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The Reincarnation of the Hieber Anion $[Fe(CO)_3(NO)]^-$ – a New Venue in Nucleophilic Metal Catalysis

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Nowadays demand for selective, energy-efficient, and sustainable chemical transformations has spurred an increasing interest in the development of "sustainable metal catalysis". This expression defines a type of catalytic transformation in which non-toxic, readily available and inexpensive, stable metal complexes are used for catalysis. The increasing prices for energy and noble metals, which are commonly used for catalysis, represent an economical and ecological dilemma. If the price for a catalyst exceeds the savings on the energy side an industrial application does not make sense. As a consequence of this dilemma, chemists are looking for exit strategies with catalysis by small organic molecules (*organocatalysis*) or by inexpensive, readily available metal complexes (*sustainable metal catalysis*) being the most prominent ones. It is an irony that these two major catalytic strategies are based on research that had been initiated several decades ago but was somehow forgotten. In the present Microreview, the story of the reincarnation of another forgotten metal complex species, that celebrates its 50th birthday this year, will be told, the $[Fe(CO)_3(NO)]^-$ anion.

Introduction

Transition metal catalysis has become an important synthetic tool in current organic chemistry.[1] The use of only small amounts of a catalytically active metal complex often allows for new and unknown bond-forming processes and hence for more efficient syntheses of complex molecular architectures. Most catalytic processes, however, rely on the use of catalysts based on late transition metals with Pd, Rh, Ru, Os, and Ir being the most popular. The increase in the price for energy has spurred a growing interest in the application of catalytic transformations on an industrial scale in order to cut down the overall energy costs. As a consequence the increasing demand tals (Table 1).

Table 1. Price increase for late transition metals from 2000 to 2008.[2]

Metal	Price [US$/ounce][a] in 2000	in 2008[b]	Price increase [%]
Gold	280	920	+ 228
Palladium	681	441	–35
Platinum	544	1900	+ 249
Rhodium	1993	8533	+ 328

[a] Data taken from https://online.kitco.com. [b] Price in June, 2008.

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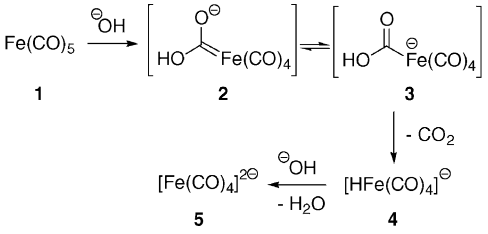
André Dieskau (right) studied chemistry in Stuttgart, Germany (2002–2004), and Strasbourg, France (2004–2006), attending the German-French double diploma study course. After working on his diploma thesis under the supervision of Bernd Plietker, he obtained his diploma from the Universität Stuttgart and from the Ecole de Chimie, Polymères et Matériaux, Strasbourg, in 2007. He is a fellow of the Studienstiftung des Deutschen Volkes and was awarded the Arthur Fischer prize 2008 by the Department of Chemistry, Universität Stuttgart. Since spring 2008, he is working toward his dissertation in the field of iron catalysis and natural product synthesis.

This development represents a serious drawback for the application of energy-saving and selective catalytic processes based on the use of late transition metals like Pd, Rh, Ru, Ir, etc. If the catalyst costs outcompete savings on the energy side, a catalytic process is not attractive for large-scale applications. In order to circumvent the problems connected with rare and expensive late transition metal complexes, the use of abundant, non-toxic and inexpensive metals as catalytically active species, like e.g. iron, could serve as a suitable alternative.[3] However, despite its advantages, reactions involving Fe-based catalysts have received less attention compared to their higher (and more expensive) homologues. This historical fact is surprising for three reasons: (i) the chemistry of iron complexes is one of the most intensively explored fields in organometallic chemistry;[4] (ii) Fe-catalysed organic reactions are ubiquitous in Nature;[5] and (iii) the first Fe-catalysed non-biomimetic transformations were already described in the early 1960s of the last century. It will remain as one of the "catalytic mysteries" why Fe catalysis has almost fallen into oblivion since then.

In the present Microreview, the chemistry of the $[Fe(CO)_3(NO)]^-$ anion will be summarized as one prominent example for the reincarnation of a potent catalytically active metal complex in organic synthesis. Starting from the origins of this chemistry, the article tries to cover the span up to the most recent applications of this complex in nucleophilic metal catalysis.

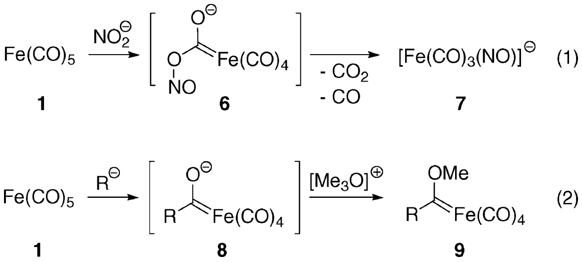
Application of the Hieber Base Reaction

The story of the $[Fe(CO)_3(NO)]^-$ anion began some 80 years ago when Walter Hieber reported and confirmed earlier reports[6–8] on the formation of nucleophilic carbonylmetalates from carbonylmetal compounds in the presence of hydroxide anions ("*the Hieber base reaction*").[9] The nucleophilic addition of hydroxide to a carbonyl ligand and the subsequent extrusion of CO_2 with simultaneous reduction of the metal centre opened a new field in organometallic chemistry that had a major influence on catalysis. Application of the Hieber base reaction to e.g. $Fe(CO)_5$ (**1**) yields the well-known $[Fe(CO)_4]^{2-}$ dianion (**5**; Scheme 1).[10]



Scheme 1. Simplified mechanism of the "Hieber base reaction".

The chemistry of tetracarbonylferrate has been extensively studied.[11–13] This anion exhibits a high degree of electron density on the metal centre, which makes it a very strong nucleophile.[14] This property has attracted the attention of organic chemists almost 40 years ago.[15] In particular, the seminal contributions by Collman[13,14,16] demonstrated the synthetic utility of these anions ("Collman's reagent"). Apart from hydroxide, different nucleophiles are amenable to the reaction. Thirty years after his initial report on the alkaline reduction of carbonylmetal compounds, Hieber reported an interesting extension of this reaction based upon some prior results patented by Hogsed.[17,18] The use of nitrite as an oxygen-centred nucleophile leads to a different reaction course, in which a CO ligand is exchanged for an NO ligand with simultaneous reduction of the metal atom [Equation (1), Scheme 2]. Although the resulting nitrosyl complex **7** might be considered as a nitrosyl analogue of "Collman's reagent", it has received considerably less attention. This particularly noteworthy complex **7** is more stable and less toxic than tetracarbonylferrate (**5**).

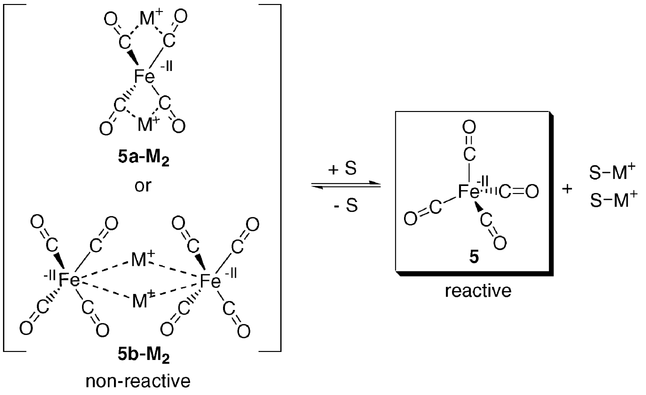


Scheme 2. Simplified mechanisms for the application of the Hieber base reaction to the formation of nitrosyl and carbene complexes from $Fe(CO)_5$.

Later, E. O. Fischer, a former student of Walter Hieber, developed the first practical synthesis of stable (carbene)-metal complexes based upon this reductive decarbonylation mechanism. He observed that, whereas oxygen-centred nucleophiles react with e.g. $Fe(CO)_5$ according to a decarbonylation/reduction pathway, softer, carbon-centred nucleophiles undergo a 1,2-addition to give metallaenolates. These can be trapped by strong alkylating reagents, e.g. Meerwein salt, to give Fischer-type carbene complexes of iron [Equation (2), Scheme 2].[19] The higher electron density at the metal centre makes these complexes more reactive and less stable than the much better investigated chromium counterparts.[20]

Structure and Reactivity of $[Fe(CO)_3(NO)]^-$

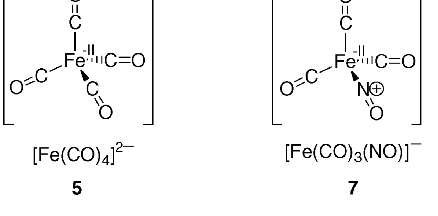
There are numerous investigations on the structure of tetracarbonylferrate by means of ESR,[21] Raman spectroscopy,[22] IR spectroscopy,[23] X-ray crystallography,[24] and quantum mechanical calculations.[25] Complexes of the type $M_2[Fe(CO)_4]$ are diamagnetic and exhibit a remarkable structural dependency on the metal cation M. In nonpolar solvents (THF etc.), a strong distortion of the ferrate from the expected tetrahedral configuration is observed due to a coordination of the metal cation M to the carbonyl carbon atoms (Scheme 3).



Scheme 3. Structures of $M_2[Fe(CO)_4]$ in different solvents (S: coordinating solvent, cryptand etc).

These contact ion pairs show a low reactivity in most organic reactions. In contrast to this, the use of stronger coordinating solvents (NMP, DMF etc.), a cryptand for complexation of the metal cation M, or a non-coordinating cation leads to the formation of separated ion pairs with the ferrate having an almost perfect tetrahedral configuration (Fe–CO bond length: 1.76 Å; OC–Fe–CO angle: 109.5°; O=C–Fe angle: 180°).[24,25] With these results in hand the observed rate acceleration in organic reactions, in which the ferrate acts as a nucleophile, is explainable. The additional coordination of the metal atom M to the carbonyl ligands or to the iron atom decreases the electron density at the iron centre and hence its nucleophilicity (Scheme 3).[26]

Similar detailed structural analyses for complexes of the general type $M[Fe(CO)_3(NO)]$ have been carried out.[27] IR spectroscopic investigations indicated a similar solvent-dependent behaviour of these complexes as described above for the carbonylferrate **5**.[28] In nonpolar solvents like THF, two distinct sets of CO and NO absorption signals are observed indicating that a mixture of tight and solvent-separated ion pairs coexist. Addition of a crown ether or a more polar, coordinating solvent leads to a single pattern attributable to a solvent-separated ion pair. The same researchers reported more investigations (X-ray crystallography, NMR and IR spectroscopy) on the structure and reactivity of $M[Fe(CO)_3(NO)]$ in solution and in the solid state and compared them to the results obtained by Bau for the related $M_2[Fe(CO)_4]$.[29] Although the disorder of the anion in the crystal packing does not allow for a clear definition of bond lengths and angles, the average values for the $[Fe(CO)_3(NO)]^-$ anion are of a similar size to those observed for the $[Fe(CO)_4]^{2-}$ dianion. The similarity of the measured parameters for both ferrate complexes suggests a structural analogy, i.e. the anions possess a tetrahedral configuration in a solvent-separated ionic form. Furthermore, the close similarity for both complexes indicates the nitrosyl ligand bound end-on with an Fe–N=O angle close to 180° (Scheme 4).[29]



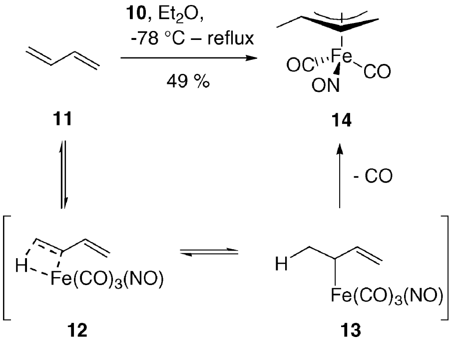
Scheme 4. Structure of $[Fe(CO)_4]^{2-}$ and $[Fe(CO)_3(NO)]^-$ in polar, coordinating solvents.

Organic Transformations Involving $[Fe(CO)_3(NO)]^-$

The reactivity of $M[Fe(CO)_3(NO)]$ depends largely on the nature of the counter cation M and on the nature of the ferrate. As pointed out above, the solvent is the reactivity-determining parameter. Little effort has so far been spent on varying the cation. In general, sodium or tetraalkylammonium cations are used. The high electron density at the iron centre in the anionic counterpart makes the metal complex both nucleophilic and basic.[30] As a consequence, reactions involving $M[Fe(CO)_3(NO)]$ can be divided according to the complex reacting as a base or as a nucleophile.

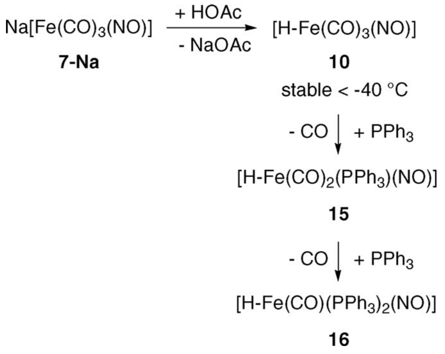
Reactions Involving $[HFe(CO)_3(NO)]$

The hydridoferrate $[HFe(CO)_3(NO)]$ (**10**) is readily accessible by protonation of the sodium salt with acetic or trifluoroacetic acid.[18] Due to the high electron density at the metal centre, this reaction might be regarded as a two-electron reduction of the proton with the hydrogen atom exhibiting a hydride character. An interesting application of $[HFe(CO)_3(NO)]$ (**10**) was reported by Chaudhari: The in situ preparation of the metal hydride according to Hieber's procedure[18] in the presence of 1,3-butadiene yielded the corresponding (π-allyl)iron complex **14** through hydrometallation (Scheme 5).[31]



Scheme 5. Hydrometallation by using $[HFe(CO)_3(NO)]$.

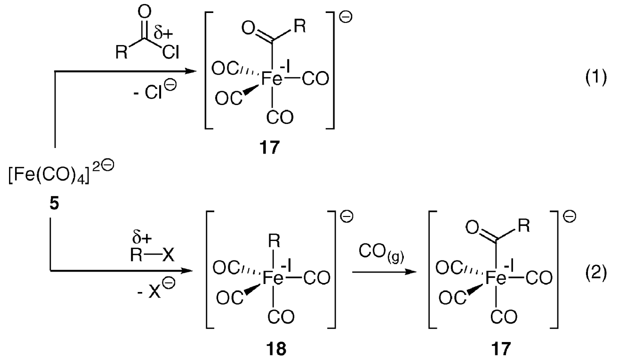
Isolation of the active iron hydride species **10** has not been achieved yet. However, addition of phosphane ligands leads to a stable hydridoiron complex (Scheme 6).[32] Use of an excess of PPh_3 yields the bis(phosphane) adduct **16**. For the latter complex detailed X-ray crystallographic, IR and NMR spectroscopic investigations have been performed indicating the hydrogen atom to be bound to the iron centre.[33]



Scheme 6. Formation of hydridoiron complexes by protonation.

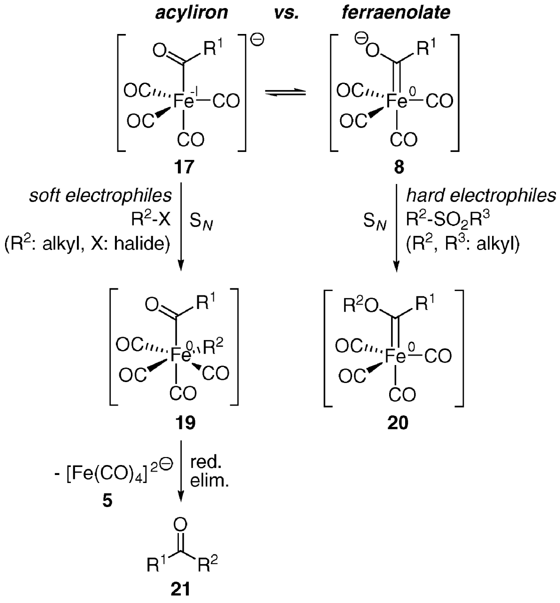
Reactions Involving Acyliron Complexes

Reactions of $M_2[Fe(CO)_4]$ to give acyl complexes have been investigated almost 40 years ago by Tsutsumi and coworkers for the potassium salt.[34] This pioneering work was followed up by Collman's seminal contributions on the use of the sodium salt as a stoichiometric reagent in organic synthesis.[13,14,16] The complexes are stable and easily accessible by nucleophilic displacement of chloride in the reaction of a carboxylic chloride **17** and ferrate **5** [Equation (1), Scheme 7]. Alternatively, nucleophilic displacement of a halide in alkyl halides followed by insertion of a CO ligand in the presence of CO gas yields acyl complexes like **17** [Equation (2), Scheme 7]. Another way to prepare acylferrates starting from Fe^0 is shown in Equation (2), Scheme 2. 1,2-Addition of alkyl- or aryllithium or -magnesium halides to one CO ligand in $Fe(CO)_5$ yields a ferraenolate **8** that might also be regarded as an acyliron complex in its tautomeric form (Scheme 8).



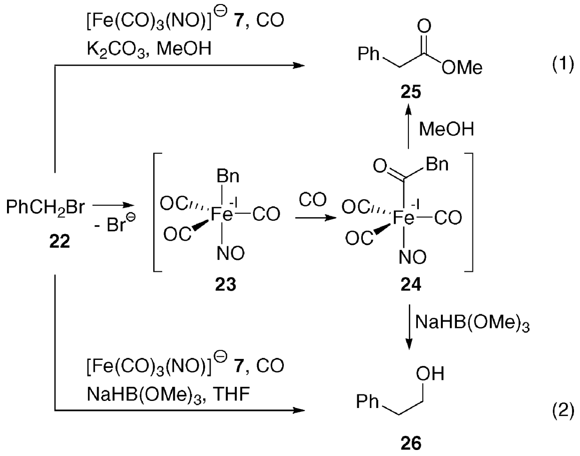
Scheme 7. Preparation of acyliron complexes.

These complexes are ambident nucleophiles. Whereas the acyl species might be regarded as a metal-centered "soft" nucleophile, in which the iron atom possesses a formal oxidation state of –I (comparable to the α-carbon atom in classical enolate chemistry), the enolate structure **8**, in which the negative charge is located on the oxygen atom, acts as a "hard" nucleophile. This paves the way for two distinct mechanistic pathways: Exposing the acyliron species to "soft" electrophiles, e.g. alkyl halides, yields non-symmetrical ketones **21** by a second nucleophilic displacement of the leaving group X through the nucleophilic Fe^{-I} centre followed by reductive elimination.[13–16,34,35] On the other hand, exposure of the acyliron complex to hard electrophiles leads to *O*-alkylation and the formation of Fischer-type carbene complexes **20**.[19,36]



Scheme 8. Acyliron complexes as ambident nucleophiles.

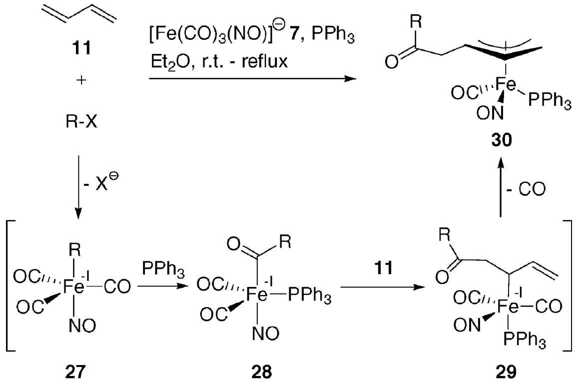
Similar to the tetracarbonylferrate, the Hieber anion $[Fe(CO)_3(NO)]^-$ (**7**) is known to form unstable acyliron complexes upon reaction with acyl chlorides [similar to Equation (1), Scheme 7].[31] Although addition of PPh_3 stabilizes these complexes by ligand exchange,[31] further studies by Eberhardt revealed these complexes to have a complex follow up chemistry leading to bi- or even trinuclear Fe clusters with the acyl group acting in part as a bridging ligand.[37] As for the tetracarbonylferrate, preparation of the acyliron species can also be performed by nucleophilic substitution/carbonylation starting from aliphatic halides. The resulting complexes are useful intermediates for a variety of transformations with the reaction in the presence of alk-



Scheme 9. Preparation and reactions involving acyl(nitrosyl)iron complexes.

oxide being the most prominent [Equations (1) and (2), Scheme 9].[38]

Chaudhari reported an interesting application of this type of complex. Formation of an acyliron species was followed by acyl metallation of a C=C bond in e.g. 1,3-butadiene to give the (π-allyl)Fe complex **30** upon decarbonylation (Scheme 10).[31]



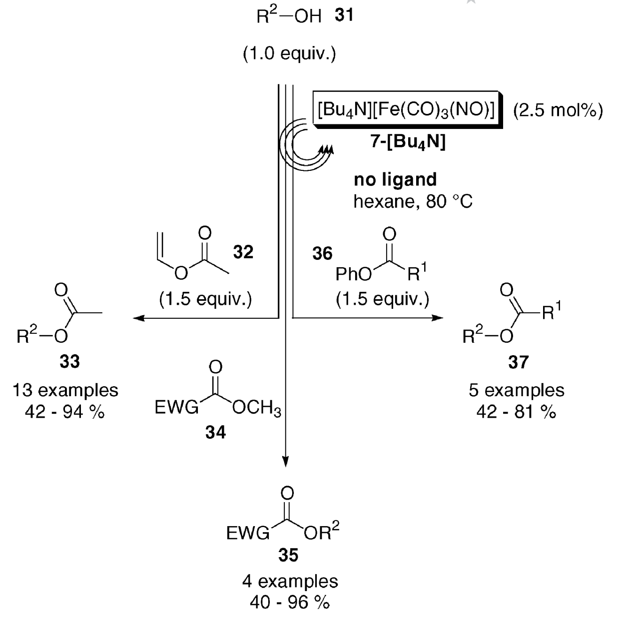
Scheme 10. Acylmetallation of 1,3-dienes.

It has to be emphasized that the mechanisms shown above are simplified. Eberhardt's work indicated the presence of more complex metal species in the reaction of $[Fe(CO)_3(NO)]^-$ with alkyl or acyl halides. Detailed mechanistic investigations have not been reported to date.

The fact that most of the reactions, in which the salt $M[Fe(CO)_3(NO)]$ is involved, are stoichiometric transformations is somewhat surprising if one considers the active species is in principal regenerated, for example under the conditions shown in Equations (1) and (2), Scheme 9. With this idea in mind, we recently started a project aiming to develop transformations, in which the *ferrate complex* **7** *is used as a catalyst*. Our attempts were guided by the following facts:

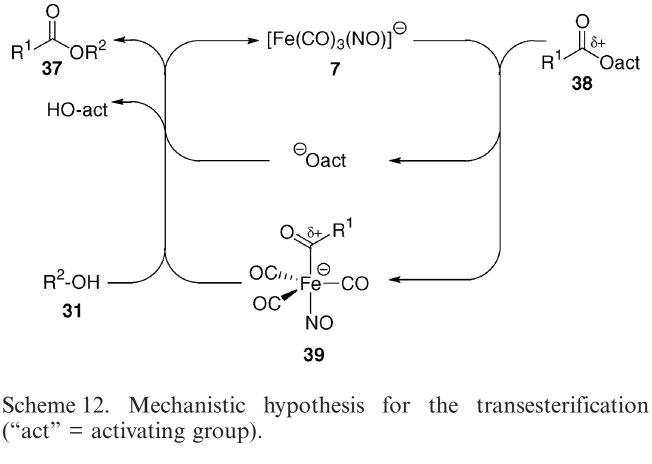
- The solvent has a strong influence on the activity. In polar aprotic solvents, a solvent-separated ion pair is present, in which the ferrate displays the highest degree of nucleophilicity.
- In nonpolar solvents the cation might coordinate to the iron centre or to the CO ligands.
- In most stoichiometric reactions, the iron atom is oxidized in intramolecular SET events. However, in the final step of the mechanism, a one-electron reduction takes place, thus regenerating the active Fe^{-II} complex.
- PPh_3 can act as suitable substitute for CO.

Hence, we turned our attention toward the development of a catalytic reaction involving acyliron complexes as reactive intermediates. We envisioned the reported low stability of these complexes to result in an increased reactivity, which therefore translates into a catalytic turnover. As a proof of concept we chose the transesterification as the model reaction. Gratifyingly, we found the catalyst to be highly active in the transesterification under neutral conditions.[39] Various acyl donors **32**, **34**, **36** can be used to give rise to diverse substituted carboxylic esters **33**, **35**, **37** in good to excellent yields (Scheme 11).



Scheme 11. Iron-catalysed transesterification.

The addition of phosphane ligands led to an inhibition of the catalytic system, which is in good agreement with the literature results, in which it was shown that acyliron complexes form di- or even trinuclear complexes upon addition of phosphane ligands.[40] Furthermore, evidence for a strong solvent effect was obtained. The reactions are best performed in a nonpolar solvent, e.g. hexane, that favours the formation of contact ion pairs. Good reaction rates were also obtained in polar coordinating solvents (DMF, NMP). A comparison of the kinetics, however, points in the direction of two different mechanisms taking place. Whereas in DMF, a solvent-separated ion pair and hence a solely nucleophilic catalyst is active, the contact ion pair present in the nonpolar solvent might act both as a Lewis acidic and Lewis basic catalyst. Although the mechanism awaits further investigations, a preliminary model has been proposed (Scheme 12). With regard to the plethora of transformations mediated by acyliron complexes derived from $M_2[Fe(CO)_4]$ or $M[Fe(CO)_3(NO)]$, these results open up a

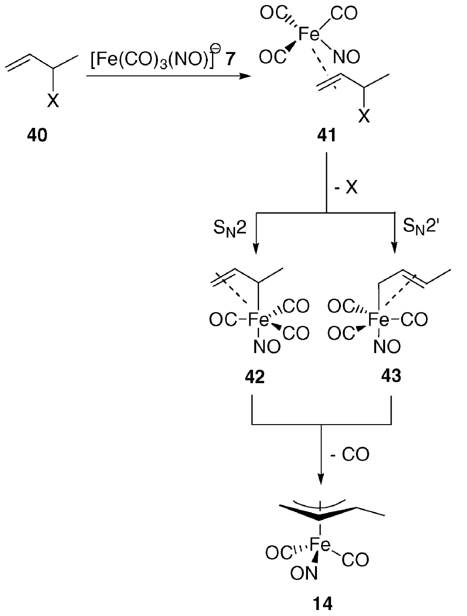


Scheme 12. Mechanistic hypothesis for the transesterification ("act" = activating group).

new field in catalysis by using them as reactive intermediates. However, at the current state of research a thorough mechanistic investigation is of utmost importance.

Reactions Involving Allyliron Complexes

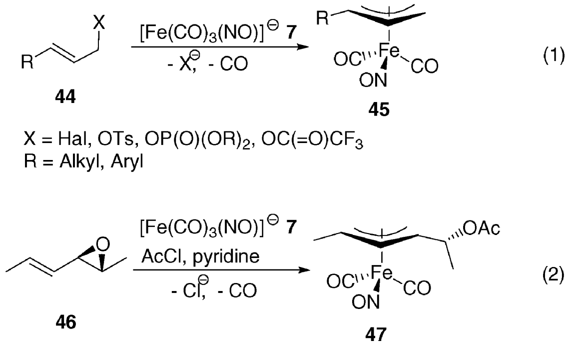
Allyliron complexes have been known for a long time and found widespread applications in organic synthesis.[41] Their major advantage is the stability, which allows their simple purification by column chromatography or distillation. Furthermore, they exhibit a dichotomous character by acting as both nucleophiles and electrophiles. The synthesis is thought to involve an initial π-coordination of the Hieber anion **7** to the double bond of the reacting substrate **40** (Scheme 13). Nucleophilic displacement of the leaving group proceeds in an S_N2 or S_N2' manner to afford the two regioisomeric (σ-allyl)Fe species **42** and **43**. Subsequent CO extrusion furnishes the corresponding (π-allyl)Fe complex **14**.



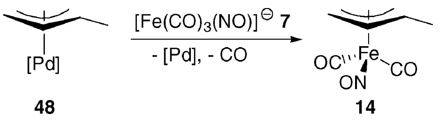
Scheme 13. General schematic pathway for the formation of (π-allyl)Fe complexes.

Several methods for the preparation of (π-allyl)Fe complexes have been published. The classical procedure is to treat the nucleophilic iron complex **7** with an allylic substrate **44** bearing a leaving group X. Usually, allylic halides, tosylates, phosphonates, and trifluoroacetates have been used [Equation (1), Scheme 14].[31,42] Moreover, vinyl epoxides like **46** are suitable substrates to form (π-allyl)Fe complexes of type **47** after trapping the alkoxide in situ with an acyl chloride [Equation (2), Scheme 14].[43]

Besides that, transmetallation has proven to be a valuable tool for the preparation of (π-allyl)Fe complexes. Nakanishi showed that reaction of (η^3-allyl)PdBr complexes like **48** with anion **7** afforded the corresponding (π-allyl)Fe complexes **14** (Scheme 15).[44]

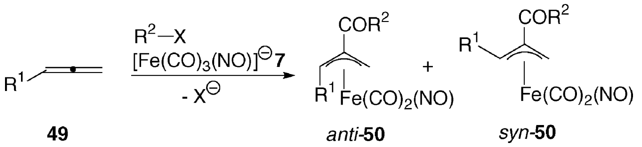


Scheme 14. Preparation of (π-allyl)Fe complexes by S_N2' reaction.



Scheme 15. Preparation of (π-allyl)Fe complexes by transmetallation.

Following up Chaudhari's work (Scheme 10),[31] Nakanishi reported the corresponding acylmetallation of 1,2-dienes leading to π-allyl complexes **50** (Scheme 16).[45] The reaction is believed to proceed via an intermediate acyliron complex like **24**, which then adds to the allene **49**.

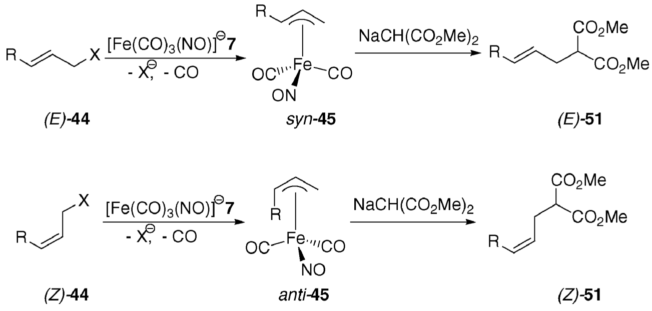


Scheme 16. Preparation of (π-allyl)Fe complexes by acylmetallation.

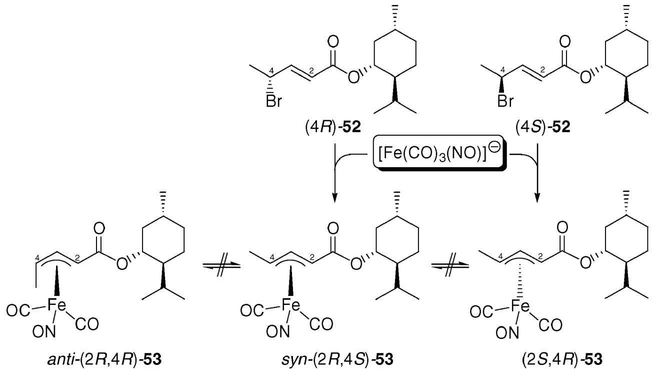
The allyl complexes **50** are formed with high *anti* selectivity due to steric interactions between the acyliron complex and the substitutents on the allene moiety. The observed regioselectivity is similar to that of the reaction of acylcobalt complexes with allenes.[46]

The structural integrity of the (π-allyl)Fe complexes is certainly one of the most intriguing characteristics and was investigated in detail by Eberhardt and Mattern (Scheme 17). They were able to show that (*syn*- or *anti*-π-allyl)Fe complexes, which are easily accessible starting from the corresponding (*Z*)- or (*E*)-allyl mesylates (*Z*)-**44**, (*E*)-**44**, are stable towards isomerization.[47] Subsequent reaction with sodium malonate as a nucleophile delivered the linear substitution products (*E*)-**51** and (*Z*)-**51** with the configuration of the double bond being conserved (Scheme 17).

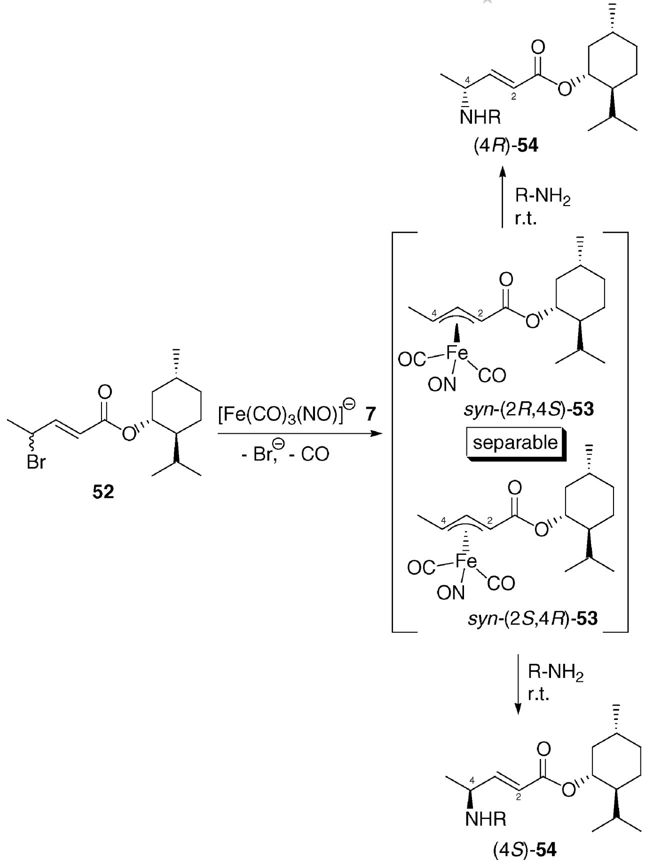
These initial results were later confirmed by the Nakanishi group.[42b] Their report focused on the properties of planar chirality in complexes of type (π-allyl)Fe(CO)$_2$(NO). The diastereoisomeric complexes **53** were chosen, due to their clearly distinguishable ^{1}H NMR spectra (Scheme 18). ^{1}H NMR spectra were recorded in a temperature range between –60 and +60 °C indicating no isomerization of the π-bond geometry or the planar chirality of the allyl ligand.



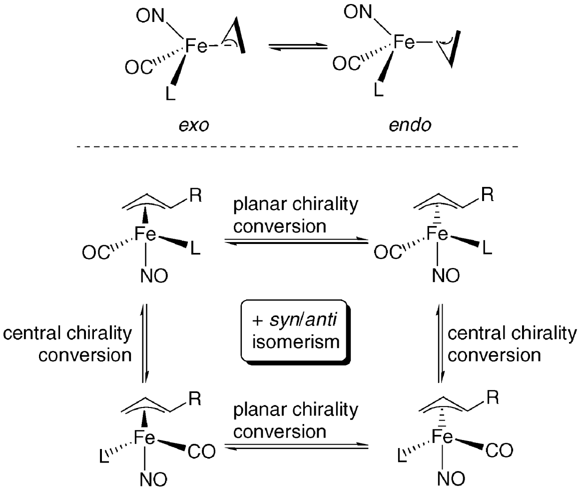
Scheme 17. Preparation of (*E*)- or (*Z*)-olefins by using stable (π-allyl)Fe complexes.



Scheme 18. Configurational stability of (π-allyl)Fe complexes **53** in solution.



Scheme 19. Diastereoselective amination of (π-allyl)iron complexes.



Scheme 20. Elements of chirality in (π-allyl)Fe(CO)(NO)L complexes.

The structural integrity and stability of (π-allyl)Fe complexes can be used for stereoselective synthesis. Treatment of a racemic mixture of γ-brominated α,β-unsaturated carboxylic (–)-menthyl esters **52** with **7** yields a diastereomeric mixture of (π-allyl)Fe complexes **53**, which can be separated by column chromatography. The isomerically pure complexes undergo nucleophilic substitutions, e.g. by reaction with amines (Scheme 19).[48] The regioselective course of the amination is mainly directed by electronic and steric factors. Depending on the nature of the leaving group and of the solvent a matched/mismatched stereodiscrimination was observed.[49]

Apart from the stability of (π-allyl)Fe complexes toward isomerization the change of one CO ligand by another monodentate ligand L, e.g. PPh_3, allows for the introduction of metal-centred chirality apart from the allyl ligand with its classical features (e.g. *endo*/*exo* and *syn*/*anti* isomerism, planar chirality) (Scheme 20).

An important result was reported by Brunner and coworkers who demonstrated that the Fe centre in (π-allyl)(carbonyl)(nitrosyl)(phosphane)iron complexes exhibits configurational stability up to 120 °C.[50] Furthermore, to elucidate the structural behaviour of these complexes in solution, temperature-dependent NMR techniques and in-situ IR techniques were applied by several research groups. Cardaci and Foffani reported[42a] that treatment of (1-H-, 1-Me-, 1-Ph- or 2-Me-allyl)$(CO)_2(NO)$Fe with a phosphane ligand leads to the formation of a *symmetrical* (π-allyl)(CO)(NO)(PR_3)Fe complex. In contrast, complexes of type (1-Cl-, 2-Cl-, 3-Cl-, 2-Br-, 2-CN-allyl)$(CO)_2(NO)(PR_3)$Fe produced by the same procedure present a five-coodinated iron centre in a pseudo-trigonal-bipyramidal geometry bearing a σ-bound allyl ligand. This was indicated by the appearance of a C=C stretching absorption at 1590–1620 cm^{-1} in the IR spectra. These results are supported by the contribution of Eberhardt and Mattern who reported the molecular structure of (1-Me-allyl)(CO)(NO)(PPh_3)Fe

(**55**) by using X-ray crystal structure analysis as shown in Figure 1.[47] The bond lengths from the metal atom to the two terminal carbon atoms (C2 and C4) of the allyl moiety are nearly equal (216.4 and 216.0 pm), and similar C–C bond lengths are present in the allyl ligand (C2–C3: 137.7 pm; C3–C4: 141.0 pm). This unambiguously proves a π-coordination of the allyl ligand to the metal centre. Similar results were reported by Nakanishi later on.[42b] Both publications have in common that complexes of type (π-allyl)(CO)(NO)(PPh$_3$)Fe present an *endo* conformation in the solid state – the allyl moiety points away from the NO ligand (cf. Figure 1).

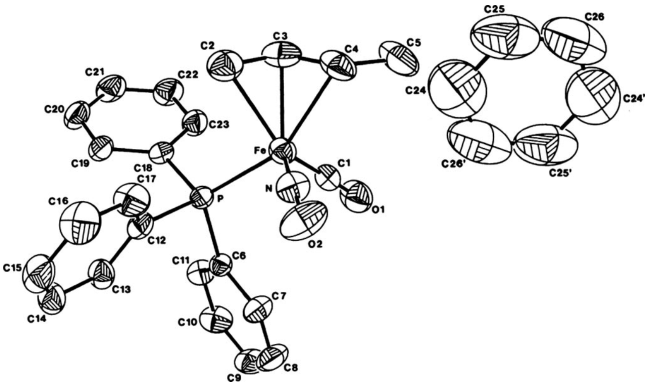
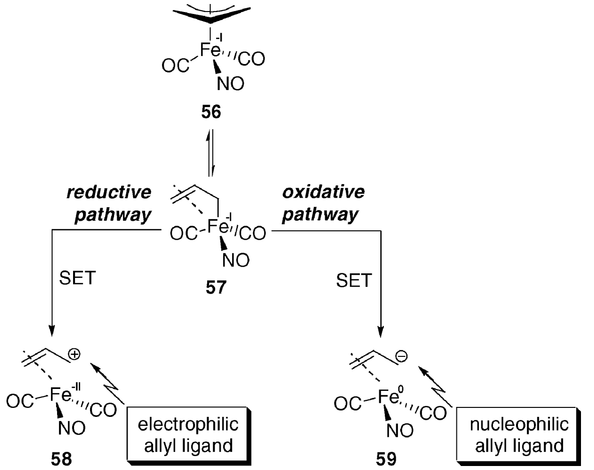


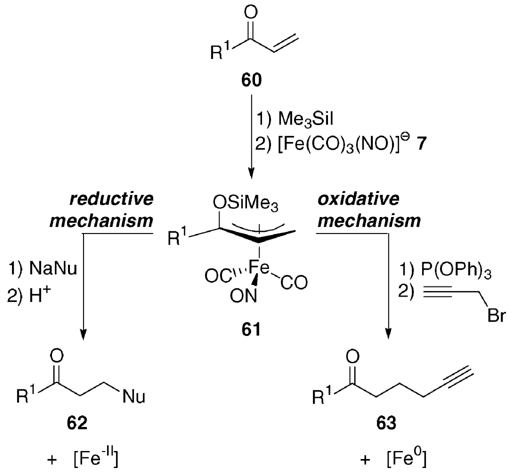
Figure 1. Molecular structure of **55**.[47]

Another striking feature of these neutral allylmetal complexes is their reactivity toward both nucleophiles and electrophiles (Scheme 21). Allyliron complexes, in which the metal centre occupies a formal oxidation state of –I, can either donate another single electron (*oxidative pathway*) or accept a single electron (*reductive pathway*). In terms of reactivity, this property translates directly to an electrophilic (oxidative) or nucleophilic (reductive) substitution mechanism. In the latter mechanism an Fe^{-II} species is regenerated, a fact that is considered to be a prerequisite for the development of a catalytic reaction as will be shown later.



Scheme 21. Reactivity modes in allyliron complexes.

There are important contributions on stoichiometric applications of (π-allyl)Fe complexes by using the Hieber anion **7** in the literature. Nakanishi found, that [1-(trimethylsiloxy)allyl]iron complexes serve as β-acyl *carbanion* equivalents (oxidative mechanism, Scheme 22).[51] The allyl complex **61** was prepared in a one-pot reaction by iodosilylation of vinyl ketone **60** and subsequent addition of the Hieber anion **7**. The (π-siloxyallyl)Fe complex **61** reacted as a β-acyl carbanion equivalent upon treatment with an electrophile (2-propynyl bromide) to lead to the substitution product **63**. Interestingly, addition of P(OPh)$_3$ considerably improved the yields, probably due to the higher electron density and hence reactivity of the metal complex. A similar reaction, in which the corresponding [1-(trimethylsiloxy)allyl]iron complexes **61** are used as β-acyl *carbocation* equivalents resulting in the formation of **62**, was reported later on by the same group (reductive mechanism, Scheme 22).[52,53]

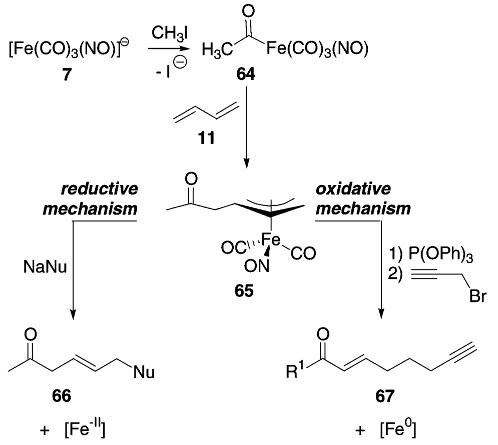


Scheme 22. [1-(Trimethylsiloxy)allyl]iron complexes serving as β-acyl carbanion and β-acyl carbocation equivalents.

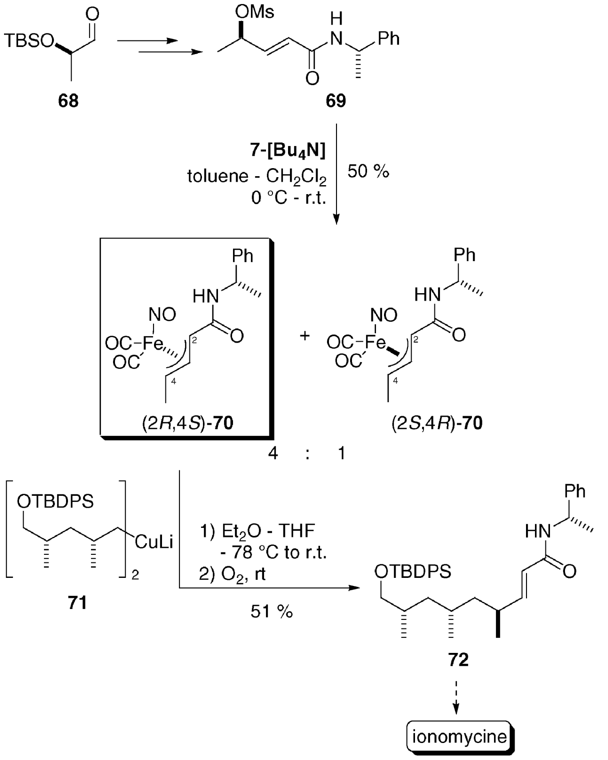
Based upon Chaudhari's seminal contribution,[31] this methodology was extended into a 1,4-functionalization of 1,3-dienes (Scheme 23).[54] Acylmetallation of a 1,3-diene **11** yielded the acylated (π-allyl)Fe complex **65**, which was treated with different C–H-acidic nucleophiles to give rise to 1,4-acylation/alkylation products of type **66**. On the other hand, treatment of **65** with 2-propynyl bromide acting as an electrophile yielded the corresponding alkyne **67**.

Recently, Kocienski and co-workers used the configurational stability of (π-allyl)Fe complexes in the synthesis of the C1–C16 fragment of ionomycine (Scheme 24).[55]

The key step in the synthesis involves the addition of [Fe(CO)$_3$(NO)]$^-$ (**7**) to the stereoisomerically pure mesylate **69**. The (π-allyl)Fe complexes **70** were obtained as a 4:1 mixture of diastereoisomers that could be separated by crystallization. Subsequent nucleophilic displacement of the Fe fragment by the organocuprate **71** led to the formation of amide **72**. The addition of the cuprate to the allyl ligand occurred *anti* to the metal centre resulting in an overall retention of configuration at C-4 (Scheme 24).

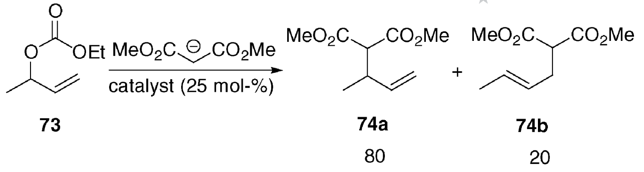


Scheme 23. 1,4-Functionalization of 1,3-dienes.



Scheme 24. Application of (π-allyl)$(CO)_2$(NO)Fe complexes in the synthesis of ionomycine.

In the reductive reactions of (π-allyl)Fe complexes presented so far the Fe^{-II} complex is regenerated during the nucleophilic addition. This paves the way for the development of a catalytic application and was recognized almost 30 years ago by Roustan. In 1979 he reported the first Fe-catalysed allylic substitution starting from readily available allyl carbonates (Scheme 25).[56] This first publication was followed up by two reports from Xu who used the more stable $[Bu_4N][Fe(CO)_3(NO)]$ salt as a precatalyst to the allylic substitution under CO gas in order to maintain the catalytic activity.[57]



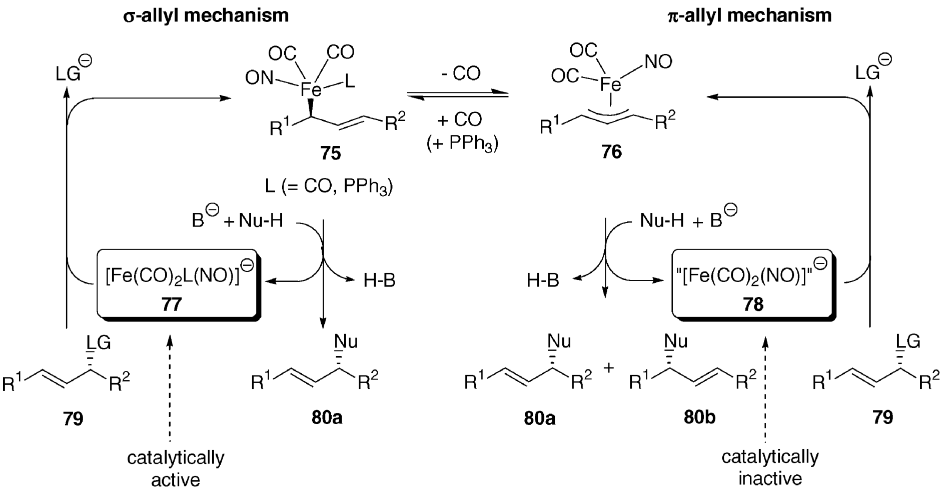
		yield
Roustan (1979):	$Na[Fe(CO)_3(NO)]$, THF, reflux	85 %
Xu (1987):	$[Bu_4N][Fe(CO)_3(NO)]$, $CO_{(g)}$, THF, reflux	35 %

Scheme 25. Fe-catalysed regioselective salt-free allylic alkylation.

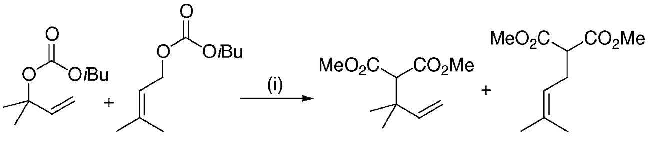
In each report the substitution occurred preferentially at the carbon atom bearing the leaving group in the starting material. Although these results provided the first examples of an Fe-catalysed allylic substitution,[58] it is somewhat surprising that no further investigations in this field have been performed although a variety of groups have used the ferrate salt **7** in stoichiometric reactions as shown above. Several reasons might be responsible for the disappearance of this catalytic reaction from the synthetic organic chemistry platform. On the one hand one might argue that the low price for the ferrate, the high catalyst loading and the CO gas conditions do not justify further research if, at the same time, more potent catalytic systems based on e.g. Pd are available. However, with regard to the most recent price explosion for late transition metals and energy a look back to such "forgotten" catalytic transformations appears to be worthwhile. Moreover, the advantages of (allyl)Fe complexes, e.g. structural integrity and stability, are of synthetic importance. With these facts in mind we recently turned our attention toward a re-examination of the allylic substitution reaction catalysed by the Hieber complex **7**. In order to "teach this old dog a new trick" we envisioned a monodentate σ-donor ligand to be a suitable and more practical replacement of the CO gas conditions. The addition of this ligand was thought to stabilize the primarily formed catalytically active (σ-allyl)Fe complex **75** (Scheme 26).

Gratifyingly the use of DMF as a coordinating solvent led to an increase in the catalyst's nucleophilicity, whereas PPh_3 improved the catalyst's stability to such an extent, that the substitution products were obtained in good yields. Moreover, excellent regioselectivities in favour of the *ipso* substitution products **74a** and **74b** were observed (Scheme 27).[59]

By using the carbonate as both a leaving group and an in-situ-generated base, no preformation of the nucleophile was necessary, which retarded the base-mediated catalyst decomposition. In summary, this transformation represented the first efficient regioselective Fe-catalysed allylic substitution under salt-free (and hence neutral) conditions. In furtherance of these studies, we were able to extend the scope of the reaction to N-nucleophiles. In order to avoid catalyst decomposition, catalytic amounts of piperidine hydrochloride (pip·HCl) were added as a buffer. Under the optimised reaction conditions, different aromatic amines were allylated with almost exclusive regioselectivities in favour of the *ipso* substitution products **83a–i** (Scheme 28).[60]

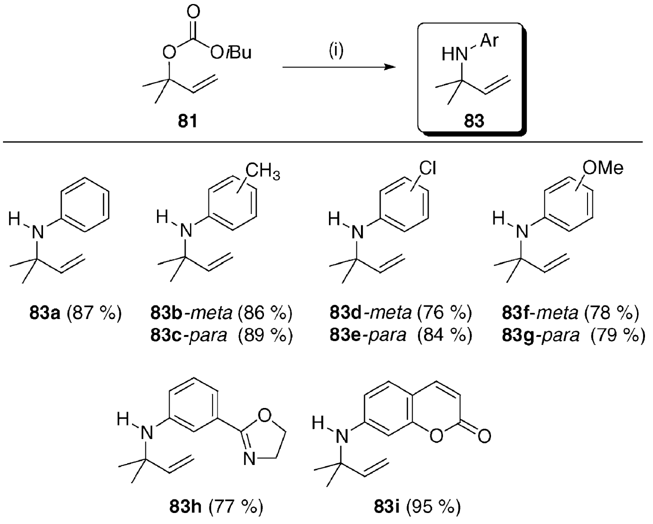


Scheme 26. Ligand effect in Fe-catalysed allylic substitutions.



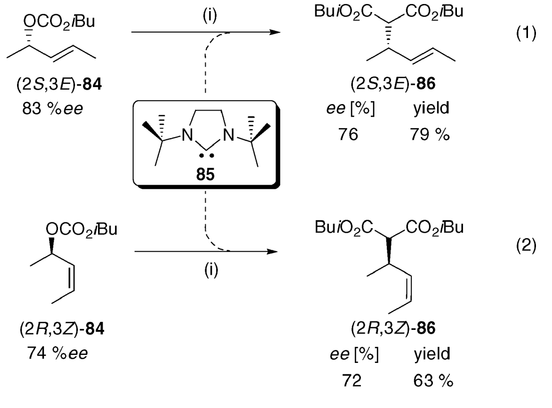
81		82	74a		74b	yield
100	:	0	98	:	2	81 %
0	:	100	7	:	93	61 %

Scheme 27. Regioselectivity in Fe-catalysed allylic alkylations. Reagents and conditions: (i) $CH_2(CO_2Me)_2$ (2 equiv.), $[Bu_4N][Fe(CO)_3(NO)]$ (2.5 mol-%), PPh_3 (3 mol-%), DMF, 80 °C.



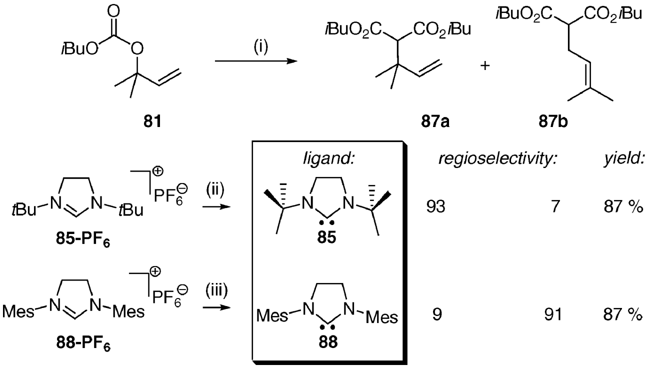
Scheme 28. Fe-catalysed allylic amination. Reagents and conditions: (i) amine (2 equiv.), $[Bu_4N][Fe(CO)_3(NO)]$ (5 mol-%), PPh_3 (5 mol-%), pip·HCl (30 mol-%), DMF, 80 °C.

Despite all the advantages, the existing protocols indicated room for improvements: (a) The use of 2 equiv. of nucleophile is not acceptable from an economical point of view. (b) The change from DMF to a less polar solvent is desirable in order to use preformed and more reactive nucleophiles under the reaction conditions. Hence, we turned our attention to N-heterocyclic carbenes as another potent ligand class, which is known for its outstanding σ-donor abilities.[61] Indeed, addition of the *tert*-butyl-substituted NHC ligand **85** allowed for full conversion in a stoichiometric reaction between the allyl carbonate and pronucleophile. Furthermore a solvent change from DMF to methyl *tert*-butyl ether (MTBE) was possible. Different C-nucleophiles were allylated in good to excellent regioselectivities in favour of the *ipso* substitution products. Most importantly the π-bond geometry in the reaction of enantiomerically enriched (*E*)- and (*Z*)-allyl carbonates **84** stayed intact with chirality transfer to the corresponding substitution products **86** (Scheme 29),[62] which is in accordance with the results reported by Eberhardt for the stoichiometric reaction.[47]



Scheme 29. Fe-catalysed regio- and stereoselective allylic substitution in the presence of NHC ligand. Reagents and conditions: (i) $CH_2(CO_2iBu)_2$ (1 equiv.), $[Bu_4N][Fe(CO)_3(NO)]$ (5 mol-%), ligand (5 mol-%), MTBE, 80 °C.

Change of the ligand's topology led to a significant change in the regioselective course of the reaction. Whereas the *tert*-butyl-substituted NHC ligand **85** allowed for a regio- and stereoselective allylic substitution, the aryl-substituted NHC ligand **88** forced the reaction to follow a π-allyl mechanism to give rise to the isomeric substitution product **87b** (Scheme 30).



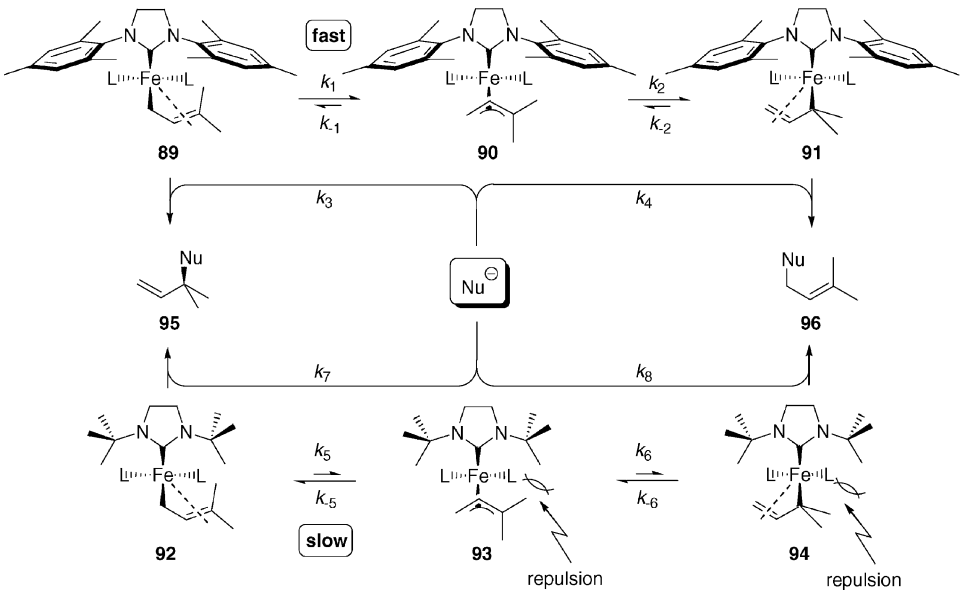
Scheme 30. Ligand-dependent regioselectivity switch in the Fe-catalysed allylic substitution. Reagents and conditions: (i) $CH_2(CO_2\text{-}i\text{Bu})_2$ (1 equiv.), $[Bu_4N][Fe(CO)_3(NO)]$ (5 mol-%), ligand (5 mol-%), MTBE, 80 °C; (ii) **85-PF$_6$** (5 mol-%), $NaNH_2$ (25 mol-%), MTBE, 80 °C; (iii) **88-PF$_6$** (5 mol-%), KO*t*Am (6 mol-%), MTBE, 60 °C.

The experimental results were summarized in a mechanistic proposal outlined in Scheme 31. By assuming that in the presence of ligand **85** or **88**, a (σ-allyl)Fe species such as **89/92** is formed initially, two subsequent reactions are possible. Species **89** and **92** could be transformed into the desired product **95** in a fast substitution reaction, or, if this reaction is slower and the ligand-created steric environment tolerates a fluctuation of the metal atom in the allyl terminus, the formation of the more easily substituted (σ-allyl)Fe species **91** from **89** is possible. A planar aryl substituent in **88** could facilitate such a fluctuation, whereas the *tert*-butyl group in **85** generates unfavourable steric interactions and thus disfavours the formation of π-allyl complex **94** from **92** (Scheme 31).

This ligand-dependent mechanistic dichotomy sets the stage for the development of an asymmetric Fe-catalysed allylic substitution. This prospect and the promising results obtained in the regioselective Fe-catalysed allylic substitution are an encouraging starting point for the development of further catalytic reactions involving the nucleophilic Hieber anion.

Conclusions

Sustainability, a keyword in current discussions in science and society, certainly represents a major challenge to the field of organic chemistry. Chemists both in academia and industry analyse processes and reactions with regard to the ecological but also economical impact on the environment, on society but also on the economy. In order to give life to the expression "sustainability", existing processes need to be optimised with regard to the cost of energy, waste, starting materials and reagents. The latter includes the catalysts. Many catalytic processes that have been developed both in academia and industry are too expensive in order to substitute a running but energy-consuming process. This holds particular true for the production of basic chemicals, which is most often performed in countries that simply cannot afford expensive catalysts and use energy-demanding large-scale applications instead. *Sustainability is a global issue.* Catalysts therefore have to be developed, that can be employed by the chemical industry worldwide. Hence, research in catalysis has not only to focus on the search for new catalytic reactions; moreover, a sustainable catalytic reaction is needed, which is characterized by the use of non-toxic starting materials, the avoidance of unnecessary and harmful waste, a low energy demand, *and* the use of non-toxic, readily available and abundant catalysts. With regard to the latter demand, two major concepts in catalysis have



Scheme 31. Mechanistic model for the ligand-dependent dichotomy.

evolved. On the one hand “organocatalysis” has faced a tremendous comeback in organic chemistry.[63] The catalysts employed in these reactions are organic molecules like amino acids, urea derivatives or chiral Brönstedt acids. On the other hand “sustainable metal catalysis” has gained increasing attention.[64] The use of non-toxic and readily abundant, inexpensive metals paves the way for a broader application of metal catalysis in industrial processes.

In the present Microreview we have summarized our most recent research efforts in the field of iron-catalysed transesterifications and allylic substitutions as examples for the potential of sustainable metal catalysis. It was an aim of this article to emphasize the fact that most of the results we obtained are the quintessence of work that was almost forgotten and had been done already several decades ago by talented and visionary chemists, who were ahead of their time.[65] It will probably be a “Catalytic Mystery” forever why two powerful and promising concepts in sustainable catalysis have fallen into oblivion for several decades. However, it is our hope that more of these “old” catalysts will face a reincarnation as is currently happening, e.g. in the field of iron catalysis in organic synthesis.

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