4.5. Hydride-induced rearrangement of **16b** (R^4 = Me) to (±)-tricarbonyl[(3–6-η^4)-(2H)pyran]iron(0) (**51**)*

A solution of 2,3-dihydrofuran (0.11 ml; 1.20 mmol) in THF (2 ml) at −78°C was treated with a 1.7 M solution of *t*-butyllithium in hexane (0.70 ml; 1.20 mmol). After 30 min the resulting mixture was allowed to warm to r.t. and then treated with a 1 M solution of triethylborane in THF (1.50 ml; 1.50 mmol). The solution thus obtained was recooled to −78°C and then added dropwise via a cannula to a slurry of complex **16b** (353 mg; 1 mmol) in THF (2 ml) kept at the same temperature. Stirring was continued for another hour and the reaction mixture was finally warmed up to r.t. again. All volatile components were removed in vacuo and the resulting residue purified by column chromatography (silica gel; diethyl ether–hexane, 1:2, v/v). Yield: 200 mg (85%) of **51** as a yellow oil. R_f (diethyl ether–hexane, 1:2, v/v) = 0.85. ^{1}H-NMR (CDCl$_3$): δ = 1.65 (s, 3H, CH$_3$), 3.32 [d, ^2J(2-H/2-H′) = 11.6 Hz, 1H, 2-H], 3.37 [d, ^2J(2-H/2-H′) = 11.6 Hz, 1H, 2-H′], 4.66 [dd, ^3J(4-H/5-H) = ^3J(5-H/6-H) = 3.6 Hz, 1H, 5-H], 5.42 [d, ^3J(4-H/5-H) = 3.6 Hz, 1H, 4-H], 5.76 [m, 1H, 6-H]. ^{13}C-NMR (CDCl$_3$): δ = 20.6 (CH$_3$), 68.1 (C5), 68.7 (C2), 74.0 (C3), 85.8 (C4), 101.5 (C6), 211.5 (FeCO). IR (film): ν = 2960 cm^{-1}, 2860, 2040, 1970, 1730, 1160. MS: m/z 236 (22) [M$^+$], 208 (73) [*236*–CO], 180 (20) [*236*–2CO], 152 (100) [*236*–3CO]. Anal. Calc. for $C_9H_8FeO_4$: C, 45.80; H, 3.42. Found: C, 45.85; H, 3.40%.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 149753 for compound **27a** and CCDC no. 148835 for compound **49**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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