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Mini Review

Carbenes with ferrocenyl substituents

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Abstract

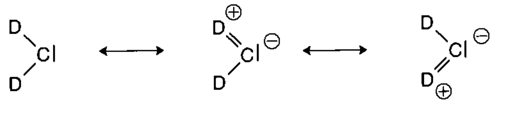
Carbenes containing ferrocenyl substituents are interesting target compounds due to the stereoelectronic influence of the metallocenyl groups in terms of steric protection, electron-donation, and reversible redox chemistry. Synthetic approaches to ferrocenyl-substituted methylidenes and *N*-heterocyclic carbenes are summarized, the reactivity of these carbenes is explored, and the spectroscopic, structural and electrochemical properties of the carbene derivatives are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbene; Methylidene; *N*-heterocyclic carbene; Ferrocene; Pentamethylferrocene; Iron

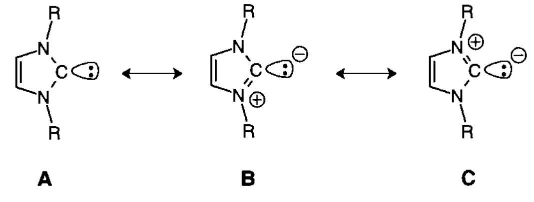
1. Introduction

Carbenes are defined as neutral organic species in which a carbon atom has a valence of only 2 and in which the two non-bonded electrons may be either paired (singlet carbene) or unpaired (triplet carbene). Due to their electron deficiency, carbenes have in general only fleeting existence and behave usually as transient electrophilic intermediates. However, H.-W. Wanzlick [1] was the first to realize in the early 1960s that the electron deficiency of the carbene center may be reduced by electron-donation of appropriate substituents (e.g. amino), resulting in stabilized and less reactive singlet carbenes with nucleophilic properties (Scheme 1).

In the extreme case, this stabilization allows not only the in situ synthesis and the study of the reactivity of such species, but also the isolation and full characterization of nucleophilic *N*-heterocyclic carbenes, a goal which was achieved by A.J. Arduengo and coworkers in 1991 [2]. This seminal report caused a renaissance of the chemistry of (stable) carbenes, and now such heteroatom-donor stabilized carbenes are known with a wide range of structural features, including imidazol-2-ylidenes (Scheme 2), imidazolin-2-ylidenes, triazol-3-ylidenes, thiazol-2-ylidenes, acyclic diaminomethylidenes, diborylmethylidenes, phosphinosilylmethylidenes, and others [3–6]. There is general agreement that zwitterions (ylides) B and C with a trivalent carbon contribute significantly to the ground state electronic structure, thereby more or less reducing the 'true' carbene character according to A with a concomitant increase in stability in comparison to simple methylidenes without donor substituents. The synthesis, structure, bonding theory, and coordination chemistry of these nucleophilic carbenes is now quite well developed [3–6], and recently the first applications in catalysis have been reported, taking advantage of the useful properties of these carbenes in terms of (i) formation of stable complexes with electrophiles ranging from electron-poor



Scheme 1. Donor-substituted carbenes.



Scheme 2. Wanzlick/Arduengo imidazol-2-ylidenes (R = alkyl, aryl).

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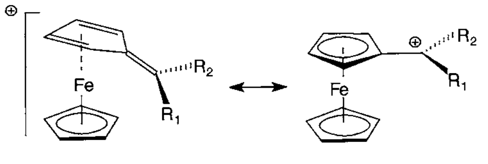
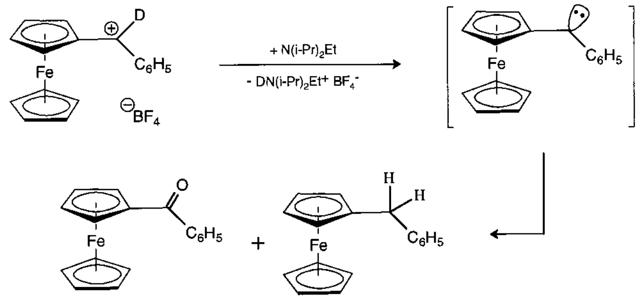
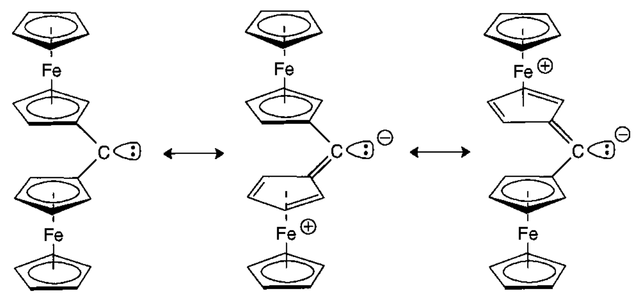


Scheme 3. Ferrocenyl-stabilized carbenium ions.



Scheme 4. Formation of an intermediate ferrocenyl carbene according to Cais et al. [13].



Scheme 5. Stabilization of methylidene by two ferrocenyl substituents.

main group elements to electron-rich transition metals, (ii) formation of stable complexes in different oxidation states of the central metal, (iii) ease of introduction of various peripheral substituents which differ in their steric bulk, electronic properties, chirality, and which may carry an additional functional group.

However, the substitution pattern of Wanzlick/Arduengo carbenes is limited so far to *purely organic* moieties with main group electron-donating substituents (e.g. N, P, O, S, etc). This report summarizes our results on the generation, reactivity, and physical properties of *organometallic* nucleophilic carbenes with ferrocenyl groups, either as the stabilizing electron-donating substituents of the carbene carbon, or as additional peripheral substituents attached to the *N*-heterocyclic Wanzlick/Arduengo carbene framework. Conceptually, ferrocenyl substituents (Fc) have been chosen because of their known extraordinary stabilization of adjacent electron deficient centers, comparable to amino substituents. The stabilization of simple carbenium ions R_2FcC^+ is effected by the delocalization of the positive charge in terms of an η^6-fulvene-η^5-cyclopentadienyl-Fe(II) resonance structure with an exocyclic bent fulvenoid double bond [7,8] (Scheme 3).

Similarly, isolable and air-stable 'elongated' carbenium ≫ cumulenium ions [8–10] $(Fc)_2C^+-(C{\equiv}C)_n(Fc)\leftrightarrow(Fc)_2C{=}(C{=}C)_n^+(Fc)$ with $n = 1, 2, 3$, and phosphenium ions Fc_2P^+ ions are known [11], but efforts to synthesize the isoelectronic nitrenium ions Fc_2N^+ met so far with failure [12].

Our interest in ferrocenyl-substituted carbenes was stimulated by Arduengo's report on the first stable carbene [2] in context with one earlier communication in 1969 which points to the possibility of stabilizing carbenes with metallocene substituents: M. Cais and coworkers reacted various ferrocenylcarbenium salts with a sterically hindered base and rationalized from the observed product mixture that a ferrocenylmethylidene has been generated in situ (Scheme 4) [13]. It is interesting to note that this reaction is quite analogous to the common synthesis of stable Wanzlick/Arduengo carbenes by deprotonation of cationic N-heterocycles.

However, when the same carbene was generated by UV irradiation of ferrocenyl(phenyl)diazomethane, a persistent EPR signal was observed, indicating a triplet state for this species [13]. Similarly, thermal decomposition of ferrocenyl(methyl)diazomethane was shown to give follow-up products consistent with a triplet nature of the corresponding ferrocenylmethylcarbene [14]. From these early results it is quite clear that only one ferrocenyl substituent is insufficient for the stabilization of a singlet nucleophilic carbene. In analogy, Wanzlick/Arduengo carbenes with only one heteroatom donor substituent are nonexistent. Therefore, our investigations were focused on the generation and possible isolation of carbenes with two adjacent ferrocenyl substituents (Scheme 5). In addition, the chemistry of *N*-heterocyclic carbenes containing metallocene substituents will be reported in the following.

2. Ferrocenyl-substituted methylidenes

Four possible synthetic routes to diferrocenylmethylidene were investigated: (i) homolytic cleavage of diferrocenyldiazomethane, (ii) Bamford–Stevens reaction of diferrocenyl tosyl hydrazone, (iii) thermolysis of diferrocenyltelluroketone, and (iv) deprotonation of diferrocenylmethylium salts. In each case the key starting material is diferrocenylketone which was prepared according to standard procedures [15,16].

2.1. Homolytic cleavage of diferrocenyldiazomethane

Diazo compounds are classical starting materials in carbene chemistry [17]. Among the various methods available for the synthesis of diazo compounds, the dehydrogenation of hydrazones and the alkaline cleavage of tosyl hydrazones (Bamford–Stevens reaction) seemed to be best suited for our purposes (Scheme 6). Unfortunately, diferrocenylketone **1** is one of the most unreactive ketones in condensation reactions, due to the steric hindrance and the electron donating properties of the two aromatic ferrocenyl substituents. In fact, all conventional methods to condense ketone **1** with hydrazine failed. Therefore a new hydrazonation method was developed [18]: metalation of 1,1-dimethylhydrazine with trimethylaluminum gave *N*-dimethylaluminum-*N′*,*N′*-dimethylhydrazide which acts as an extremely powerful hydrazonation reagent due to the highly oxophilic dimethylalumino group. The resulting dimethylhydrazone was obtained in almost theoretical yield and could be easily converted to the unsubstituted hydrazone **2** by a standard exchange reaction with anhydrous hydrazine.

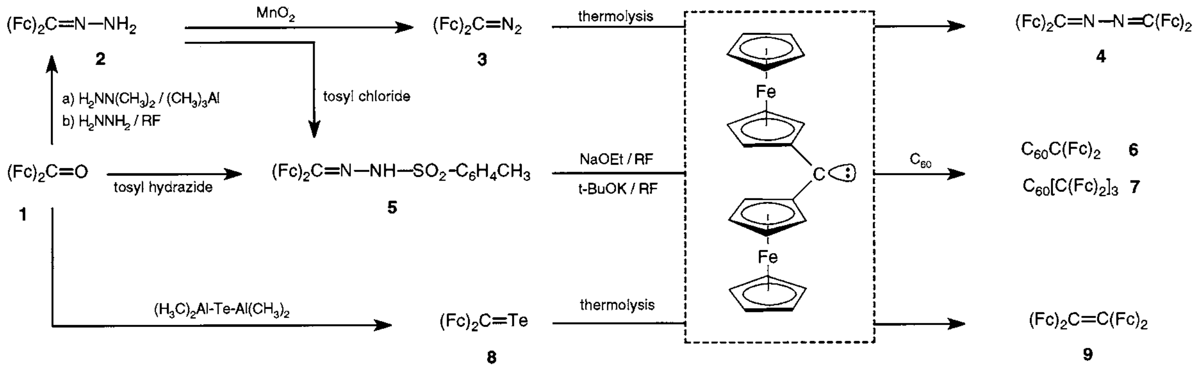
Dehydrogenation of **2** was investigated with various oxidants, including silver oxide, iodosobenzene diacetate, dimethyldixorane, and active (freshly prepared) manganese dioxide. Only the latter reagent gave reproducible results allowing the synthesis of diferrocenyldiazomethane **3** in 93% isolated yield [19]. This yellow diazo compound ($\nu_{C=N=N} = 2025$ cm^{-1}) is quite sensitive toward air and is very easily protonated to the corresponding blue diferrocenylmethylium cation (see below), preventing its further purification and characterization. When **2** was heated in an inert solvent under strictly anhydrous conditions until no more N_2 was formed, none of the desired diferrocenylmethylidene $(Fc)_2C$ could be detected, instead quantitative conversion to tetraferrocenylazine **4** was observed. This indicates that this method of carbene generation is obviously not suited for our purposes in terms of getting access to isolated diferrocenylmethylidene.

2.2. Bamford–Stevens reaction of diferrocenyl tosyl hydrazone

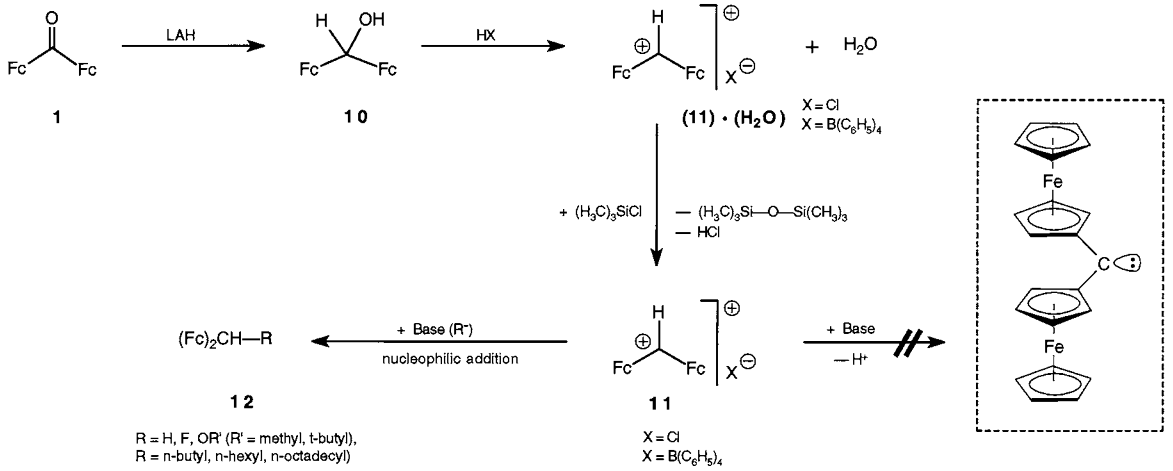
Hyrazone **2** served also as the starting material for the corresponding tosyl hydrazone **5** which was easily formed by reaction with tosyl chloride (Scheme 6). In contrast to the air sensitive diferrocenyldiazomethane **3**, this tosyl hydrazone is a stable and storable progenitor of diferrocenylmethylidene: alkaline cleavage of **5** under standard Bamford–Stevens conditions (toluene, *t*-BuOK, reflux) generated diferrocenylmethylidene in situ [20] which can be reacted with typical carbene trapping reagents. We chose fullerene C_{60} as one of the more interesting electrophilic trapping reagents and obtained tris(diferrocenylmethano)fullerene **7** according to FAB mass spectroscopy in 21% isolated yield. Due to the existence of various steroisomers of **7** no informative further spectral properties are available and attempts to purify this mixture by HPLC met with failure. Interestingly, under our reaction conditions the tris addition product **7** was formed selectively, whereas other workers recently succeeded in synthesizing the corresponding mono(diferrocenylmethano)fullerene **6** under slightly different reaction conditions [21] starting from tosyl hydrazone **5** which was prepared by hydrazonation of diferrocenylketone **1** with tosyl hydrazide.

2.3. Thermolysis of diferrocenyltelluroketone

Because diferrocenyldiazomethane **3** did not fulfill our expectations as a useful starting material for the synthesis of diferrocenylmethylidene, we turned our attention to bis(ferrocenyl)telluroketone **8** as a possible carbene precursor (Scheme 6). Telluroketones are in general extremely thermo- and photo-labile compounds which can only be isolated if electronically or kinetically stabilized or coordinated to transition metal moieties [22], otherwise decomposition by elimination of elemental tellurium takes place. On the other hand, this high reactivity might allow a clean and non-high energy pathway to diferrocenylmethylidene. Accordingly, bis(ferrocenyl)telluroketone **8** was synthesized [23] from diferrocenylketone **1** using bis(dimethylaluminum)telluride [24] as the effective oxygen–tellurium exchange reagent. Telluroketone **8**, a dark blue compound, is besides 1,1,3,3-tetramethylindane-2-tellone



Scheme 6. Generation and reactivity of diferrocenylmethylidene (Fc = ferrocenyl).



Scheme 7. Reaction of anhydrous diferrocenylmethylium salts with bases (Fc = ferrocenyl).

[25] the only room temperature stable telluroketone, indicating some degree of steric and electronic stabilization by the two bulky and electron-donating ferrocenyl substituents. Nevertheless, **8** proved to be still very reactive: exposure to air led to immediate reformation of ketone **1**, and heating a carefully deoxygenated solution of **8** to approximately 50°C resulted in formation of a shiny mirror of metallic tellurium, indicating (formal) redox disproportination of telluroketone **8** to elemental Te and the desired diferrocenylmethylidene $(Fc)_2C$. However, the other product besides elemental tellurium was tetraferrocenylethylene $(Fc)_2C{=}C(Fc)_2$ (**9**), an unusual chiral sterically highly congested olefin [26], which might be considered as the formal dimerization product of diferrocenylmethylidene. Mechanistically, olefin **9** is formed most likely by a twofold Te extrusion from a preformed telluroketone [2 + 2] cyclodimer, and not from the bimolecular reaction of two intermediate diferrocenylmethylidenes [26]. This could be proven by attempted trapping of diferrocenylmethylidene with transition metal moieties: reaction of telluroketone **8** with various substitution-labile metal carbonyl complexes yielded only olefin **9** and no indications of diferrocenylcarbene metal carbonyl complexes [23].

From the results discussed so far one can conclude that neither diferrocenyldiazomethane nor diferrocenyltelluroketone are suitable starting materials for the unambiguous synthesis of diferrocenylmethylidene.

2.4. Deprotonation of diferrocenylmethylium salts

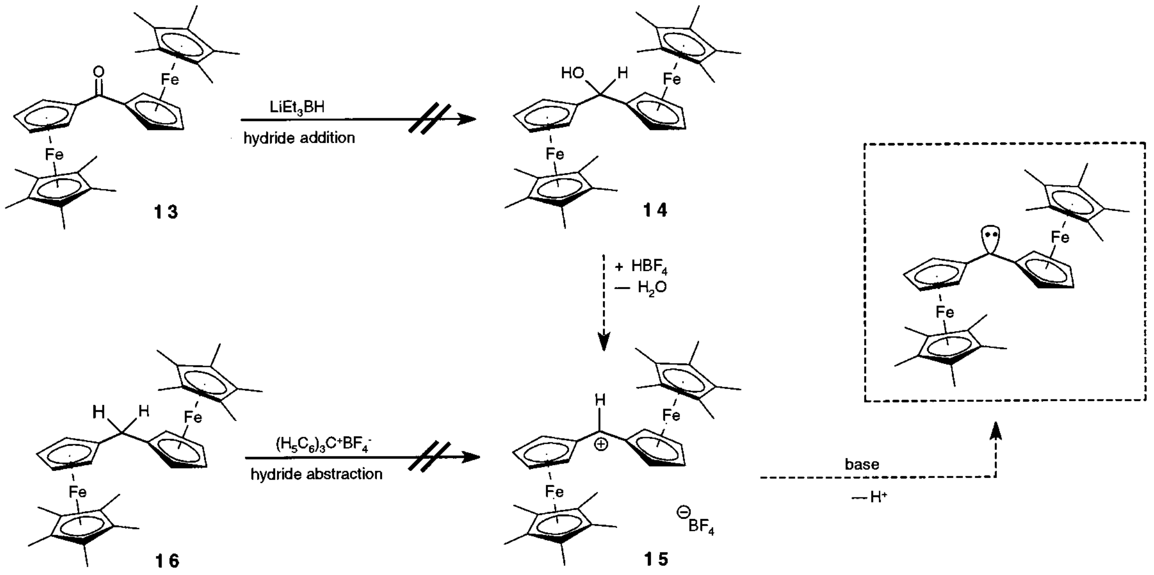
As already outlined in the Section 1, deprotonation of ferrocenylmethylium salts (Scheme 4) has been reported as a possible pathway to ferrocenylmethylidenes [13], analogous as the deprotonation of cationic N-heterocycles to the corresponding Wanzlick/Arduengo carbenes [3–6]. Due to the a-carbenium stabilizing capacity of ferrocenyl substituents in general [7] (Scheme 3), diferrocenylmethylium salts containing two such stabilizing substituents are very stable and easily synthesized [27] by acid-induced dehydration of diferrocenylmethanol **10** which in turn may be obtained by lithium aluminum hydride reduction [28] of diferrocenylketone **1** (Scheme 7).

When ferrocenyl carbinols are dehydrated with strong acids to the corresponding ferrocenylmethylium salts, water is inherently present in the product mixture or the ferrocenylmethylium salts may be formulated as hydrated salts, respectively [27]. For the use of these salts in the following reaction with strong bases aiming at the removal of the proton it is imperative that these salts are completely anhydrous, otherwise no successful outcome is possible. In analogy to a convenient method of converting metal chloride hydrates to unsolvated anhydrous metal chlorides [29] we obtained the dry methylium salts **11** by treatment of the hydrated salts (**11**) · (H_2O) with trimethylchlorosilane, thereby removing all water in the form of volatile hydrogen chloride and hexamethyldisiloxane. Reacting these methylium compounds **11** with various bases differing in basicity, nucleophilicity, and steric bulk *never did effect deprotonation to the desired diferrocenylmethylidene*, instead nucleophilic addition to the corresponding substituted diferrocenylmethane $(Fc)_2CHR$ (**12**) was always observed [27]. This result clearly shows that anhydrous ferrocenylmethylium salts are quite electrophilic and, more important, that *diferrocenylmethylidene cannot be generated by deprotonation of diferrocenylmethylium salts.*

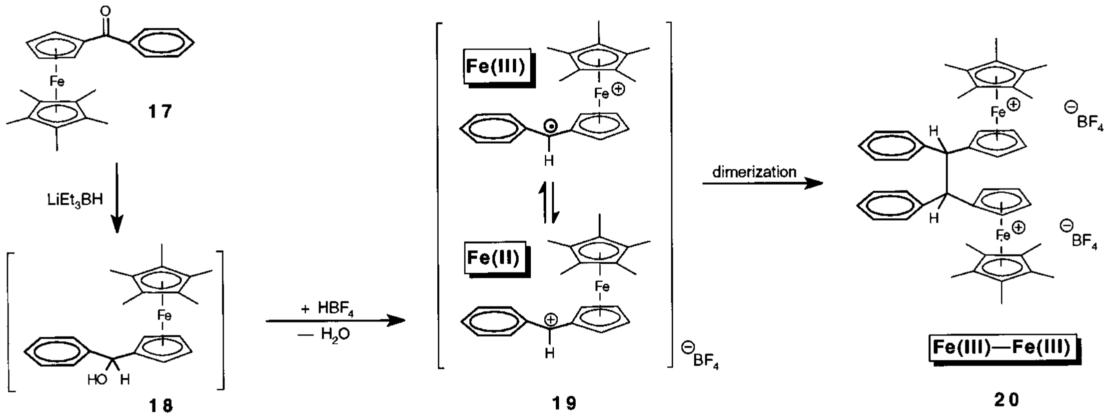
To increase the steric protection at the carbene carbon and to enhance the donor capacity of the metallocenyl substituents, we developed methods to synthesize functionalized pentamethylferrocenyl compounds [30] aiming at the preparation of bis(pentamethylferrocenyl)methylidene (Scheme 8). However, neither reduction of bis(pentamethylferrocenyl)ketone **13** to the corresponding alcohol **14**, nor oxidation of bis(pentamethylferrocenyl)methane **16** to the corresponding methylium salt **15** proved possible. In the first case steric hindrance by the two very bulky pentamethylferrocenyl substituents prevented nucleophilic addition of hydride, and in the second case no hydride abstraction was possible, due to competing metal-centered oxidation of the electron-rich pentamethylferrocenyl moiety [30]. Therefore bis(pentamethylferrocenyl)methylidene is not accessible by these synthetic routes.

Based on these results another possible starting material containing only one bulky pentamethylferrocenyl substituent and one phenyl group was prepared [30]. Starting from pentamethylferrocenyl(phenyl)ketone **17** reduction to the alcohol **18** did succeed, although this compound was only stable in solution (Scheme 9). Removal of water by reaction with fluoroboric acid afforded a green cation, presumably pentamethylferrocenyl(phenyl)methylium tetrafluoroborate **19**. However, in contrast to diferrocenylmethylium salts, this carbenium salt was unstable and dimerized in solution to the paramagnetic 1,2-bis(pentamethylferrocenium)-1,2-diphenylethane ditetrafluoroborate **20** by an intramolecular redox disproportionation followed by intramolecular radical coupling [30]. Also, we note that carbenium salt **19** is the pentamethylated analog of ferrocenyl(phenyl)carbenium salts reported by Cais et al. [13] as a precursor of ferrocenyl(phenyl)methylidene, and obviously it is not possible to synthesize the corresponding pentamethylferrocenyl(phenyl)methylidene.

To conclude this section, all the available evidence from different synthetic attempts starting with different possible starting materials indicates that *ferrocenylmethylidenes cannot be isolated in condensed phase*. Hence, two or one ferrocenyl substituents are not capable of stabilizing a carbene center resulting in a nucleophilic singlet carbene according to Scheme 1. However, it is possible to get access to ferrocenyl carbenes in situ and trap them with suitable reagents. Therefore, it is most likely that such carbenes are (reactive) triplet species, similarly to purely organic aryl-substituted methylidenes.



Scheme 8. Bis(pentamethylferrocenyl)methylidene progenitors.



Scheme 9. Pentamethylferrocenyl(phenyl)methylidene progenitors.

3. Ferrocenyl-substituted *N*-heterocyclic carbenes

As noted in the introduction, the chemistry of *N*-heterocyclic carbenes [3–6] is limited so far to representatives with purely organic N-substituents (compare Scheme 2). Therefore, we were interested in synthesizing Wanzlick/Arduengo carbenes containing electroactive ferrocenyl substituents and to study the influence of the metallocenyl group on the reactivity and properties of these organometallic carbenes and/or their metal complexes. From an application oriented view, the ferrocenyl groups might give rise to useful properties of catalytically active transition metal complexes [e.g. Pd(II), Ru(II), Rh(I)] in terms of their reversible redox couple and with regard to their unique steric shielding.

3.1. (Benz)imidazol-2-ylidenes with pendant ferrocenyl substituents

N-Heterocyclic carbenes are usually prepared by deprotonation of their precursors, cationic N-heterocycles [3–6]. These, in turn, are most easily accessible by N-alkylation of the corresponding heterocycles. Accordingly, imidazole or benzimidazole was mono- and bis-alkylated with appropriate electrophiles Fc-$(CH_2)_nX$ [$n = 1$ or 2; X = $N(CH_3)_3^+$, Br] yielding imidazolium and benzimidazolium salts **21a**,**b**, **22a**,**b**, and **23** (Chart 1). We used mainly benzimidazole as the parent heterocycle due to better yields and ease of workup [31] as compared to imidazole, used independently from us by others [32]. As anticipated, azolium salts **21a**,**b**, **22a**,**b**, **23** had normal spectroscopic properties and solid state X-ray structures, showing that the remote metallocenyl groups effect no unusual structural properties in comparison to simple organic azolium compounds. However, the presence of the peripheral metallocenyl groups allowed electrochemical comparisons of different combinations of cations and anions, showing that the Fc/Fc$^+$ couple is sensitive to the cation–anion coulomb interaction which may be correlated with the varying size of the substituents and/or anions [31,32]. Similarly, NMR titrations of **22a** (X = PF_6^-) with different tetrabutylammonium salts $Bu_4N^+X^-$ (X = Cl, Br, I, NO_3, HSO_4) showed significant different anion–cation interactions, suggesting the usage of such ferrocenyl imidazolium compounds as new anion receptors [32]. Also, we note that one further objective to prepare ferrocenyl azolium salts was their potential use as electroactive 'molten salts' similar to the prototypical 1-ethyl-3-methyl-1H-imidazolium salts [33], however, the compounds synthesized so far did not show such a behavior. One might anticipate that ferrocenylimidazolium salts with longer N-alkyl spacers will have lower melting points and behave as room-temperature ionic liquids.

From the ferrocenyl azolium salts **21a**,**b**, **22a**,**b**, **23**, *N*-heterocyclic carbene derivatives **24**–**31** (Chart 1) were easily synthesized by in situ deprotonation and subsequent trapping following established methods in *N*-heterocyclic carbene chemistry [3–6]. In comparison to

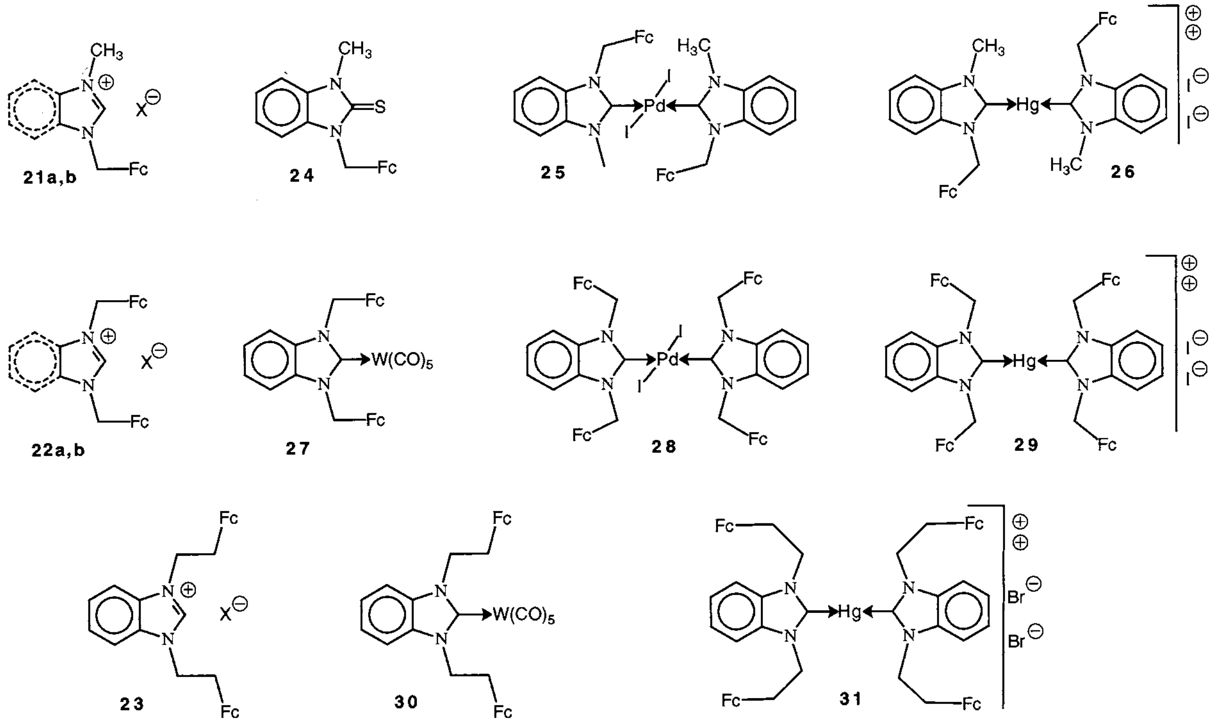


Chart 1. Ferrocenylalkyl(benz)imidazolium salts and their carbene derivatives (Fc = ferrocenyl, X = Br, I, $B(C_6H_5)_4$; a = benzimidazole, b = imidazole).

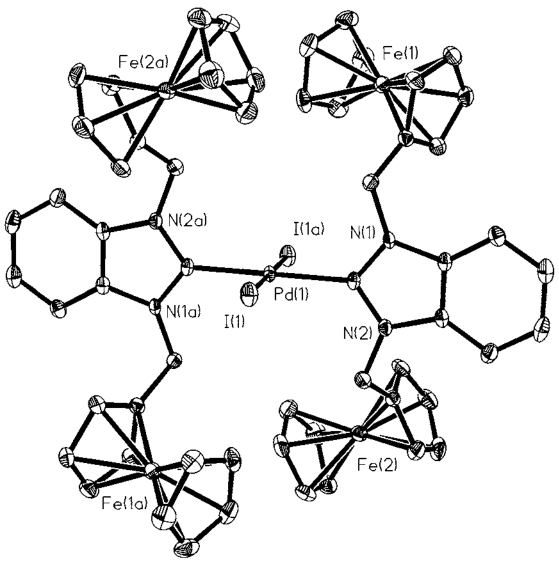


Fig. 1. Molecular structure of **28** [31].

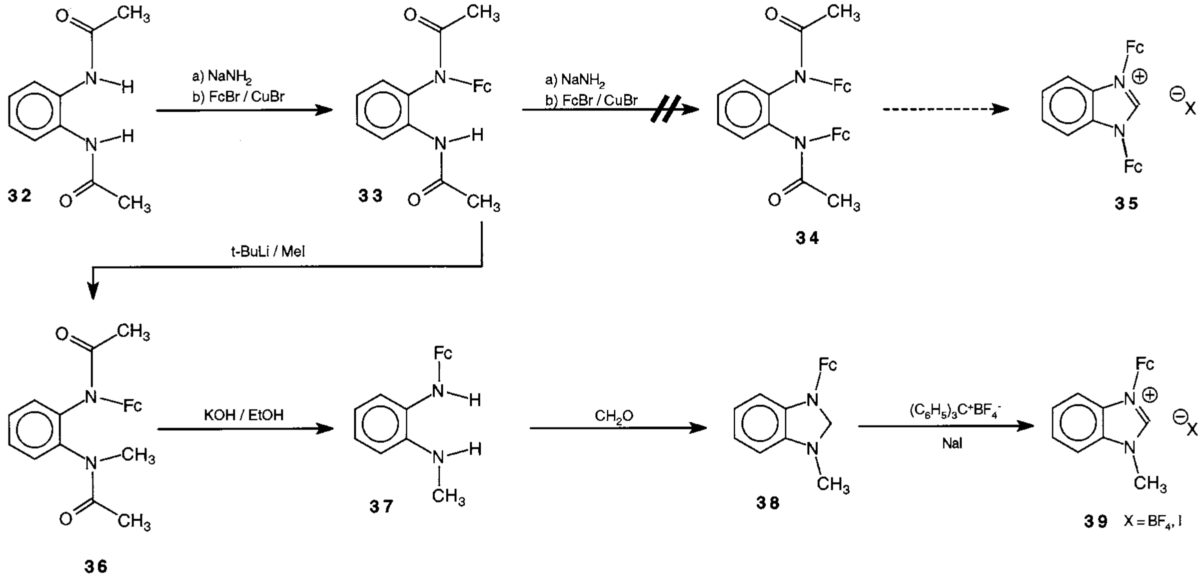
non-ferrocenylated but otherwise analogous carbene derivatives, compounds **24**–**31** showed very similar properties in terms of structure and spectroscopic parameters [31]. The single crystal X-ray structure of one representative, **28**, is shown in Fig. 1, illustrating the steric bulk of the metallocenyl groups.

3.2. Benzimidazol-2-ylidenes with one N-ferrocenyl substituent

The synthesis of *N*-heterocyclic carbene progenitors containing one non-spacered *N*-ferrocenyl group is more difficult but may be achieved by a synthetic sequence involving (i) linking of the ferrocenyl moiety to a non-cyclic precursor, (ii) subsequent ring closure, and (iii) oxidation to the target *N*-ferrocenyl benzimidazolium salt (Scheme 10) [34]. Ferrocenylation of **32** as an activated orthophenylenediamine yielded monosubstituted **33** (which is sterically too hindered to allow the synthesis of bis-ferrocenylated **34**, therefore no *N*,*N*′-diferrocenyl-benzimidazolium salts **35** were accessible by this pathway). On the other hand, introduction of the much smaller *N*-methyl group proved possible and subsequent alkaline hydrolysis of **36** gave deprotected diamine **37**, condensation with formaldehyde afforded benzimidazoline **38**, and oxidation or hydride-abstraction with trityl salts yielded benzimidazolium salts **39**. Spectroscopically and structurally, these benzimidazolium compounds showed no unusual features, ruling out any potential participation of the *N*-ferrocenyl substituent in the delocalization of the positive charge [34], thereby indicating that the metallocene group behaves analogous to an aromatic organic group (e.g. phenyl).

Therefore, we anticipated that the ‘free’ carbene *N*-ferrocenyl-*N*-methyl-benzimidazol-2-ylidene should be accessible by deprotonation of **39** with a suitable base. However, despite many attempts with various non-nucleophilic bases and with different solvent mixtures, no stable carbene could be detected in solution, only decomposition was observed.

On the other hand, in situ deprotonation and derivatization afforded carbene derivatives **40**–**45** (Chart 2) without difficulties [34]. Thiourea **40** was mainly pre-



Scheme 10. Synthesis of *N*-ferrocenyl-*N*′-methyl-benzimidazolium salts.

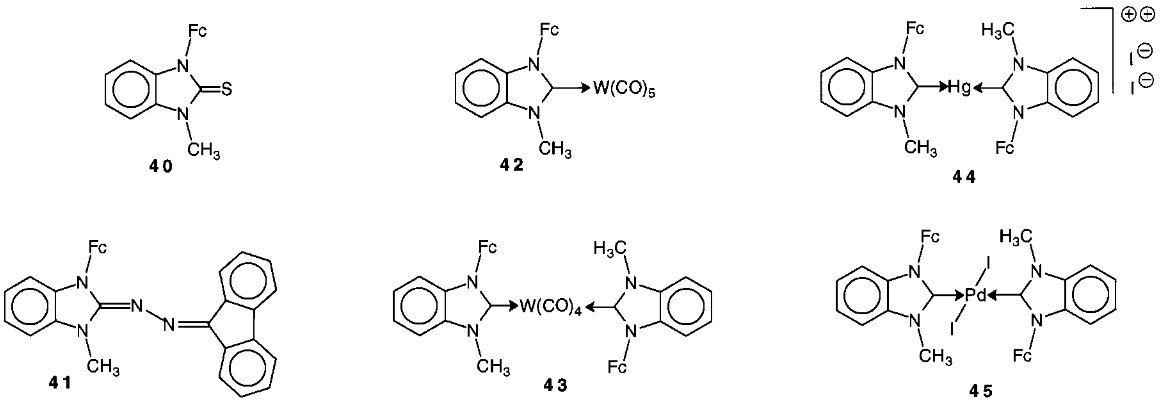


Chart 2. Carbene dereivatives of N-ferrocenyl-N'-methyl-benzimidazol-2-ylidene.

pared as a possible starting material for the synthesis of the free carbene by reduction with elemental potassium following Kuhn's procedure [35], but no reaction was observed when a mixture of **40** and two equivalents of potassium was refluxed in THF for 2 days. The failure to obtain the free carbene by this reduction pathway indicated that not steric hindrance but rather electronic effects were responsible for the limited stability or inaccessability, respectively, of N-ferrocenyl-N'-methyl-benzimidazol-2-ylidene.

Yellow azine **41** was synthesized from **39** by reaction with methyl lithium followed by 9-diazofluorene, showing that such donor–acceptor compounds containing a conjugating azine bridge are (in principle) easily accessible. However, performing the same reaction with the extremely electrophilic 4,5-dicyano-2-diazo-imidazole gave a dark red solution, presumably containing an ylidic benzimidazolium-azo-dicyanoimidazolide which proved too unstable to be isolated [34].

Carbene metal derivatives **42**–**45** were prepared by established methods in N-heterocyclic carbene chemistry [3–6]. Structurally and spectroscopically, these compounds showed properties quite similar to otherwise analogous but non-ferrocenylated compounds [34], indicating that there is no principal difference between N-ferrocenyl-N'-methyl-benzimidazol-2-ylidene and other simple (non-ferrocenylated) N-heterocyclic carbenes. Sterically, the N-ferrocenyl substiutent is quite bulky, as can be seen from the X-ray crystal structure of **43** (Fig. 2) where the two carbene ligands are cis to each other.

Cyclic voltammetry of compounds **39**–**43** showed a number of resolved redox processes, indicating that the N-ferrocenyl substituents are electronically coupled to the remaining molecular framework. For example, azine **41** showed five distinct redox waves, and biscarbene complex **43** showed two reversible couples in accordance with the number of ferrocenyl groups [34].

3.3. *Imidazol(in)-2-ylidenes with two N-ferrocenyl substituents*

At first sight, one might assume that N,N'-diferrocenyl azolium salts are most easily synthesized by ring-closure condensation of two equivalents of aminoferrocene with paraformaldehyde, ammonium chloride, and glyoxal, but no such reaction proved possible in our hands. In addition, direct N-ferrocenylation of suitable functionalized imidazole compounds (e.g. N-halogeno or N-diazonium imidazole) gave no positive outcome. Therefore, a new synthetic route had to be developed [36] (Scheme 11): first, aminoferrocene **46** was condensed with paraformaldehyde to the purple diferrocenyl-1,4-diazabutadiene (Fc-DAB) **47** which is an interesting compound on its own due to the well known and rich coordination chemistry of diazabutadiene ligands (R-DAB, R = alkyl, aryl) in general. For example, multimetallic redox-active transition metal carbonyl complexes (Fc-DAB)M$(CO)_4$ were synthesized [37] and the corresponding Ni and Pd halide complexes

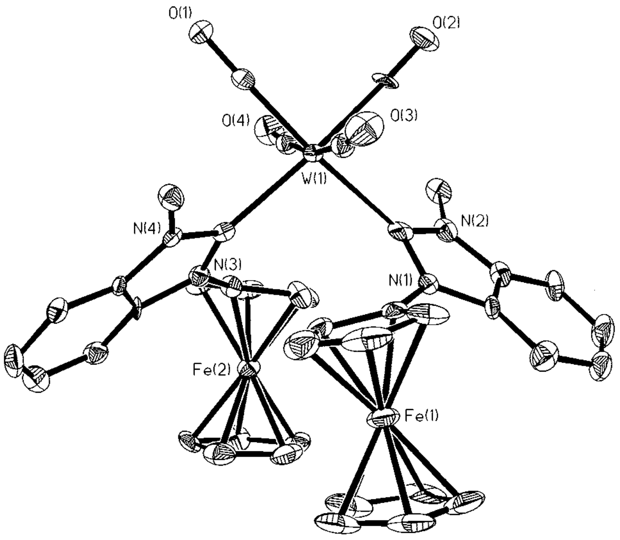
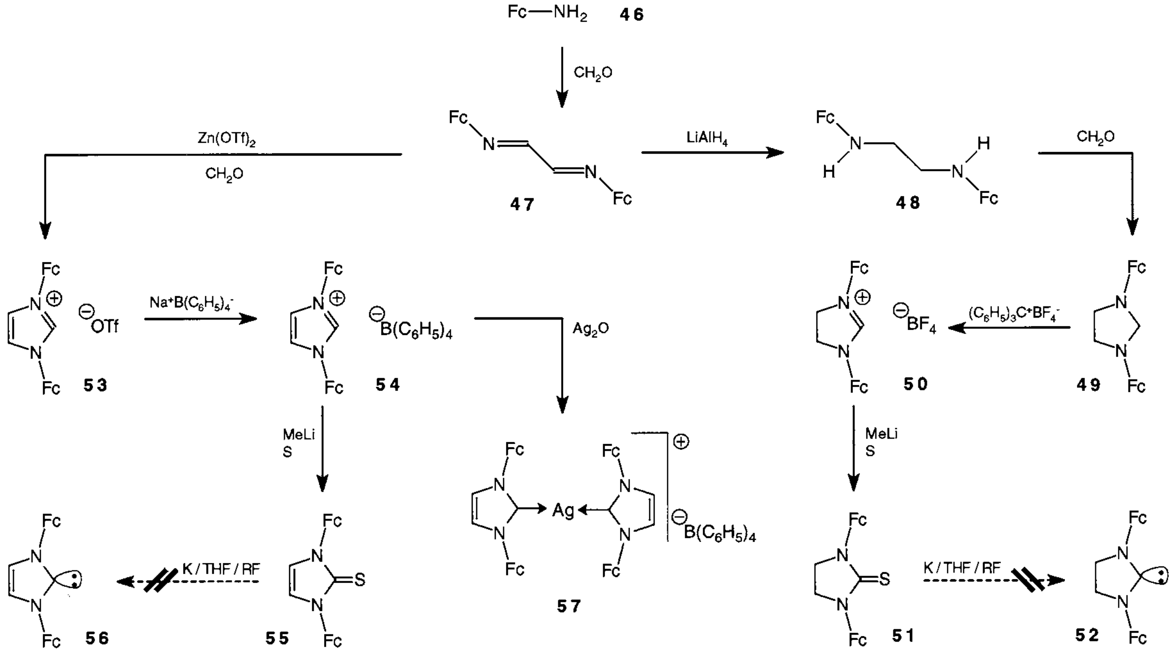


Fig. 2. Molecular structure of **43** [34].

(Fc-DAB)MX_2 have been evaluated for their catalytic performance in the methylaluminoxane-activated polymerization of olefins [38]. Second, Fc-DAB **47** was reduced by LAH to diferrocenylethylenediamine (Fc-en) **48** which again is a new ligand with interesting properties due to the presence of the two redox-active *N*-ferrocenyl groups [39]. Third, ring-closure condensation of Fc-en **48** with paraformaldehyde afforded imidazolidine **49** which was oxidized with trityl salts to the corresponding carbene precursor diferrocenylimidazolinium tetrafluoroborate **50**.

Similarly as the mono-ferrocenylated imidazolium salt **39**, this compound showed regular spectroscopic and structural properties, indicating that the positive charge is delocalized on the N–C–N amidinium subunit only with no non-classical stabilization by the two adjacent *N*-ferrocenyl substituents. Starting from this carbene progenitor, attempts were made to synthesize the corresponding 'free' diferrocenylimidazolin-2-ylidene **52**, but no suitable base for the deprotonation of **50** could be found. However, in situ deprotonation by methyl lithium and trapping with elemental sulphur afforded cyclic thiourea **51**, but its attempted reduction with potassium according to Kuhn's method [35] met with failure. The reason for the inaccessability of the free carbene **52** is most likely the low acidity of the amidinium N–CH–N subunit, which needs a sufficiently strong base which reacts further with the carbene if no trapping reagent is present. In line with this interpretation, all our attempts to synthesize metal carbene derivatives by in situ reactions of **50** with transition metal compounds containing weaker bases (e.g. $Pd(OAc)_2$, $Hg(OAc)_2$, Ag_2O, etc.) did not yield any carbene complexes [36].

Because aromatic *N*-heterocyclic carbenes show in general superior stability [3–6] and because the non-aromatic imidazoline compounds **49**–**51** did not yield the desired carbene derivatives, we focused our attention on the preparation of *N*,*N*′-diferrocenylimidazol-2-ylidene compounds. In an interesting and mechanistically complicated one-pot reaction, Fc-DAB **47** was activated by complex formation with the very Lewis-acidic zinc triflate and condensed subsequently with paraformaldehyde directly to *N*,*N*′-diferrocenylimidazolium triflate **53** which may be converted to the corresponding tetraphenylborate **54** [36] (Scheme 11). Both these imidazolium salts are 'normal' azolium salts without involvement of the *N*-ferrocenyl substituents in the delocalization of the positive charge, similarly as all other *N*-ferrocenyl (benz)imidazol(in)ium salts discussed above. Contrary to our expectations, reaction of **54** with various non-nucleophilic bases did not allow the synthesis of *N*,*N*′-diferrocenylimidazol-2-ylidene **56**, but in situ deprotonation and reaction with sulphur afforded thiourea **55**. However, the reduction of **55** with two equivalents of elemental potassium failed, only decomposition but no spectroscopic evidence for the existence of carbene **56** was observed. Therefore, one can draw the (preliminary) conclusion that *N-ferrocenyl substituents in general are incompatible with isolable N-heterocyclic carbenes.* On the other hand, the successful synthesis of thiourea **55** showed that deprotonation of imidazolium salt **54** and trapping of the intermediate carbene is in principle possible. Accordingly, **54** was reacted with various basic transition metal



Scheme 11. *N*,*N*′-Diferrocenylimidazol(in)-2-ylidene precursors and derivatives.

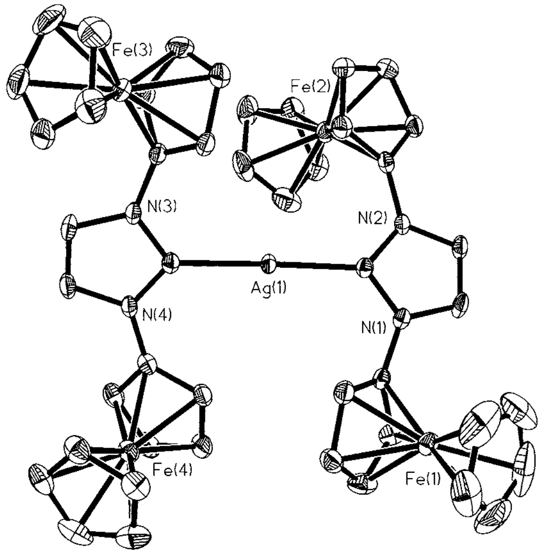


Fig. 3. Molecular structure of the cation of **57** [36].

compounds: Whereas the interaction of imidazolium salt **54** with $Pd(OAc)_2$ or $Hg(OAc)_2$ did not afford any metal carbene complexes, the reaction with Ag_2O did allow the synthesis of the corresponding silver complex **57**. The failure to obtain metal carbene complexes of Pd(II) and Hg(II) can be attributed to the insufficient basicity of the (weak) base acetate and to steric hindrance by the *N*-ferrocenyl substituents which prevent the formation of a square planar Pd(II) complex. Interestingly, attempted synthesis of such metal complexes by deprotonation of **54** with methyl lithium followed by interaction with transition metal halides (e.g. $PdCl_2$, $HgCl_2$) were also unsuccessful, most likely due to the limited lifetime of the intermediate carbene **56** and due to the heterogenous reaction conditions. Recent work by Lin [40] has shown that Ag(I) *N*-heterocyclic carbene complexes are efficient carbene transfer reagents [41] and in analogy one would expect that also compound **57** may be used in such reactions. However, attempted transfer of carbene **56** by interaction of complex **57** with Au(CO)Cl or $PdCl_2$ met with failure and this lack of reaction is probably due to steric hindrance.

Silver(I) complex **57** is an air-stable yellow solid, noteworthy spectroscopic properties include its NMR chemical shifts and coupling constants of ^{1}H, ^{13}C, ^{10}B, ^{11}B, ^{107}Ag, ^{109}Ag, and its Raman stretching vibration of the carbene–Ag^{+}–carbene subunit [36]. An X-ray structure analysis showed the expected linear coordination of the two *N*-heterocyclic carbene ligands bearing twisted *N*-ferrocenyl substituents (Fig. 3). Taken together, these spectroscopic and structural properties of **57** are quite similar to other analogous but non-ferrocenylated Ag(I) complexes, indicating again that the incorporation of *N*-ferrocenyl substituents in such complexes effect no unusual electronic features. Cyclic voltammetric comparison of compounds **50**, **51**, **54**, **55**, **57** revealed the presence of two slightly separated redox waves in the case of **50**, **51**, **54**, **55**, indicating some degree of electronic communication of the two ferrocenyl groups, whereas for silver complex **57** only a single four-electron oxidation was observed, meaning that the central metal cation essentially prevents any form of conjugation between the two *N*-heterocyclic carbene ligands [36].

The following conclusions can be drawn from the results discussed in this section: (Benz)imidazol(in)ium salts containing one, two, and spacered or unspacered ferrocenyl substituents have been prepared by various synthetic routes which involve rather unusual reactions in the case of unspacered *N*-ferrocenyl-substituted systems. From these starting materials for the synthesis of *N*-heterocyclic carbenes, the ‘free’ carbenes cannot be generated by interaction with bases, due to either insufficient acidity of the (benz)imidazol(in)ium salts or due to the quite limited stability of the ferrocenyl *N*-heterocyclic carbenes. However, in situ generation of the carbenes and trapping with suitable electrophiles is possible, affording typical carbene metal complexes [Hg(II), Pd(II), W(0), Ag(I)] and non-metal derivatives (thione, azine). In contrast to other non-ferrocenylated analogs, the ‘free’ carbenes cannot be synthesized by reduction of ferrocenyl-substituted heterocyclic thiones, suggesting that ferrocenyl substituents are unfavourable for *N*-heterocyclic carbene species. On the other hand, the spectroscopic and structural properties of the ferrocenyl *N*-heterocyclic carbene derivatives show values which are quite similar to those of analogous non-ferrocenylated compounds, indicating that ferrocenyl substituents behave to a major degree like simple organic groups (e.g. phenyl). However, due to the unique steric bulk of the metallocenyl moiety, some otherwise established *N*-heterocyclic carbene chemistry is in some cases prevented (e.g. formation of square planar Pd(II) complexes, carbene transfer reactions of Ag(I) complexes). The ferrocenyl groups in these carbene derivatives can be oxidized reversibly and, in cases where two ferrocenyl substituents are present, they show minor electronic coupling through the N-heterocycle. Finally, all the available evidence suggests that *ferrocenyl groups are not capable of electronically stabilizing N-heterocyclic carbenes.*

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