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Review

Recent chemistry of the η^5-cyclopentadienyl dicarbonyl iron anion

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Contents

Abstract

The distinctive nucleophilicity of the η^5-cyclopentadienyl dicarbonyl iron (Fp) is reviewed from 1994 to present. In addition to its nucleophilic reactivity, other distinguishing reactivity characteristics such as basicity and oxidizability are discussed. A section is included concerning various

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synthetic means used in generating the Fp anion. Substitution and addition reaction sections concerning both organic and inorganic electrophiles are covered. Fp anion reactions with organic electrophiles are explored according to sp^3-, sp^2-, and sp-hybridized electrophilic carbon bonds in forming new carbon–iron bonds. Besides intriguing mechanistic studies, applications of newly formed Fp complexes including, but not limited to, catalysis, asymmetric and regiospecific reactions, vapor pressure deposition, optical filtration, and polymerization are reviewed.
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Keywords: η^5-Cyclopentadienyl dicarbonyl iron anion (Fp anion); Supernucleophilicity

1. Introduction

This article represents a modern overview of the η^5-cyclopentadienyl dicarbonyl iron anion (i.e., Fp anion) that extensively covers the literature from the year 1994 to present. Although there are two notable reviews on organoiron transformations [1] and Fp chemistry [2] prior to 1994, there are no comprehensive reviews since then. Thus, we focused our attention on the more recent advances since 1994 comprising over 250 original references. By no means do we assume that prior research on Fp anion is unimportant, rather we hope to give credit to earlier work in this area by several pioneering researchers. Without the early work of notables such as Fischer, Rosenblum, Wojcicki, Casey, Davies, Liebeskind, Gladysz, Brookhart, Nesmeyanov, Pannell, King, and others, the foundation for the current level of research in this area would not exist.

Iron is abundant, inexpensive, and relatively nontoxic in comparison to many other transition metals, thus making it an ideal and practical choice for the study of transition metal-based organometallic compounds. Since the synthesis and discovery of ferrocene in 1951 [3–7], iron complexes have been central to the discipline of organometallics. Ferrocene and related "piano stool" complexes have been studied extensively due to their unique properties, stability, and ease of characterization. The iron dicarbonyl cyclopentadienyl (Cp) complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]$, has been incorporated into so many compounds that it has come to be symbolized as Fp [8]. The most notable Fp derivative, the η^5-cyclopentadienyl dicarbonyl iron metalate (Fp anion), was first reported in 1955 by Fischer (Fig. 1) [9,10]. At that time, Fischer was exploring reactions of Cp ligated metal complexes. Since that first report, use of the Fp anion has grown steadily to the point where over 1600 papers have been published incorporating this species in some aspect of a chemical transformation.

The Fp anion, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]^-$, itself is an 18-electron complex. The complex acts as a strongly nucleophilic Lewis base and is often used as a starting material or precursor to other Fp complexes [11]. In addition, the complex is inexpensive to synthesize and readily accessible [12]. In the past, this complex has been used as a starting material to form a variety of reactive cationic and carbene precursors. It has also been used as a stoichiometric auxiliary in a wide range of organic and inorganic species.

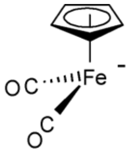


Fig. 1. Typical structural representation of the Fp anion.

Some of the more recent advances using Fp anion as a reagent now involve such diverse fields as materials science where application of its analogs in vapor deposition methods has shown promise. Electrocatalytic methods for generating the anion also provide intriguing possibilities. Furthermore, the Fp anion has been applied toward an even broader range of asymmetric and regiospecific reactions than ever before. A host of inorganic compounds have also been reacted. We envision that this review will continue to advance the development of the Fp anion as a unique reagent in organic and inorganic synthesis.

For the sake of simplicity, this review concerning the Fp anion has been divided into four main sections, these are: reactivity, synthesis, substitution reactions, and addition reactions. In addition to recent advances since 1994, the reactivity and synthesis sections borrow heavily from earlier material. The substitution and addition sections focus solely on material published from January 1994 to June 2006.

2. Reactivity of the $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}$ metalate

2.1. Nucleophilicity of the $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}$ metalate

The cyclopentadienyl dicarbonyl iron metalate (Fp^-) is one of the most nucleophilic transition metal anions. Although an underlying reason or explanation for its nucleophilicity has not been fully explained, several studies have been performed. King et al. compared nucleophilic displacement reactions between various electrolytically generated transition metal carbonyl anions with organic halides (methyl iodide, ethyl bromide, and isopropyl bromide) and found the Fp metalate to be the most reactive of the anions tested (Table 1) [13].

This remarkable variance in reactivity of the various metalates was attributed to three factors. First, King [14] had found earlier that: "In the cases of transition metals which form sta-

Table 1
Reactivity comparison of metalates with organohalides

Anion	Relative nucleophilicity
CpFe(CO)_2^-	70,000,000
CpRu(CO)_2^-	7,500,000
CpNi(CO)^-	5,500,000
Re(CO)_5^-	25,000
CpW(CO)_3^-	500
Mn(CO)_5^-	77
CpMo(CO)_3^-	67
CpCr(CO)_3^-	4
Co(CO)_4^-	1

ble carbonyl derivatives, a coordination number [C.N.] of six is generally more favorable than a coordination number of five or seven in the absence of changes in electronic configuration." This idea is based on the stability of the final complex after nucleophilic displacement. For instance, a metal carbonyl complex will increase its coordination number by one following a nucleophilic displacement reaction. Therefore, a metal carbonyl complex anion such as $Co(CO)_4^-$ (C.N. = 4) will have a coordination number of 5 after reaction, whereas the more nucleophilic $Mn(CO)_5^-$ (C.N. = 5) will have a final coordination number of 6 after reaction. As a second factor, the nucleophilicity generally increased as the size of the central metal increased. Thus, the nucleophilicity of the group 6 elements (Cr, Mo, and W) increased down the periodic table as the size of the central atom increased. Third, the weaker the ligands were at accepting electron density from the metal, the greater the negative charge on the central atom and consequently, the greater its nucleophilicity. Although these factors explained the reactivity trends for many of the anions, they did not completely explain the extraordinary nucleophilicity of the Fp anion, especially its increased nucleophilicity over the ruthenium analog ($[Cp(CO)_2Ru]^-$). Despite numerous studies, the extraordinary nucleophilicity of the Fp anion is still not completely understood (*vide infra*).

A more recent study suggested that ion pairing between the transition metal anion and its counter cation may influence reactivity [15]. Ion pairing apparently distorts the structure of the anion, the extent of which depends on the solvent, thus affecting reactivity. In essence, a "more naked" anion may be responsible for the increased reactivity of $[Cp(CO)_2Fe]^-$ over $[Cp(CO)_2Ru]^-$.

In this context, Pannell and Jackson [16] had previously studied ion pairing of NaFp by infrared spectroscopy. They found that in tetrahydrofuran (THF) solutions this complexed anion existed as a dynamic equilibrium of three species having carbonyl stretching frequencies of 1877, 1806; 1862, 1770; and 1862, 1786 cm^{-1} corresponding to the tight ion pair, the contact ion pair and the solvent separated ion pair, respectively (Fig. 2). Gradual addition of a crown ether to a THF solution of the NaFp salt resulted in partial removal of the tight ion pair and an increase in the carbonyl stretching frequencies characteristic of the contact and solvent separated ion pairs. Furthermore, addition of dimethoxyethane as a stronger cationic solubilizer than THF, also reduced the concentration of the tight ion pair. Interestingly, a THF solution of the potassium metalate, KFp, exhibited carbonyl stretching frequencies at 1865 and 1788 cm^{-1}, characteristic of the solvent separated ion pair.

Based on classical organic chemistry [17], one might expect a "more naked" anion such as that formed from KFp to be thus more reactive than the NaFp, which exhibits a higher degree of tight ion pairing. Indeed, a small decrease in the rate was exhibited for the more interactive Na cation with the related manganese pentacarbonyl anion used as a model [18]. In this same study, changes in the solvent had little effect on the nucleophilicity of common carbonyl anions.

Dessy and Pohl [19] observed no difference between the nucleophilicities of MFp (M = Li, NBu_4) with $(CH_3)_2CHBr$ in diglyme. In comparison to carbanions, it was demonstrated that in THF solutions the lithium salt of the fluorenyl carbanion ($C_{13}H_9^-$) was more reactive, as a result of solvent separated ions, than $NaC_{13}H_9$ [20]. The $NBu_4C_{13}H_9$ demonstrated even less solvent-separated ion pairing than the sodium salt and thus by inference less reactive than $NaC_{13}H_9$. Therefore, LiFp would be expected to have been a more reactive nucleophile than NR_4Fp. At least with MFp (M = Li, NBu_4), this was not the case.

Apparently the greater nucleophilicity of the Fp anion is a result of several properties, including high charge density at the metal center, an even coordination number (C.N. = 4) following a nucleophilic displacement reaction, and the nature of ion pairing. Furthermore, in the case of alkyl halides, several studies [18,21–24] have confirmed the reactivity trend followed in Table 1.

Much of the earlier work on Fp anion nucleophilicity centered on reactions with alkyl-substituted electrophiles. However in 1996, Beletskaya et al. prepared a comprehensive review of carbonyl metalates, including the Fp anion, in aromatic and vinylic nucleophilic substitution reactions [21]. In addition to comparing carbonyl metalates with traditional carbanion nucleophiles, they investigated the composition of the reactants (nature of the counterion and leaving group), the stability of the products (tendency toward dimerization), and the reaction conditions (the type of solvent and the reaction temperature).

Beletskaya and coworkers found carbonyl metalates to be altogether different than traditional carbanion nucleophiles. For instance, unlike other metal carbonyls, LiFp exhibited greater nucleophilicity than KFp in THF solution toward aryl and vinyl electophiles. The explanation for this behavior was that LiFp exists in THF solution mainly as distinct tight ion and contact ion pairs (see Fig. 2). In general, the reactivity of aryl and vinyl halides toward the Fp anion increased as the size of the leaving group increased, i.e., I > Br > Cl > F. These findings were the reverse of traditional carbanion reactivity in vinylic and arylic

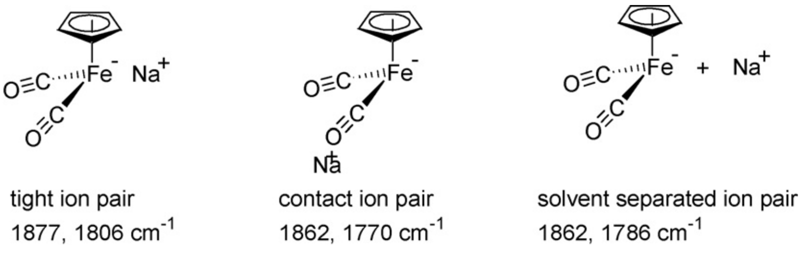
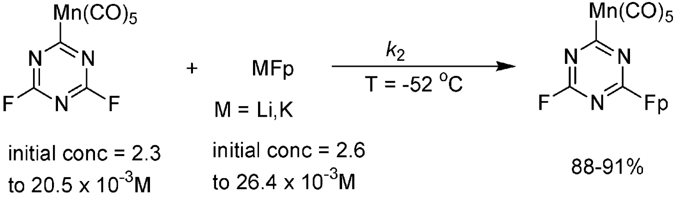


Fig. 2. Types of ion-pairing.

Table 2

Results of factors that effect the Fp anion reaction rate



Solvent	Additive (mol/mol MFp)	M	k_2 ($\times 10^2$ mol^{-1} s^{-1})
THF	None	K	397
THF	18-Crown-6 (2)	K	107
THF	HMPA (20)	K	88
Ether	None	K	Too high
THF	None	Li	580
THF	HMPA (20)	Li	89

substitution reactions where the carbanion reactivity increased as the size of the leaving group decreased, i.e., F > Cl > Br > I.

The Fp anion showed a decrease in reaction rate in the presence of cation solvating additives such as HMPA or 18-crown-6 ether (Table 2). The rate also decreased on addition of other salts such as $KBPh_4$ with KFp. Use of less polar ethers such as diethyl ether also increased the rate (Table 2). Factors that decreased the reaction rate were readily explained by the loss of tight and contact ion pairs to solvent separated pairs. A higher temperature tended to increase the reaction rate at the expense of unwanted Fp_2 dimer formation. Even though solvents less polar than THF increased the reaction rate, they also produced more Fp_2 dimer, whereas addition of 18-crown-6 ether to KFp at room temperature decreased dimer formation at the expense of the reaction rate. In essence, it appears that formation of tight and contact ion pairs is critical to increasing the reactivity of Fp anion, although increased reactivity also favors dimer formation.

The authors gave two plausible routes for Fp_2 dimer formation in their study. The first route involved a radical mechanism by a redox process called a single electron transfer (SET) mechanism (Scheme 1, SET mechanism). The second route called a halogen metal exchange (HME) mechanism involved formation of FpX (X = Cl, Br, I) followed by attack of another Fp anion to give the Fp_2 dimer (Scheme 1, HME mechanism).

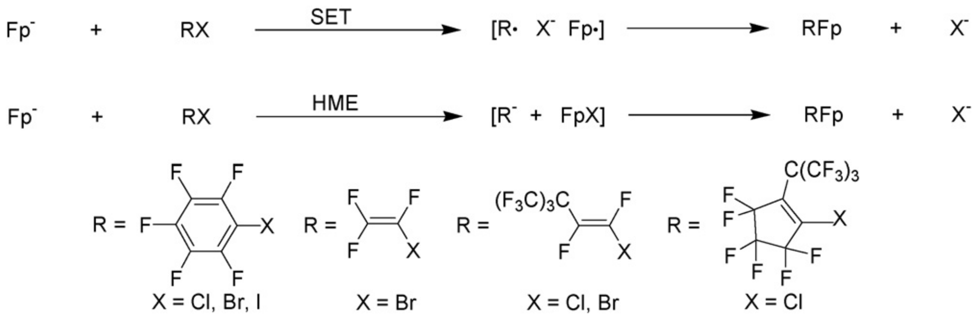
In more recent work, researchers Beletskaya, Artamkina, and Sazonov have further studied the role of metal carbonyl anions in reactions with aryl and vinyl halides. By the use of anion traps (i.e, proton donors) and radical traps [25] they have been able to put forth a mechanism that challenges the traditional SET mechanism in favor of a HME mechanism (Scheme 1) [26]. The HME mechanism was shown to be the major pathway for Fp anion substitution of polyfluorinated aryl and alkenyl halides. The major difference in these mechanisms lies in the first step where either a radical pair (homolytic cleavage, SET) or a carbanion (heterolytic cleavage, HME) is indicated in the transition state.

2.2. *Basicity of the (η^5-C_5H_5)(CO)$_2$Fe metalate*

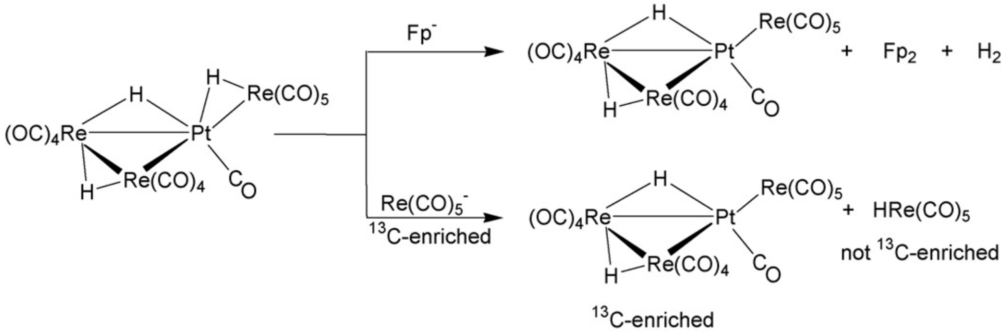
Nucleophilicity aside, the Fp anion also displays Brønsted basic tendencies [27]. The tendency to act as a Brønsted base interfered with the work of Bergamo et al. while establishing an order of thermodynamic nucleophilicity for several metal carbonyl nucleophiles. In this case, the bridging rhenium pentacarbonyl hydride ligand ($HRe(CO)_5$) of the model compound $Re_2Pt_2(\mu\text{-}H)_2(CO)_9\{HRe(CO)_5\}$ is strongly labile and rapidly exchanges with free $HRe(CO)_5$ at the Pt center, allowing for thermodynamic comparison in ligand displacement studies of the model compound by $[Re(CO)_5]^-$ or Fp anion (Scheme 2). Their thermodynamic nucleophilicity results were similar to the kinetic nucleophilicity results listed in Table 1, but the nucleophilicity of Fp anion, unlike the other metal carbonyl anions, could not be established due to deprotonation of the model compound. The authors noted that the reactivity of the Fp anion as a base was unexpected because it is less Brønsted basic than $[Re(CO)_5]^-$ according to the order of Brønsted basicity derived from thermodynamic acidity constants: $Re(CO)_5^- > Fp^- > WCp(CO)_3^- > Mn(CO)_5^-$ [27]. The deprotonation of the model compound by $[Re(CO)_5]^-$ had been discounted earlier due to results of C^{13}-enrichment NMR studies, which favored nucleophilic displacement of $HRe(CO)_5$ by the $[Re(CO)_5]^-$ anion [28].

2.3. *Oxidizability of the (η^5-C_5H_5)(CO)$_2$Fe metalate*

In addition to its nucleophilicity and basicity characteristics, the Fp anion is also easily oxidized and thus is a good reducing agent [29]. In fact, solutions of Fp anion readily undergo oxidation when exposed to air and should be kept free of oxygen. For this reason, the compound is best prepared and reacted in degassed solvents. The solids of MFp (M = Li, Na, and K) may



Scheme 1.



Scheme 2.

be pyrophoric when exposed to air or moisture depending on the counter ion used: the potassium salt is the least stable. Polar protic solvents will degrade Fp anion solutions by deprotonation since the Fp anion reacts with Brønsted acids to form the neutral hydride complex (FpH). The hydride complex is unstable and thermally decomposes to the Fp_2 dimer and hydrogen gas, that is, an overall redox reaction occurs.

Despite these unwanted tendencies, the reducing ability of the Fp anion has been useful in explaining its reactivity according to researchers Beletskaya and coworkers [26]. These researchers characterized the Fp anion as having "supernucleophilicity, supersoftness, and high reducing power." This "supersoftness" is exemplified by the nature of the leaving group in the aforementioned HME mechanism of vinyl and aryl halides, where the Fp anion prefers soft leaving groups such as the iodo anion. These researchers have found that Fp anion prefers a "reverse leaving group order" where $I > Br \gg Cl > F$. This order is contrary to ordinary nucleophiles and the reverse of the classical S_N2Ar mechanism [25]. The authors note the extraordinary capacity of the Fp anion to reduce organic substrates (R group in HME mechanism of Scheme 1) to carbanions. As mentioned earlier, this reduction can also result in a subsequent, unwanted reaction of the neutral complex FpX, where X = Cl, Br, or I, with an available Fp anion to give the Fp_2 dimer.

2.4. *Other characteristics of the (η^5-C_5H_5)$(CO)_2$Fe metalate and its derivatives*

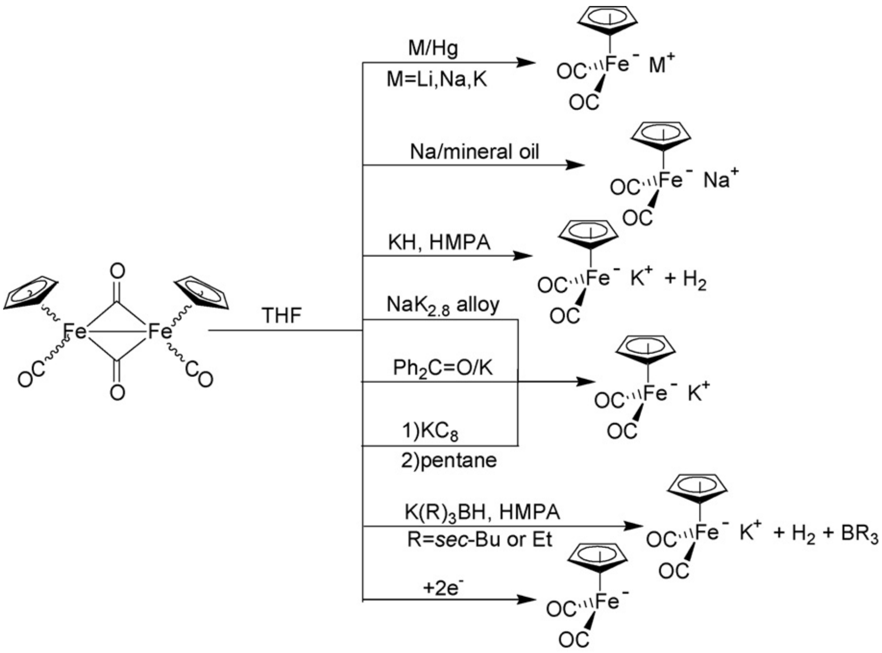
Even with its high reactivity, the Fp anion can be readily adapted by ligand exchange and it and its derivatives are soluble in many organic solvents. Sunderlin and Squires calculated the Fe–CO bond strength in Fp anion to be 184 ± 16 kJ/mol at 0 K and 188 ± 16 kJ/mol at 298 K [30]. Despite this high bond strength, the CO ligands can be exchanged with other neutral donor ligands such as phosphines after reaction with an appropriate electrophile. This provides a unique method for preparation of asymmetric complexes. Although outside the scope of this review, modification of the aromatic Cp ligand with electron donating groups (EDG) further enhances the nucleophilicity of the anion. This increased nucleophilicity has been well-noted with Fp* anion, where the Cp* ligand (i.e., $C_5(CH_3)_5$) replaces the Cp ligand (i.e., C_5H_5). As with other organometallic compounds, and despite being a salt, MFp is highly to slightly soluble in many organic solvents such as THF, ether, diglyme, hexane, and others regardless of the counterion M.

3. Synthesis of the (η^5-C_5H_5)$(CO)_2$Fe metalate

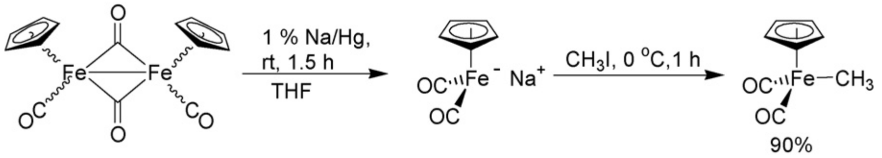
In addition to its greater nucleophilicity, the Fp anion is also the least expensive metalate to synthesize, of those in Table 1. Commonly, these anions are prepared by reduction of the corresponding dimer or trimer (bi- or trimetallic complex) at room temperature with a dilute sodium in mercury amalgam in THF [13] and used *in situ* [11]. In addition to the Fp anion, the bimetallic complex di-μ-carbonyldicarbonylbis(η^5-cyclopentadienyl)diiron, $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)_2]$, or Fp_2 dimer is a valuable starting material in the synthesis of other mononuclear and bimetallic complexes [11]. One example is the formation of $[Fp]_2(\mu\text{-}Se)$ from elemental selenium and Fp_2 dimer [31]. Of the starting dimers or trimers which are commercially available to synthesize the anions in Table 1, the Fp_2 dimer is the least expensive per mole. The Fp_2 dimer is also readily soluble in many organic solvents such as THF. An overview of some of the reactions used to produce the Fp anion from the Fp_2 dimer in THF is presented in Scheme 3.

The aforementioned mercury amalgam procedure has been used with various metals including Li, Na, and K. A typical procedure is that from Mapolie, Moss, and Smith whereby Fp_2 dimer (1.00 g, 2.83 mmol) is stirred over sodium amalgam (0.30 g Na; 4.0 mL Hg) in THF (20 mL) at room temperature [32]. In another method reported by Mahmood and Hossain, 6.0 g (0.017 mol) of Fp_2 dimer is dissolved in 45 mL of THF and a 1% Na/Hg amalgam containing 1.28 g (0.055 mol) of Na metal is added and stirred at room temperature for 1.5 h. The reaction mixture is then cooled to −78 °C, whereby the amalgam solidifies and the NaFp/THF solution is transferred to another flask. Upon warming to 0 °C, 8.0 g (0.056 mol) methyl iodide is added dropwise and allowed to stir for 1 h. Removal of the THF solvent, chromatographic separation by pentane, and removal of the pentane solvent provided 5.85 g of the Fp methyl complex in 90% yield (Scheme 4) [33].

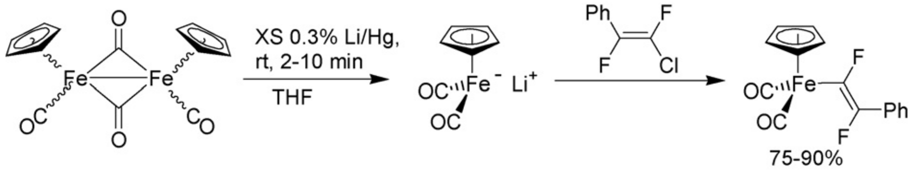
Contamination of the Fp metalate by Fp_2Hg [34] has been one disadvantage of the mercury amalgam procedure. Another noted disadvantage is the low solubility of alkali metals in mercury (e.g., Li = 0.05% (w/w) [35]) thus requiring the handling of large quantities of mercury. Despite these disadvantages,



Scheme 3.

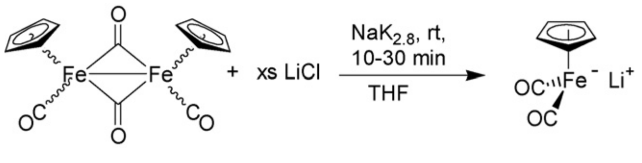


Scheme 4.



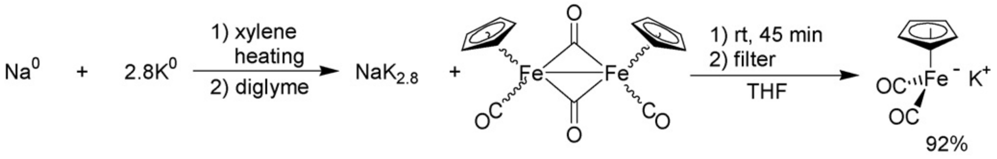
Scheme 5.

the mercury amalgam procedure is simple, rapid (10–30 min), and widely used. Sazonov et al. have prepared the LiFp salt from Li–Hg amalgam (Scheme 5). In this procedure, 10 mg of Fp_2 dimer in 1–3 mL of THF was reduced with an excess (0.05–0.07 mL) of 0.3% Li/Hg amalgam under vigorous stirring. The reaction was complete within 2–10 min. As expected, their product also contained impurities and yields were in the range of 75–90% after reaction with (*Z*)-β-chloro-α,β-difluorostyrene (Scheme 5). Alternatively, these researchers also produced the lithium metalate by transmetallation of KFp in THF (Scheme 6) [35]. This was accomplished by reacting a 0.03–0.06 M THF solution of Fp_2 dimer with $NaK_{2.8}$ alloy in the presence of a small excess of LiCl. After 10–30 min the LiCl dissolved completely and the colorless KCl solid precipitated.



Scheme 6.

Several other heterogeneous procedures are actually available for generating the Fp metalate from the Fp_2 dimer in addition to the mercury amalgam methods. Other heterogeneous methods include use of a sodium mineral oil dispersion [36] and the aforementioned $NaK_{2.8}$ alloy, i.e., 1 mol Na:2.8 mol K [37]. The latter is reported to be superior to Na/Hg amalgam since it is a more rapid reaction and gives uncontaminated solutions of KFp. The alloy is prepared by gently heating 77 g potassium metal and 16 g sodium metal in 100 mL of xylene. Upon coalescence of the metals, 50 mL of diglyme is added causing the alloy to form a globule. The liquid alloy is also easily transferred from the globule and measured by syringe at room temperature to a THF solution of Fp_2 dimer, and after 45 min, the alloy partly solidifies and is readily filtered. The yield is 92% based on Fp_2 dimer



Scheme 7.

(Scheme 7) [37]. This method has also been used extensively by researchers Beletskaya, Artamkina, and Sazonov et al. in their work with Fp anion in nucleophilic aromatic substitutions by the aforementioned HME mechanism (Section 2) [25,26,38]. Rück-Braun and coworkers have reviewed the procedures for Fp anion formation and report the Na/Hg amalgam and $NaK_{2.8}$ alloy procedures have both been used in large scale applications [39].

Researchers Mayr et al. have experimentally prepared KFp in 81% yield by reaction of Fp_2 with potassium–graphite laminate (KC_8) in THF (Scheme 3) [40]. A similar procedure has also been performed by Fischer et al. [41]. The group of Lapinte has been able to effectively sonicate potassium metal into a THF solution to give a blue-grey colloidal suspension that effectively generates the reactive Fp anion *in situ* within 15 min [42]. Researchers Pinkes and Cutler have also used a similar method to generate KFp in a standard ultrasonic cleaning bath [43].

Homogeneous methods include the use of hydride reducing agents. Shore [44] prepared the Fp anion by reduction of Fp_2 using potassium hydride in HMPA/THF. Addition of HMPA to THF increases the solubility of potassium hydride and reduces $K^+ Fp^-$ ion-pair formation in the reaction product. No separation is required since the hydrogen byproduct is evolved upon formation (Scheme 3). Gladysz et al. [45] used the trialkylborohydride K-Selectride® [(sec-$C_4H_9)_3BH^-$] K^+ to achieve the same goal, although in this procedure the trialkylborane must be removed (Scheme 3) [39]. Rück-Braun has used the Gladysz procedure to efficiently prepare an Fp cationic carbene complex from Fp anion in one pot [46].

A very important homogeneous method for preparing the potassium salt of the Fp anion was reported by Shore and Plotkin [47]. Reduction of the Fp_2 dimer was conveniently achieved by use of potassium benzophenone ketyl (Scheme 3). The salt was isolated and stored for months under an inert atmosphere. In regard to other homogenous methods, it should be mentioned that naphthalene–sodium [48] and potassium silicides [49] have also been employed.

Although not new (see Table 1), another method for the synthesis of Fp anion directly from its dimer involves electrolysis. In this method, electrons are transferred from a metal electrode to the Fp dimer to form salts of the Fp anion in an electrochemical oxidation–reduction reaction. The electrochemical oxidation–reduction reactions were found to be reversible [22,50]. The electrolytic method is sometimes used to generate Fp anion when it is required as a catalyst (e.g., in electrocatalysis). One such example is that of Tanji et al. for selective carboxylation of olefins (see Section 4.2.3, Scheme 180) [51]. Several authors have recently used electrolytic methods to generate the Fp anion. Citing ecological reasons in lieu of mercury amalgams and alkali metals, researchers Astruc et al. were able to produce the Fp anion using a consumable Mg anode, a stainless steel grid cathode, and n-Bu_4NBr as electrolyte in THF solution. Magdesieva, Butin, Beletskaya, Artamkina, and others investigated the use of various mediators to reductively activate organohalides for reaction with Fp anion in homogeneous redox catalysis [52]. Their work is derived from earlier research on the Fp anion generated by electrolytic reduction of the Fp_2 dimer [53,54].

Besides the classical alkali earth salts of Fp anion, other cations have been employed. Voskoboinikov and Beletskaya have formed the ytterbium salt $(THF)_4Yb[Fp]_2$ salt in 42% yield by reaction of Fp_2 dimer with Yb metal in liquid ammonia followed by dilution in THF after evaporation of ammonia. A subsequent IR spectrum revealed absorptions for carbonyl ligands with stretching frequencies of 1934 and 1860 cm^{-1}. The authors conclude that the salt contained two equivalent Yb–Fe bonds, and the Yb is not coordinated with the bridging carbonyl ligands [55]. Ellis and Flom, originators of the aforementioned $NaK_{2.8}$ alloy method, found in 1975 that a KFp solution in THF readily reacted with n-tetrabutylammonium perchlorate to form the [(n-$Bu)_4N$]Fp salt in 92–95% yields. This was the first isolation and characterization of this extremely reactive anion originating from the Fp_2 dimer [37]. The $NaK_{2.8}$ alloy method was also used to generate [ZnCl]Fp salt *in situ* simply by the addition of $ZnCl_2$ to the reaction mixture [29]. The authors claim this salt is useful for avoiding side reactions because the Fp anion is a good reducing agent.

Schuman and workers were able to form the Grignard salt, FpMgBr, from Fp_2 dimer, 1,2-dibromoethane, and magnesium turnings in THF solution within 5 h at room temperature [56]. It should be mentioned that the research group of Maslennikov was able to form a Grignard salt of the type FpMgCl from FpCl instead of directly from the Fp_2 dimer. The group reacted FpCl with magnesium metal in DMF solution for 24 h followed by precipitation with dioxane. Analysis of the filtrate indicated the presence of the $Mg[Fp]_2$ salt. This led the researchers to suggest equilibrium between FpMgCl and $Mg[Fp]_2$ in the reaction mixture [57].

4. Reactions of the (η^5-C_5H_5)$(CO)_2$Fe metalate

Besides being inexpensive to synthesize and demonstrating higher rates of reaction, the Fp anion also reacts with a range of electrophiles. The Fp anion has undergone a plethoric range of reactions with electrophiles. Many novel and synthetically significant organometallic complexes have been prepared from the Fp metalate. Electrophiles have been reacted with the Fp anion via substitution and addition mechanisms. These reactions and their applications will be reviewed. A concise list of the reactions in tabulated form (Tables 3–16) is available as supplementary data.

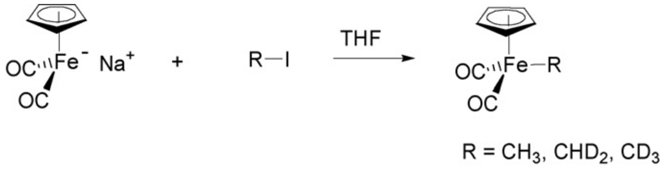
4.1. Substitution reactions of the (η^5-C_5H_5)$(CO)_2$Fe anion

In substitution reactions with the Cp$(CO)_2$Fe metalate, the halide, tosylate, or triflate group in many electrophiles have been replaced by the Cp$(CO)_2$Fe moiety to form new iron bonds. The new bond that is formed with Fp is often a carbon–iron bond. The electrophiles that form new iron–carbon bonds can be separated into those that react with the Fp anion at a carbon that has a specific hybridization, that is, sp^3, sp^2, or sp. Therefore, the various electrophiles that form new Fe–C bonds will be separated and discussed based on the reactive carbon's hybridization. In the first section, electrophiles with the reactive carbon having sp^3 hybridization will be studied, for example, such electrophiles as alkyl halides, allyl tosylates, or haloalkyl silanes. In the second section, electrophiles with the reactive carbon having sp^2 hybridization will be studied, for example, such electrophiles as vinyl triflates, aryl halides, and acyl halides. In the third section, electrophiles with the reactive carbon having sp hybridization will be studied, for example, such electrophiles as alkyne or allene tosylates.

Increasingly, complexes are being discovered containing new bonds that are not Fe–C bonds. Many of these compounds contain new Fe–Si, Fe–B, Fe–Sn, as well as other new Fe-metal bonds. These new complexes will be discussed in a separate section that follows the Fe–C section. Each group of reagents will be individually reviewed.

4.1.1. Fe–C (sp^3) bond formation (Table 3)

Alkyl halides and tosylates combined represent possibly the largest single group of electrophiles used to form new Fp to carbon bonds. Although many of the procedures used today represent those established before 1994, the compounds are being employed in varied and elegant ways.



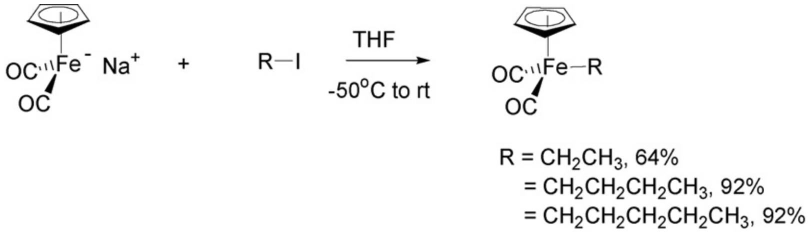
Scheme 8.

As the simplest of Fp compounds, McQuillian and coworkers prepared [58] isotopomers of the methyl complex to study their vibrational spectra, geometry, and bond properties (Scheme 8). The methyl complex has even found its way into the educational laboratory experience. Mocellin et al. had their student's prepare [59] the Fp methyl complex as part of an undergraduate laboratory experiment to provide students with a more realistic view of experimental science.

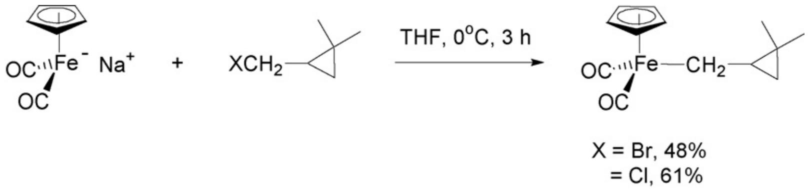
Hossain and Mahmood synthesized [33] the methyl Fp complex for conversion to an iron Lewis acid ($Fp^+\cdot$THF BF_4^-) catalyst. The catalyst promoted reactions between aromatic aldehydes and ethyl diazoacetate to form acrylic acid ethyl esters and β-keto esters. The $Fp^+\cdot$THF BF_4^- complex has found wide-spread utility as a catalyst for Diels–Alder reactions, cyclopropanations, epoxidations, and aziridinations. Its usefulness as a catalyst for these reactions has been reviewed [60].

The ethyl complex (Fp-CH_2CH_3) is a gateway to the π-complex. Thus, to study the synthesis and characteristics of bimetallic complexes, Gibson et al. prepared [61] the Fp η^1-ethyl complex by a known procedure as a means to forming the π-complex $Fp^+C_2H_2$ BF_4^-.

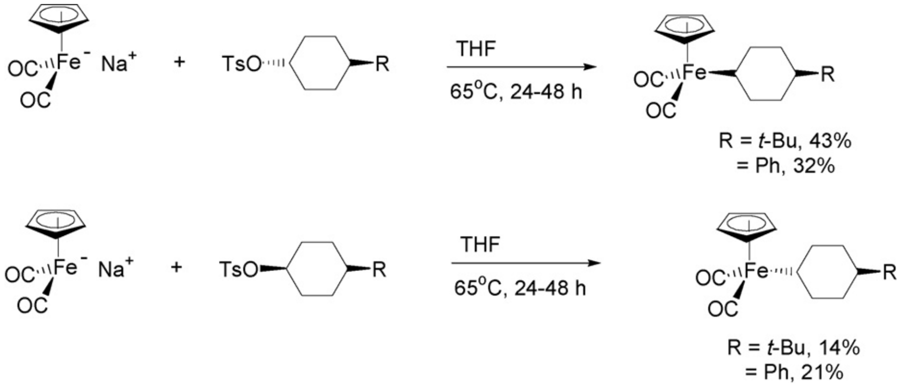
Two researchers converted the ethyl complex to phosphine derivatives. Idmoumaz et al. transformed [62] the ethyl complex to the phosphine analog CpFe(CO)$(PPh_2Me)CH_2CH_3$ to study alkyl migration. Brookhart and Scharrer synthesized [63] several Fp–alkyl complexes (Scheme 9) as intermediates in the preparation of phosphine ligated carbene complexes. The carbenes were employed in insertion reactions with organosilanes.



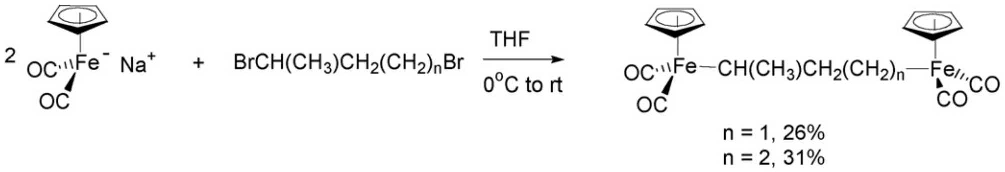
Scheme 9.



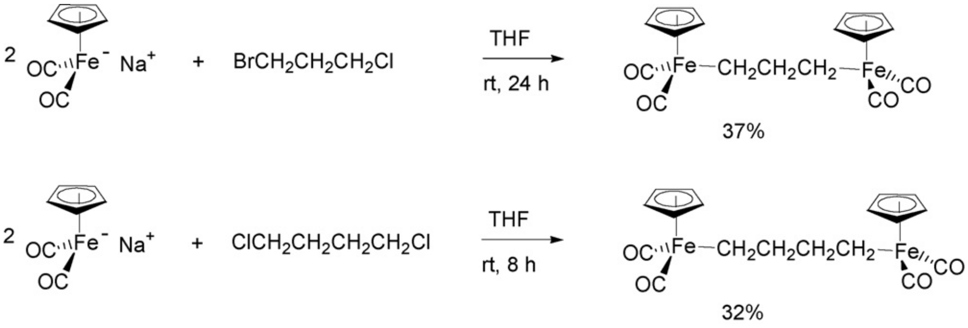
Scheme 10.



Scheme 11.



Scheme 12.



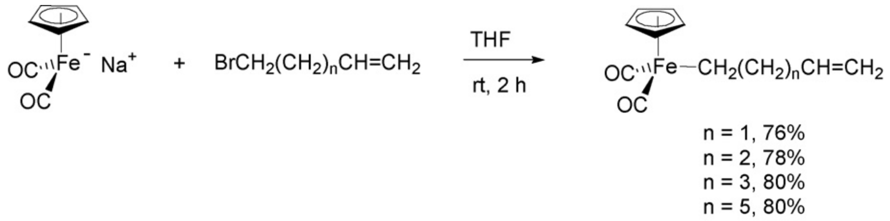
Scheme 13.

In order to understand the mechanism of ring-opening in the 2,2-dimethylcyclopropylmethyl Fp complex, Hill and Li prepared [64] a complex from the Fp anion and 2,2-dimethylcyclopropylmethyl halide (Scheme 10).

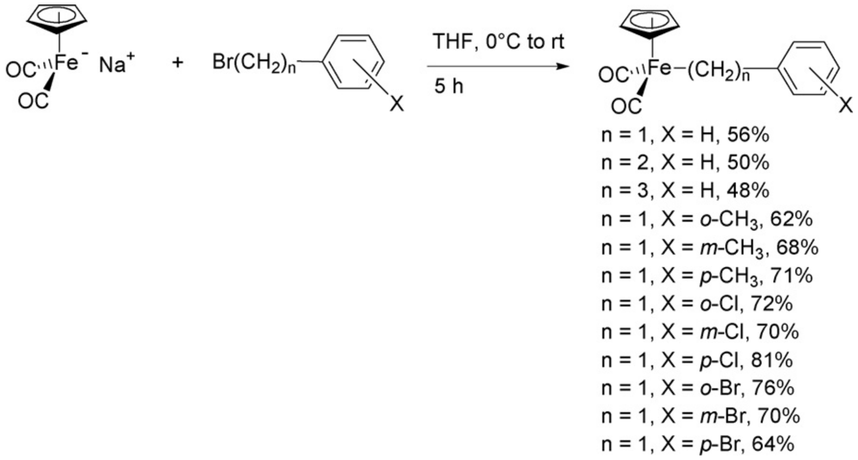
The *cis*- and *trans*-isomers of both 4-phenyl- and 4-*t*-butylcyclohexyl *p*-toluenesulfonates were individually reacted [65] with the Fp anion via S_N2 displacement by Stessman and coworkers (Scheme 11). These 4-substituted cyclohexane Fp complexes were prepared to determine the conformational energy using variable-temperature ^1H NMR.

Binuclear Fp complexes were prepared by two different research groups. In order to study alkyl migration reactions, Cammell and Andersen prepared [66] two binuclear Fp complexes using a modification to a known procedure (Scheme 12). Upon treatment with PPh_3, alkyl migration to form the acyl complex occurred at the branched end of the molecule via CO insertion. Safiullah et al. synthesized and characterized [67] two similar Fp binuclear complexes from the Fp anion and alkyl dihalides (Scheme 13).

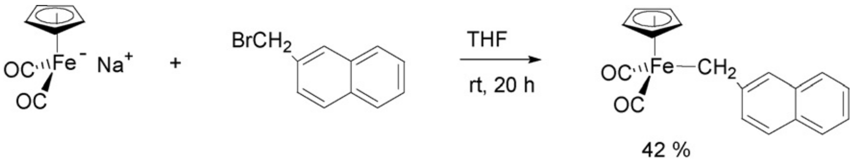
Mapolie and coworkers have prepared a number of Fp complexes that contain a terminal double bond (Scheme 14). The earliest examples of these Fp η^1-alkenyl complexes were used [68] to study their reactivity toward hydrogenation, hydroboration, hydroformylation, and Lewis acids. Two more complexes



Scheme 14.



Scheme 15.



Scheme 16.

were subsequently prepared [69] and converted [70] to their cationic iron η^2-(α,ω-diene) analogs for reactivity studies with various nucleophiles.

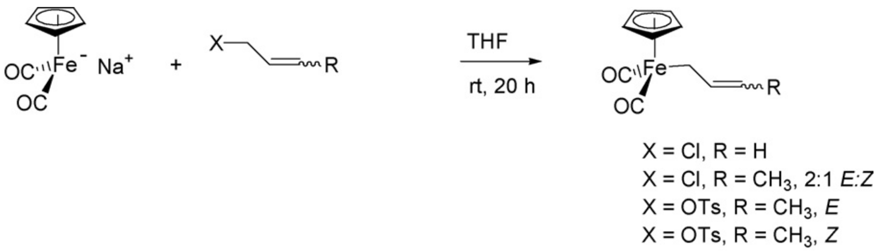
Many researchers have prepared Fp complexes having unsaturation alpha to the methylene or methine group. Benzylic and allylic halides and tosylates have served as electrophiles in the majority of these reactions. Zamojski and Guo prepared [71] the Fp benzyl complex (Fp-CH_2Ph) as an intermediate to the acyl complex, CpFe(CO)(PPh_3)($COCH_2Ph$). Alkylation, aldol condensation, and decomplexation reactions were then studied.

Moss and Andersen prepared [72] a range of ring substituted benzyl iron complexes (Scheme 15) to study the substituent effect on CO insertion to form the corresponding acyl complexes. Ullah et al. synthesized [73] the Fp η^1-2-methylnaphthalene complex to characterize and study its photochemical reactivity (Scheme 16).

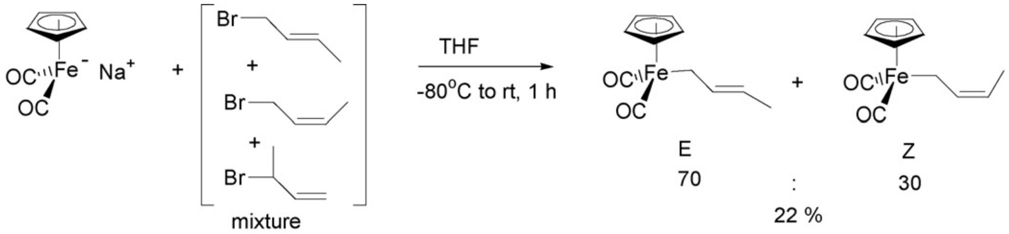
Undoubtedly, the allylic complex is one of the most studied unsaturated Fp compounds. Many research groups have studied allylic complexes as reagents for additions to aldehydes and ketones as well as cycloaddition reactions. Agoston prepared [74] Fp η^1-allylic complexes to study their use in BF_3-promoted addition to aldehydes forming homoallylic alcohols (Scheme 17). Jiang synthesized [75] the Fp η^1-allylic complex (Fp–CH_2–CH=CH_2) to study BF_3-promoted addition to ketones. Van Steen and coworkers used the Fp η^1-allylic complex to study the reaction pathway for chain growth in the Fischer–Tropsch synthesis [76,77]. Bohac prepared *E*,*Z* mixtures of η^1-(crotyl)Fp from NaFp and an isomeric mixture of commercially available crotyl bromide. The η^1-(crotyl)Fp compounds were prepared [78] (Scheme 18) and used in a regio- and stereoselective [3 + 2] cycloaddition reaction with a $Fe(CO)_3$ complexed tropylium ion to generate hydroazulene skeletons related to sesquiterpene.

Mayr and coworkers studied [40] the effect that the Fp moiety had on the reactivity of the π bond in allyl complexes. They synthesized (Scheme 19) the allyl complexes and reacted them with various electrophiles to discover that there was a six- to ninefold increase in nucleophilicity. Welker et al. prepared [79] Fp–CH_2CH=CHR (R = H, CH_3) from the allyl chlorides and the Fp anion using previously reported procedures. The resulting complexes were used to form thiosulfinate esters which have potential as inhibitors for cancer and HIV type 1 replication.

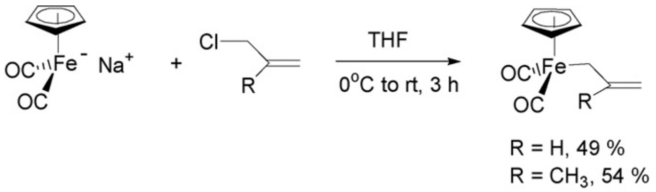
Welker's research group has also developed the use of alkynylic halides and tosylates as electrophiles in substitu-



Scheme 17.



Scheme 18.



R = H, 49 %
R = CH_3, 54 %

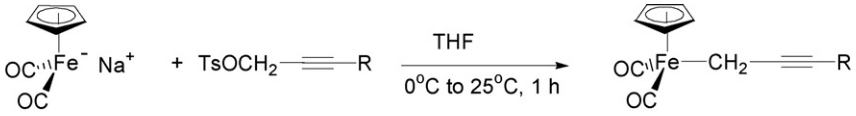
Scheme 19.

tion reactions with the Fp anion and applied the complexes to organic synthesis. Welker et al. prepared [80] the Fp η^1-allylic complex (Fp–CH_2–CH=CH_2) and the Fp η^1-alkynylic complex (Fp–CH_2–$CCCH_3$) by known procedures so they could be reacted with ketenes as a means to cyclopentenones. Welker et al. utilized 2-propyne tosylate electrophiles to prepare [81–84] the corresponding Fp complexes (Scheme 20) for [3 + 2] cycloadditions with sulfur dioxide and sulfur trioxide. The iron-mediated complexes were employed as precursors to sulfur heterocycles such as sulfenate esters which are potential inhibitors of cancer and HIV type 1 replication.

A third major area of research has been electrophiles that form new Fe–C bonds but often also contain an element (e.g., silicon, oxygen, or nitrogen) or group of elements (e.g., carbonyl or ester group), besides just carbon and/or hydrogen, which impact the compounds' reactivities or properties. The largest such group are the haloalkyl silanes and they will be discussed together. All the other electrophiles will be discussed individually.

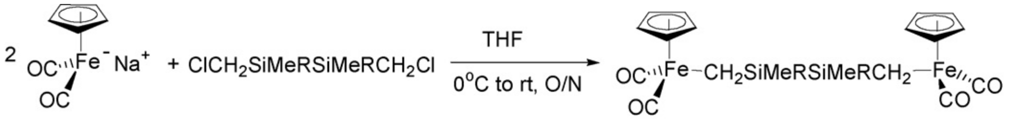
Pannell's research group has been very instrumental in the development of Fp-containing alkyl silanes, much of it related to photochemical transformations. Pannell and coworkers prepared [85] oligosilyl-containing bimetallic Fp complexes and reported that these complexes quantitatively undergo photochemical conversion to 1,3-disilacyclobutanes. To study the factors that control the photochemically induced eliminations and rearrangements, Pannell et al. synthesized [86] additional oligosilyl diFp derivatives with silyl groups in various positions relative to iron (Scheme 21). Complexes with both Fe–C and Fe–Si bonds were prepared.

In further studies to understand the nature of photochemical-induced eliminations and rearrangements, Pannell and cowork-

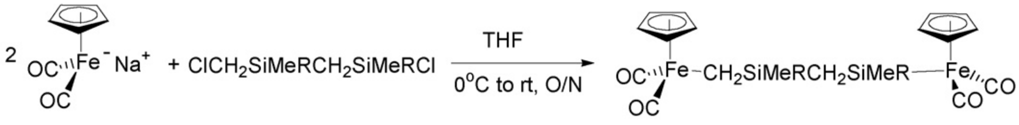


R = 4-CH_3OPh, 72 %
R = 4-t-BuPh, 97 %
R = 3-*c*-C_6H_9, 84 %
R = CH_3, 70 %
R = Ph, 66 %
R = 2-Cl-*c*-C_6H_8, 58 %
R = 4-CH_3COPh, 58%
R = 4-CF_3Ph, 33 %

Scheme 20.

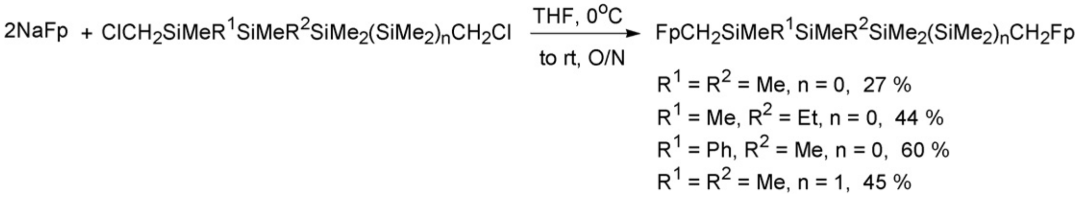


R = Me, 64 %
R = Ph, 24 % (*meso/dl*, 5:1)

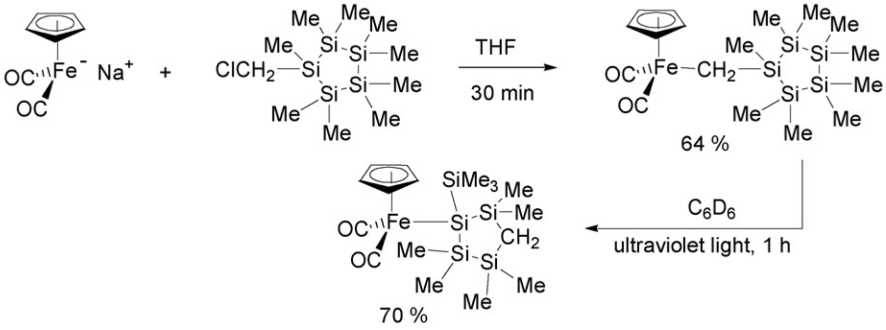


R = Me, 35 %
R = Ph, 71 %

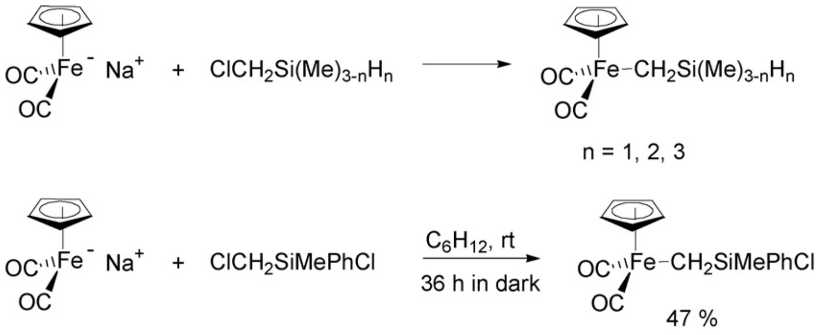
Scheme 21.



Scheme 22.



Scheme 23.



Scheme 24.

ers synthesized [87] diFp derivatives of tri- and tetrasilane complexes (Scheme 22). This same group prepared [88] an Fp η^1-methylcyclic polysilane (Scheme 23) and studied its reactivity toward ultraviolet irradiation. Only a single rearranged product resulted from irradiation.

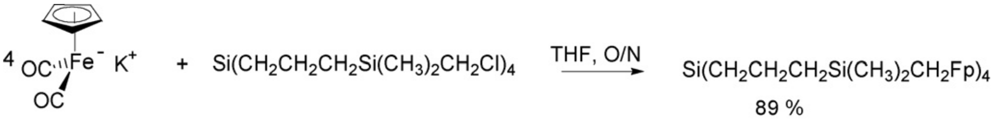
Malisch and coworkers synthesized [89] Fp-containing α-methylsilyl complexes for conversion to the corresponding Fp-containing silanols and siloxanes (Scheme 24). The Fp α-methylsilylmethylphenylchloro complex was also later prepared [90] then subsequently converted to the silanol derivative (Scheme 24).

Moss and coworkers reacted [91] the Fp anion with a chloromethyl terminated silane dendrimer (Scheme 25). The dendrimer was isolated in high yield, characterized, and various other reactions were attempted. The authors cited many applications for dendritic polymers, including use as an immobilization phase for homogeneous catalysts.

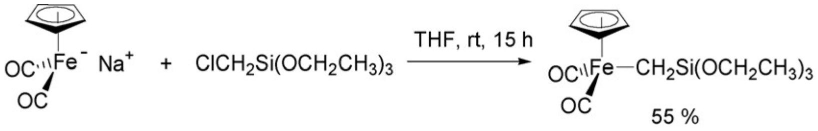
In an attempt to prepare an organoiron oxetane, Enders and coworkers synthesized [92] the α-triethoxysilylmethyl Fp complex (Scheme 26) and subsequently treated the complex with either Me_3NO or irradiation.

Turnbull et al. prepared [93] a wide range of $CpFe(CO)_2$-containing complexes in order to determine the ^{13}C NMR chemical shift effect of the Fp moiety. Fp-substituted cyclohexanes and tetrahydropyrans were synthesized in low to moderate yields from the corresponding tosylate or halide electrophiles (Scheme 27).

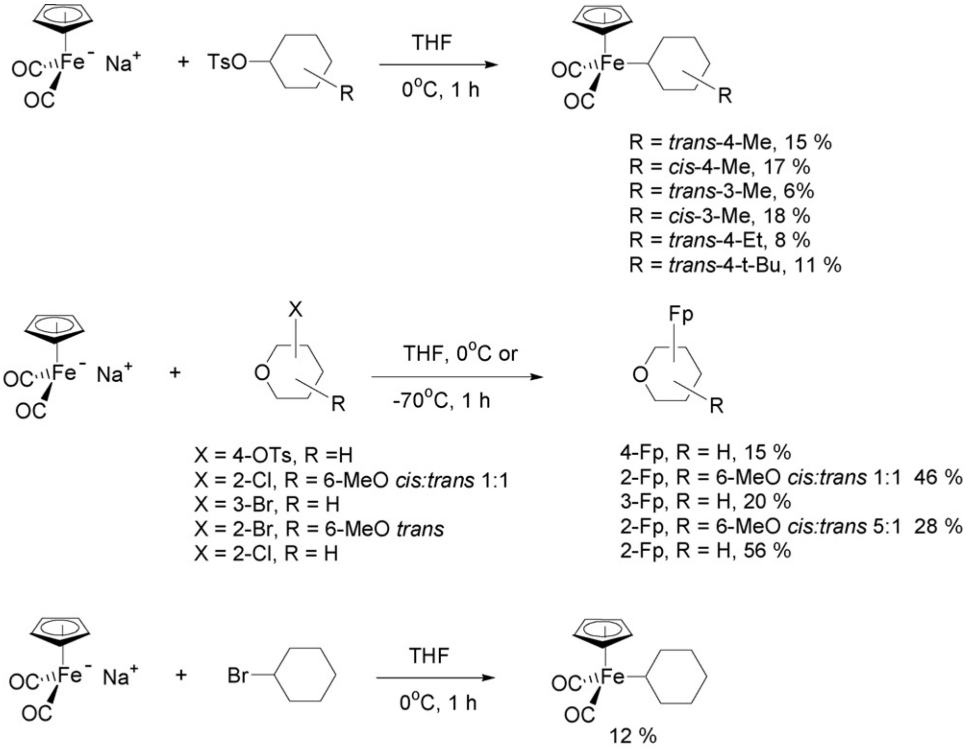
Two ester complexes were prepared by different research groups. Cotton and Schmid prepared [94] $FpCH_2CO_2SiMe_3$ by modification of a known procedure (Scheme 28). The



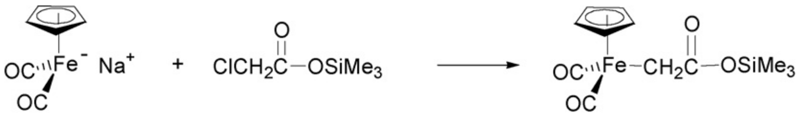
Scheme 25.



Scheme 26.

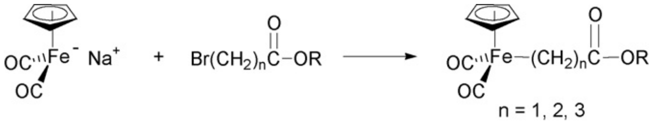


Scheme 27.



Scheme 28.

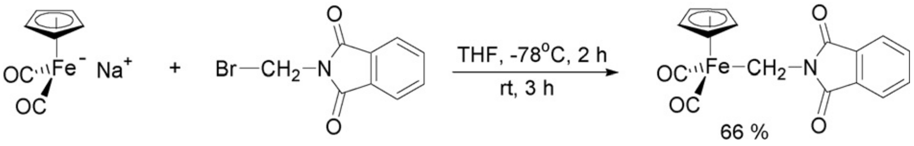
silylester served as a precursor to the weakly acidic carboxylic acid complex. The latter functioned as a chromium ligand which allowed preparation of the $Cr_2(\mu\text{-FpAc})_4(FpAcH)_2$ complex without axial ligation. Saidi et al. reacted [95] the Fp anion with alkyl bromoesters as a means to diesters via oxidative carbonylation with ceric ammonium nitrate (Scheme 29).



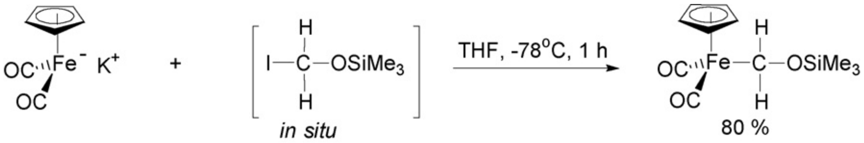
Scheme 29.

A rather unusual phthalimidomethyl Fp complex was reported by Enzmann et al. [96] after they reacted the Fp anion with bromomethylphthalimide (Scheme 30). This complex was prepared as part of a study to understand *N*-protected groups and their role and use as catalysts in amidocarbonylation reactions for potential use in peptide synthesis.

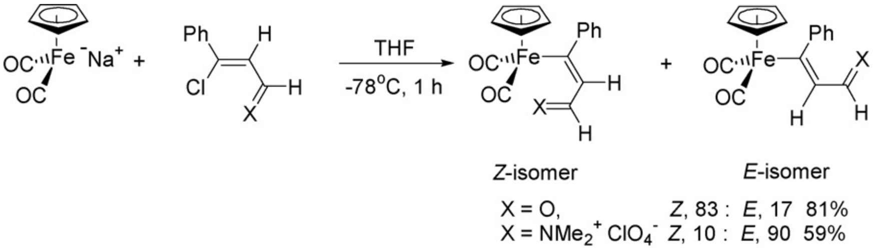
Hossain and coworkers generated α-siloxyiodomethane, either *in situ* from iodotrimethylsilane and formaldehyde or from



Scheme 30.



Scheme 31.



Scheme 32.

other sources of formaldehyde, and subsequently reacted it with the Fp anion to provide [97] the α-siloxymethyl Fp complex (Scheme 31). This complex served as an efficient precursor to the corresponding carbene in reactions with alkenes to form cyclopropanes.

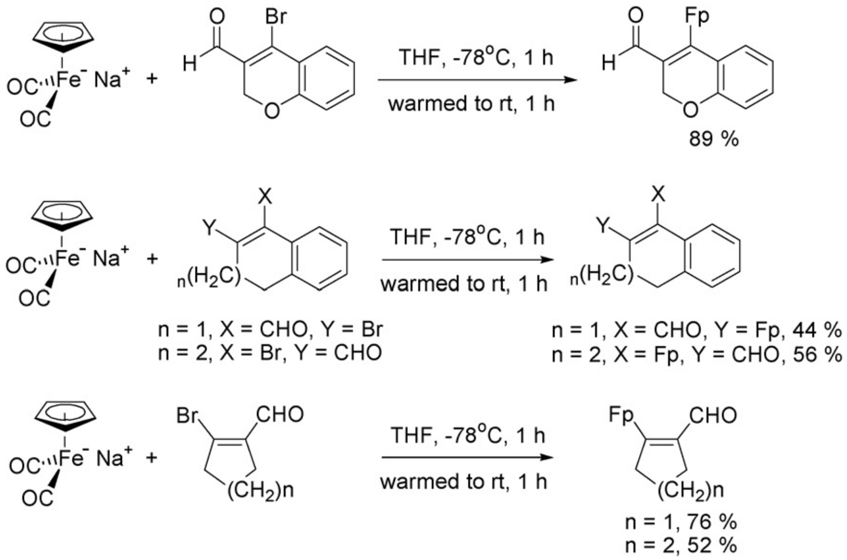
4.1.2. Fe–C (sp^2) bond formation (Tables 4 and 5)

In this section, electrophiles with the reactive carbon having sp^2 hybridization will be discussed; these are the vinyl, aryl, and acyl halides, and the triflates, and tosylates. Many of these reactions have been carried out to prepare precursors for further synthetic transformations and others simply performed to study and understand the mechanisms involved in substitution reactions by the Fp anion. The latter studies have added to the growing evidence for the supernucleophilicity of the Fp anion.

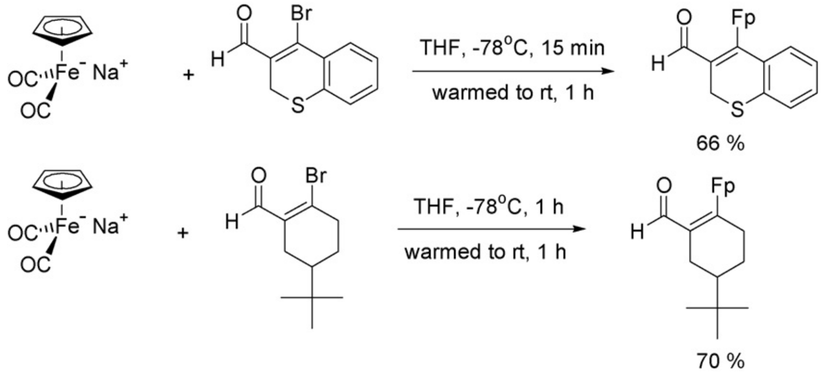
Rück-Braun et al. have reviewed [98] the use of organoiron compounds for selective organic transformations. In addition, many of the reactions involving Fp vinyl complexes as intermediates in various cyclizations have been developed by the Rück-Braun research group. Rück-Braun prepared [99] vinylogous iron complexes (Scheme 32) in order to transform them into α,β-unsaturated γ-lactams. The α,β-unsaturated γ-lactams were the target molecules in a later publication using additional Fp-substituted vinyl aldehydes (Scheme 33) as intermediates prepared [100] from the Fp anion and vinylhalo aldehydes.

Novel intramolecular cyclocarbonylations were achieved by Rück-Braun and Möller using Fp-substituted cyclic vinyl aldehydes (Scheme 34) [101]. These Fp complexes were subsequently transformed into α,β-butenolides and γ-butyrolactones.

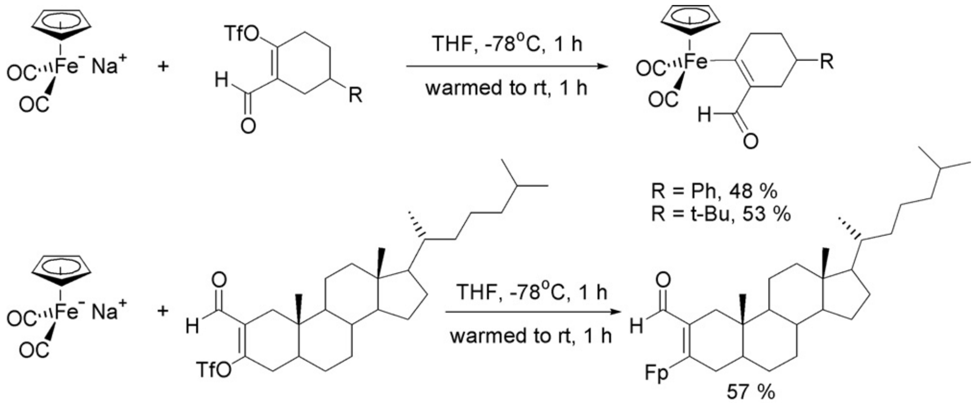
Rück-Braun and coworkers have also employed triflate as the leaving group to prepare [102] cyclohexene carbaldehyde Fp complexes (Scheme 35). Reaction of the Fp anion with β-trifluoromethyl(sulfonyloxy)-substituted cyclic enals provided the complexes in 48–57% yield. The cyclic iron-substituted compounds were used as intermediates to 5-substituted α,β-butenolides but have potential as precursors for the synthesis of other lactone or lactam derivatives.



Scheme 33.



Scheme 34.



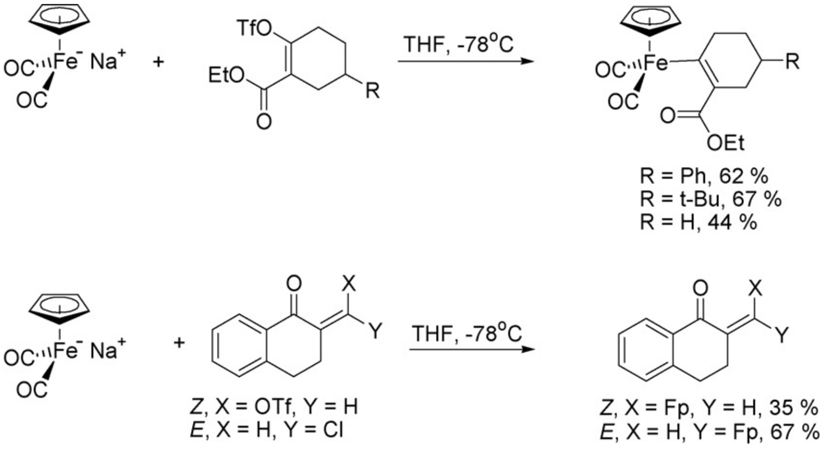
Scheme 35.

As part of their attempts to increase the scope of reactions with vinyl triflates and halides, Rück-Braun and coworkers extended [103] their Fp anion reaction to ethoxycarbonyl cyclohexenes and tetralones (Scheme 36). These compounds served as precursors to α,β-butenolides and γ-lactams.

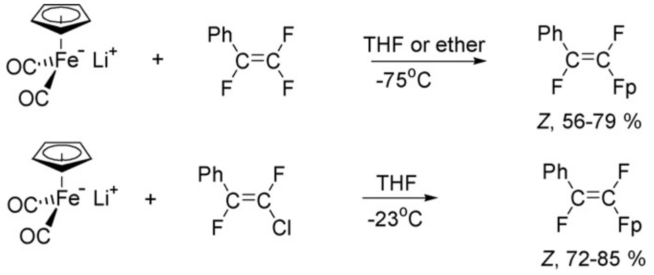
Besides lactones and lactams, the Rück-Braun group extended the use of Fp-substituted vinyl aldehydes to 5-substituted dihydropyrrolones. The Fp anion was reacted [104] with cyclic carbaldehyde bromides (see Scheme 33) and the complexes formed were converted to *N*-sulfonyl azadienes for further reaction with carbon nucleophiles.

Another research group that has studied vinyl electrophiles extensively is the Beletskaya research group. Whereas the Rück-Braun group focused their attention on use of the Fp complexes for organic synthesis, the Beletskaya group has focused on understanding the mechanism and reactivity of the Fp anion with vinyl halides.

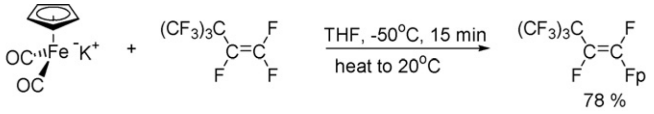
Beletskaya et al. studied [35] the effect of the lithium cation on the reactivity of the Fp anion with vinyl electrophiles via nucleophilic vinyl substitution (Scheme 37). Solvent effects indicated that the reaction rate increases as the fraction of solvent-separated ion pairs and free ions increases.



Scheme 36.



Scheme 37.



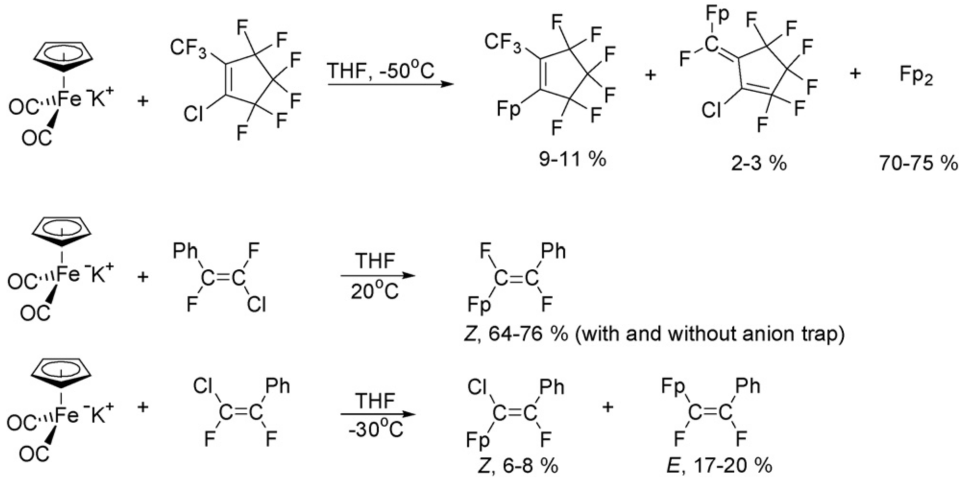
Scheme 38.

In their continued studies of anionic transition metal carboxylates in nucleophilic vinyl substitution reactions, Beletskaya and coworkers reacted [105] the Fp anion with perfluoro(3,3,-dimethyl-1-butene) (Scheme 38). They attributed the factor responsible for the predominantly *trans* isomer to be strong steric shielding of the double bond by the $(CF_3)_3C$ group. They note that the reaction of the "supernucleophilic" Fp anion with this perfluorovinyl electrophile to be very fast even at −50 to −80 °C.

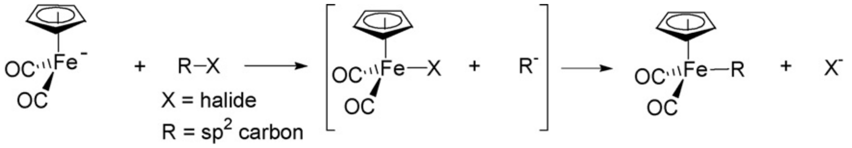
To extend the scope of their study of the mechanism involved in aromatic substitutions to vinyl substitutions, Beletskaya et al. studied [106] the reactions between anions of transition metal carbonyls and two alkene halides. These researchers reacted the highly electrophilic 1-chloro-2-(trifluoromethyl)-hexafluorocyclopent-1-ene with various carbonylates including the Fp anion (Scheme 39). Their study confirmed that the Fp anion reacts more rapidly than the carbonylates $CpW(CO)_3{}^-$, $CpMo(CO)_3{}^-$, $Re(CO)_5{}^-$, and $Mn(CO)_5{}^-$. In fact, the reaction is so rapid that these researchers could not establish the exact mechanism by which the main product (Fp dimer) was formed. They also studied the reactivity of the vinyl electrophiles, *Z*- and *E*-β-chloro-α,β-difluorostyrene. If the vinyl substitution mechanism was similar to aromatic substitution mechanisms, then an "anionic trap," e.g., *t*-BuOH or α-PhCH(Et)CH, would capture the alkenyl carbanion intermediate and confirm that the first step was halogen exchange with the Fp anion. Indeed, this did not happen as evidenced by the absence of any effect on the product distribution with *Z*-β-chloro-α,β-difluorostyrene. Thus, at least with these electrophiles, the previously assumed S_N2 nucleophilic substitution mechanism was consistent with their results.

More recently, Beletskaya et al. have shown [107] that a HME mechanism (Scheme 40) is the most plausible route to products formed from reaction between Fp anion and certain vinylic substrates. In an attempt to demonstrate a correlation between the HME mechanism and Fp anion reaction with trifluorohaloethene or 1-halo-1,2,4,4,4-pentafluoro-3,3-bis(trifluoromethyl)-1-butenes, these researchers monitored the reaction products in the absence and presence of the "proton donors," *t*-BuOH or α-PhCH(Et)CN (Scheme 41). The low yields of substituted products in the presence of the "proton donors" and the presence of FpBr supported the HME mechanism for these electrophiles.

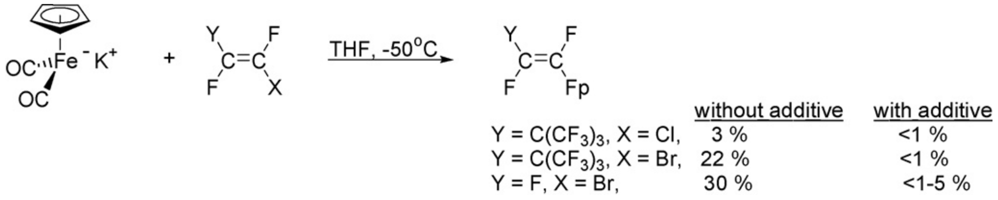
Reasoning that high halogen electrophilicity makes the HME mechanism particularly facile for polyfluorinated substrates, Beletskaya and coworkers provided [26] additional examples using common, non-fluorinated vinyl halides. An α-activated methyl *Z*-α-bromocinnamate, an active heterocyclic 2-bromo-



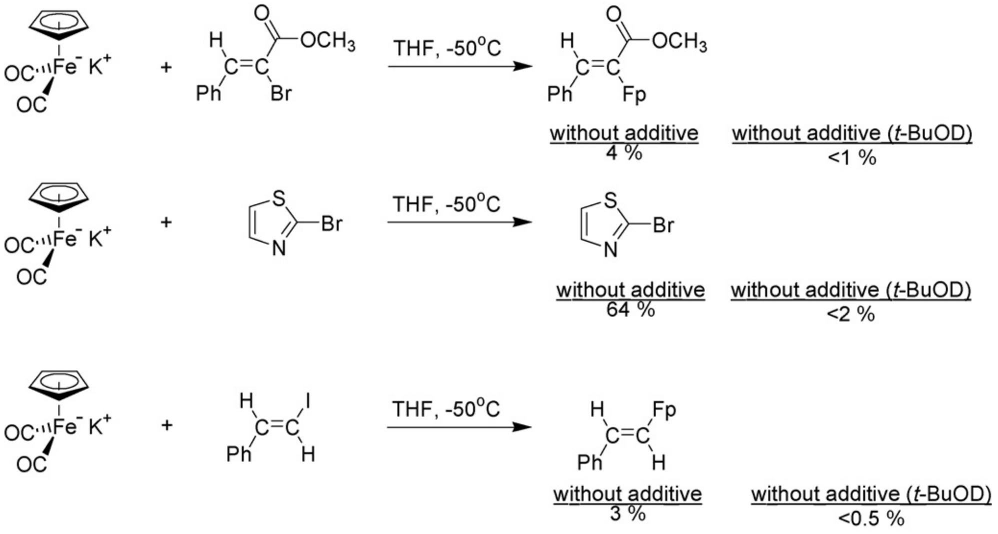
Scheme 39.



Scheme 40.



Scheme 41.



Scheme 42.

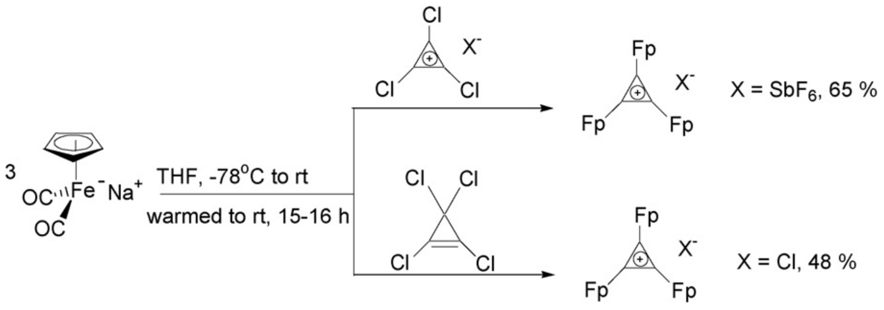
1,3-thiazole, and an unactivated β-iodostyrene were treated much like the polyfluorovinyl electrophiles. Although the nucleophilic substitution yields in most cases were rather low, treatment with the anionic trap *t*-BuOD led in every case to lower yields and accompanying formation of monodeuterated alkenes. Both of these outcomes are supportive of a HME mechanism (Scheme 42).

Other researchers have employed vinyl halides or vinyl halide-like electrophiles for various purposes. Selegue and coworker synthesized and characterized [108] a cyclopropenium cation with three Fp moieties (Scheme 43). Despite repeated attempts using reductants and nucleophiles to generate new derivatives of this trimetallic cyclopropenium complex, the complex was unreactive.

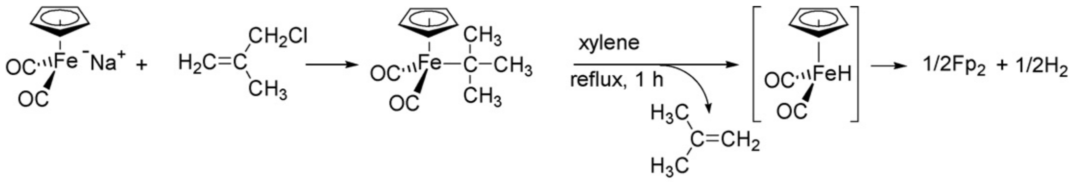
Ganter and coworkers prepared [109] an Fp-substituted *tert*-butyl complex by a known procedure in order to determine the products of thermal decomposition in refluxing xylene (Scheme 44). In this way, these researchers were able to corroborate a proposed mechanism for break-up of a phosphole-substituted iron dimer.

Magdesieva et al. employed [52] mediator assisted (*ortho*-dicyanobenzene) electrochemical activation of both aryl and vinyl halides to react with the Fp anion via nucleophilic substitution of the halide (Scheme 45). Magdesieva's group expanded [110] these electrochemical reactions to fluorovinyl halides and aryl halides for generation of Fp-substituted analogs (Scheme 46).

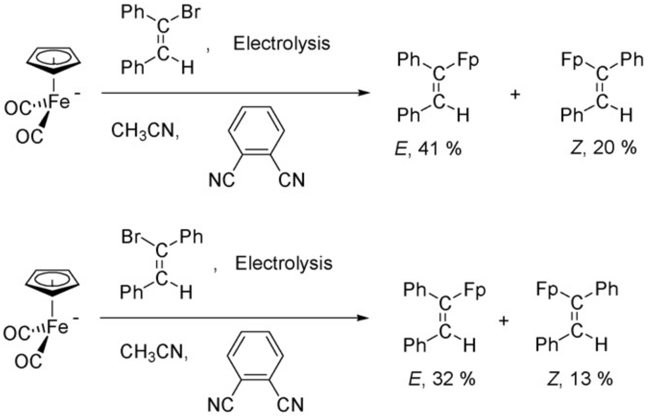
Magdesieva further extended the application of electrochemically generated Fp anion reactions to three other aryl halides. The FpC_6H_4CN complex was prepared [53] in 45% yield via nucleophilic aromatic substitution of bromide in 4-bromobenzonitrile (Scheme 47). Magdesieva et al. also reacted [54] 1,4-diiodobenzene via electrochemically induced substitution to study the conditions for mono- versus disub-



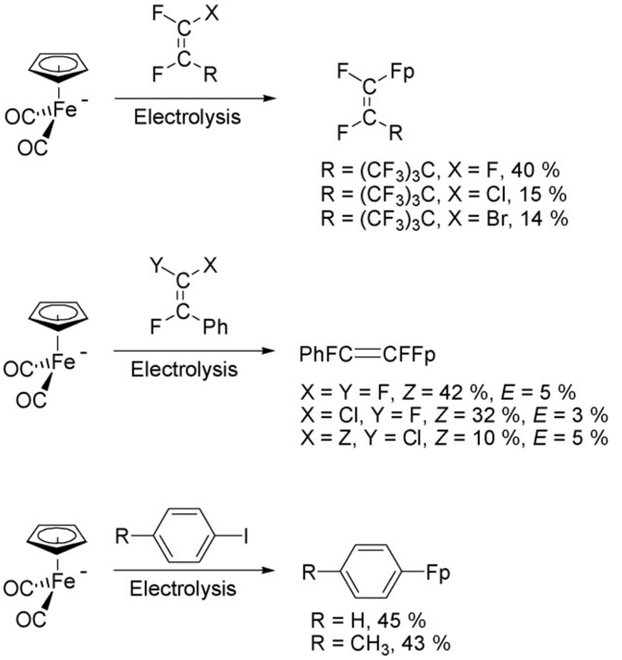
Scheme 43.



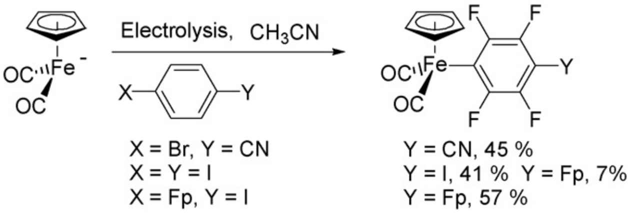
Scheme 44.



Scheme 45.



Scheme 46.



Scheme 47.

stitution with Fp anion. To confirm that 1,4-disubstituted Fp benzene results from the monosubstituted Fp intermediate, 4-cyclopentadienyldicarbonyliron-1-iodobenzene was reacted separately with the Fp anion (Scheme 47).

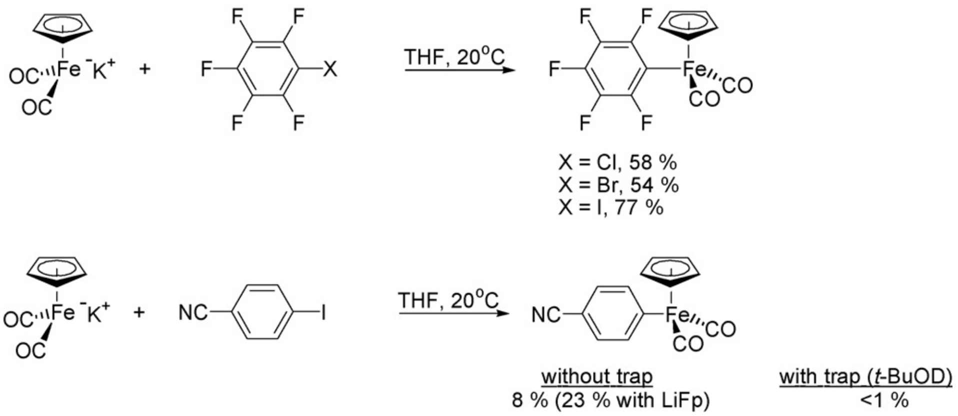
Much like Magdesieva, Beletskaya recognized a similarity in the reactivity of vinyl electrophiles and aryl electrophiles with the Fp anion. To study the mechanistic similarity, Beletskaya and coworkers prepared [26] a number of Fp aryl complexes (Scheme 48). As with the vinyl halides, anionic traps were shown to reduce the yield using aryl halides. Reduced yields in the presence of anionic traps provided evidence to support a HME mechanism proposed by Beletskaya for aryl halides with the Fp anion.

Recognizing a cationic impact to the product yield led Beletskaya to study [25] other counter ions instead of potassium in addition to other reaction conditions (Scheme 49). Beletskaya investigated in great detail the factors (reactant ratio, solvent, counter ion, and temperature) that control the yield from reaction between Fp anion and chloropentafluorobenzene. The highest yield occurred in THF at room temperature with 25% excess C_6F_5Cl. Mechanistic implications were investigated using “anionic traps,” sometimes termed “proton donors,” such as *t*-BuOH or α-PhCH(Et)CN; and it was determined that the reaction proceeded through a $C_6F_5^-$ intermediate via the aforementioned halogen metal exchange mechanism (see Scheme 40).

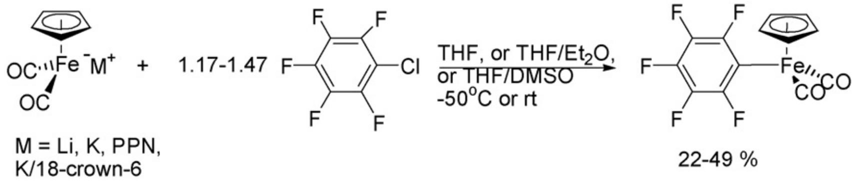
Beletskaya and coworkers continued their investigation [111,112] of the halogen-exchange mechanism (HME) by studying the reactions between transition metal anions ($Cp(CO)_2Fe^-$, $Mn(CO)_5^-$, $Re(CO)_5^-$) and polyfluoroinated arenes containing heavier halogen atoms (Cl, Br, I). A number of Fp-containing polyfluoro complexes were isolated or detected in the process of their investigations (Scheme 50). In their studies, other mechanistic pathways (addition–elimination, S_N2, and free radical) were eliminated. Interestingly, when a tosylate group replaced the heavy halogen atom, the fluoride ion was the better leaving group and only *meta*- and *para*-toluenesulfonylate Fp complexes were detected.

To provide a useful route to mono-, di-, and trinuclear σ-aryl iron complexes via palladium catalysis, Beletskaya and coworkers reacted [29] FpZnCl with triiodobenzenes or diiodobenzenes (Scheme 51). Many factors such as reaction times, equivalents of FpZnCl, types of catalysts ($PdCl_2(PPh_3)_2$ and $Pd_2(dba)_3$), solvents (THF and $CHCl_3$), and catalyst ligands (trifurylphosphine and $AsPh_3$) were varied.

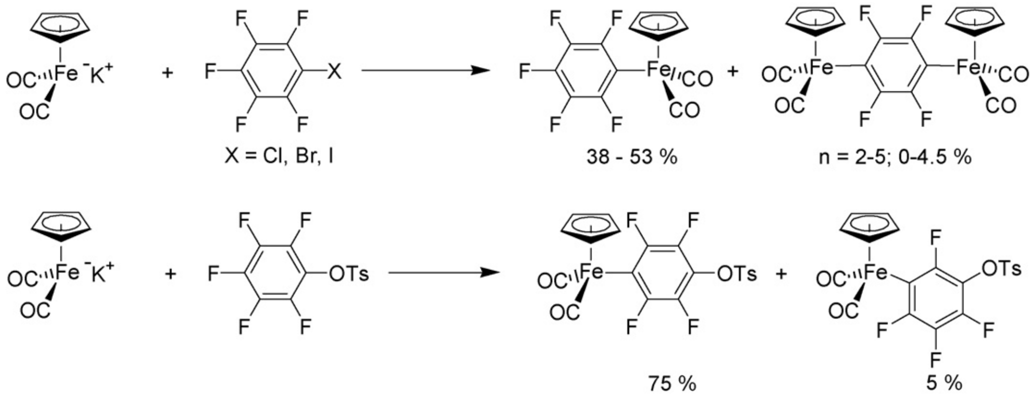
To explore the impact that fused aromatic rings would have on their reactivity toward Fp anion, Hunter and coworkers prepared, characterized, and studied [113] Fp substituted derivatives of



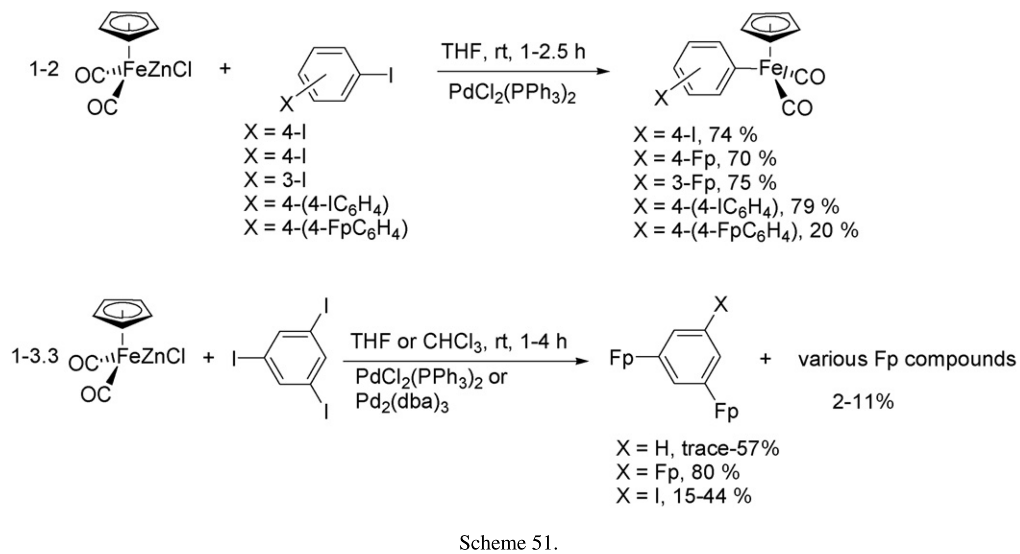
Scheme 48.



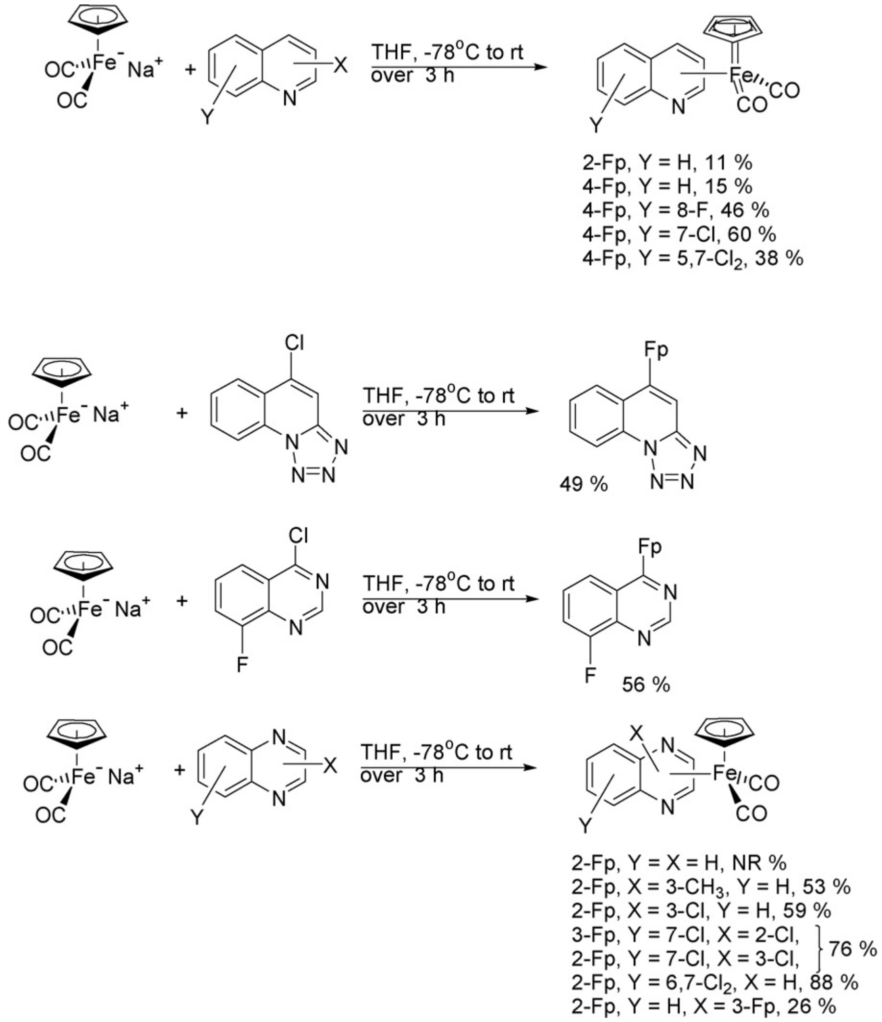
Scheme 49.



Scheme 50.



Scheme 51.



Scheme 52.

fused heteroarenes. A wide range of Fp complexes having quinoline, quinazoline, and quinoxaline functionality were synthesized (Scheme 52).

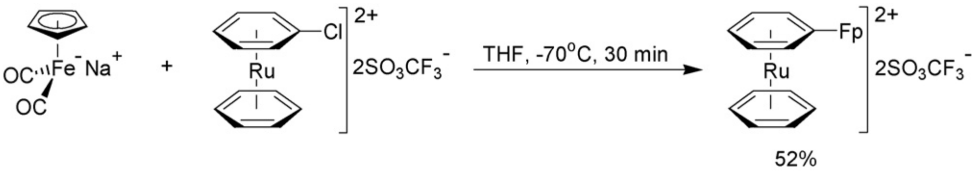
As part of their study of various ruthenium complexes, Beck and coworkers prepared [114] an unusual Fp η^1-phenyl bound ruthenium complex via an addition-elimination reaction (Scheme 53).

The final group of electrophiles that are used to form new Fe-C (sp^2) bonds are acyl chlorides and alkylchloroformates as well as anhydrides (Table 5), that is, each has a reactive sp^2-hybridized carbon atom as part of a carbonyl group. The carbonyl carbon is attacked by the Fp anion with elimination of a halide or alkanoate to generate an Fp acyl complex.

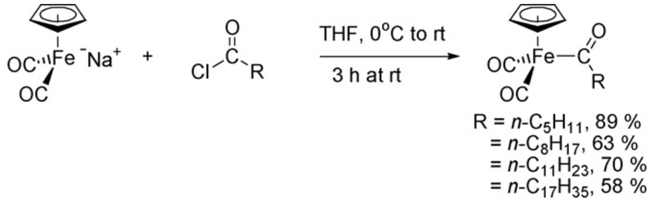
Alkyl, alkenyl, aryl, and some rather unusual acid chlorides have been employed as electrophiles in reactions with Fp anion. The simplest group of these electrophiles is the acid halide group that contains alkyl substitution, that is, FpCOR (R = alkyl group).

Yin and Moss synthesized and characterized [115] a number of long chain Fp acyl complexes from acyl chlorides and the Fp anion (Scheme 54). To study their thermal behavior, one of the representative complexes ($R = n\text{-}C_{11}H_{23}$) was investigated by differential scanning calorimetry and thermal gravimetric analysis. The complex studied was stable to 210 °C even though its melting point was rather low at 38–41 °C.

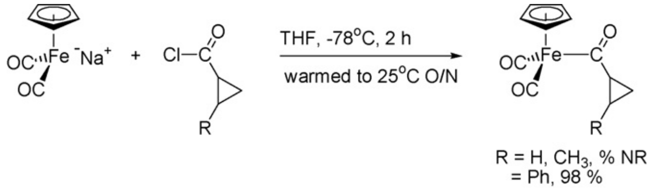
Welker and coworker prepared [79] acyl cyclopropyl Fp complexes from the Fp anion and the acid halides by either a



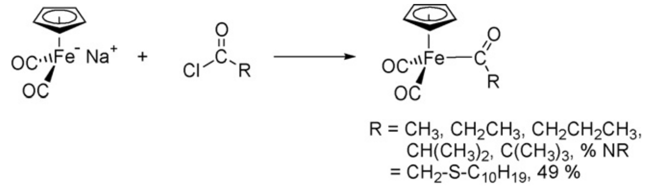
Scheme 53.



Scheme 54.



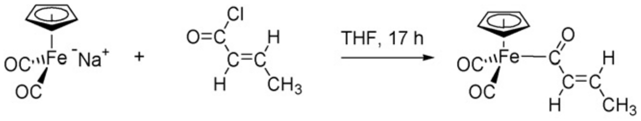
Scheme 55.



Scheme 56.

known procedure or extension of that procedure (Scheme 55). However, their target molecules were not the acyl complexes but rather the alkyl complexes. The unsubstituted Fp acyl cyclopropyl complex underwent efficient photolytic decarbonylation and subsequent 3 + 2 cycloaddition with SO_2 to form a diastereomeric mixture of sulfenate esters. Attempts to use the substituted cyclopropyl complexes in similar SO_2 reactions could not be undertaken because the photolytic decarbonylation resulted in decomposition of the acyl complexes.

Danikiewicz and coworkers prepared [116] a number of Fp acyl complexes by previously reported methods or extension of the same in order to study the mass spectrum fragmentation pattern by electron impact (Scheme 56). A common fragmentation pattern with $m/z = 205$, 177, 149, 121, 95, and 56 was observed and the structures were assigned for each Fp acyl complex. The pattern depends strongly on the stability of a radical of the alkyl group. If the radical of the alkyl group is highly stabilized, for example a tertiary group, then loss of the alkyl group is facile and occurs at the front end of the fragmentation pattern. Thereafter, three sequential CO groups are lost before the Cp group is lost or fragmented. If the radical of the alkyl group has low stability, for example an ethyl group, then three sequential CO groups are typically lost before the alkyl or Cp groups are lost or fragmented.



Scheme 58.

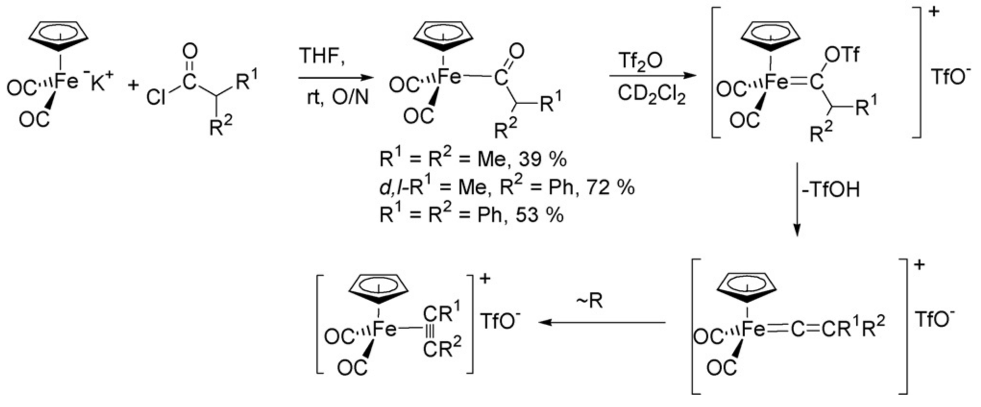
Bly and coworkers synthesized [117] three Fp disubstituted acetyl complexes to convert them to Fp η^1-vinylidene complexes. The latter complexes were reported to isomerize to the corresponding Fp η^2-acetylenes in the presence of triflic anhydride (Scheme 57).

Arguably, a more important group of acid halide electrophiles from the stand point of downstream organic transformations and mechanistic studies are those that contain unsaturated substitution, that is, FpCOR where R is an unsaturated group, the so-called Fp acyl alkenyl and Fp acyl aryl complexes.

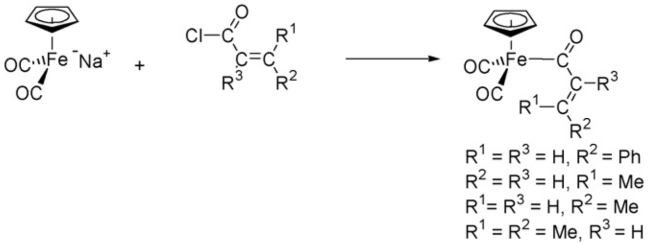
Van Steen et al. reacted [77,118] the Fp anion with *trans*-crotonyl chloride by modification of a known procedure to generate the corresponding acyl complex (Scheme 58). Decarbonylation of the acyl complex via irradiation in acetone allowed isolation of the vinyl complex, Fp–CH=CHCH_3. The possible thermal isomerization of the vinyl complex to the allyl complex was studied to help understand the chain growth mechanism in the Fischer–Tropsch synthesis.

Kwon and Ojima prepared [119] Fp α,β-enoyl complexes from acid chlorides and Fp anions by a known procedure (Scheme 59). These acyl complexes were employed as intermediates to give the α,β-enoyl chiral complexes of $CpFe(CO)(PPh_3)$. The latter have shown promise as effective reagents in stereoselective organic transformations.

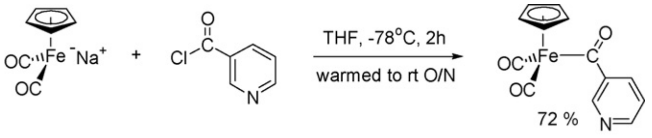
Davies et al. have also generated [120] α,β-unsaturated Fp acyl complexes by a known procedure. These acyl complexes underwent conjugate addition with a homochiral lithium amide



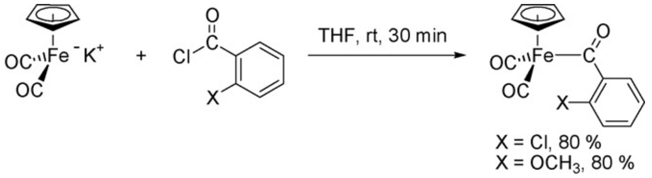
Scheme 57.



Scheme 59.



Scheme 61.



Scheme 62.

to afford Fp β-amino acyl complexes (Scheme 60). Deallylation of a substituent on the amino moiety and subsequent oxidative decomplexation resulted in homochiral β-lactams.

Davies and coworkers also reacted [121] the Fp anion with nicotinyl chloride to form the nicotinoyl Fp complex (Scheme 61). This acyl complex served as an intermediate in photolytic phosphorylation to afford CpFe(CO)(PPh_3)CO-3-pyridyl. This pyridyl chiral auxiliary reacts stereoselectively with various nucleophiles to provide 4-substituted-1,4-dihydronicotinoyl complexes.

Guerchais et al. reacted [122] the Fp anion with *ortho*-substituted benzoyl chlorides to form acyl complexes (Scheme 62). The acyl complexes were treated with methyl triflate to generate Fischer-type carbene complexes. The reactivity of the carbene complexes toward alkoxides was investigated.

Butler et al. prepared [123] the Fp-9-anthracenoyl complex (Scheme 63) as an intermediate to ferrocenyl anthracenes, which are synthons for the construction of molecular sensing devices.

Magdesieva et al. reacted [124] pentafluorobenzoyl chloride with the Fp anion to isolate and characterize various products (Scheme 64). The two main products were benzoyl derivatives and a third product implied its formation was from a radical species.

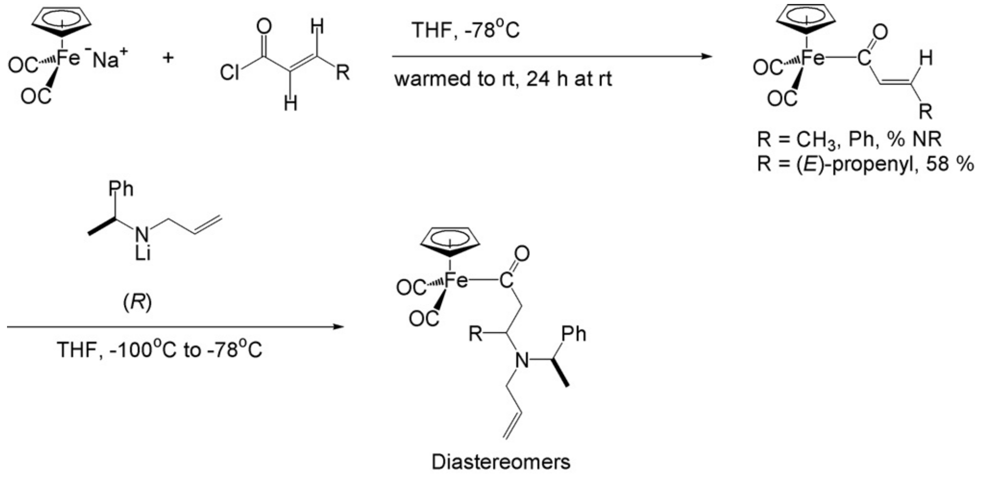
Beck and coworkers synthesized [125] the diFp acyl complex of a diacyl chloride of ethenoanthracene to study its thermal and photolytic decarbonylation products (Scheme 65). Under both thermal and photolytic conditions, decarbonylation produced ethenoanthracene and Fp dimer. Phthaloyl chloride was also reacted with Fp anion using a known procedure. Although an acyl complex was proposed as the intermediate, only Fp dimer and (*E*)-[1,1′]biisobenzofuranyliden-3,3′-dione were isolated.

Beck and coworkers also prepared [96] an Fp phthaloylacetyl complex from Fp anion and phthaloylacetyl chloride (Scheme 66). The *N*-protected aminoacetyl Fp complex could be useful for the synthesis of peptides.

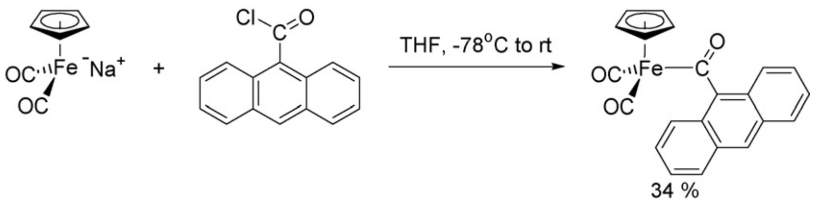
Dotz and coworkers synthesized [126] some rather exotic Fp sugar acyl complexes from the Fp anion and aldonic acid chlorides (Scheme 67). These researchers were interested in whether incorporation of the Fp fragment would impact the conformation along the carbohydrate skeleton. In fact, the Fp moiety did not significantly alter the conformation along the carbohydrate skeleton.

Alkylchloroformates and anhydrides represent the final group of carbonyl-containing electrophiles that have been successfully reacted with the Fp anion. Cutler et al. synthesized [127] the Fp methoxycarbonyl complex by modification of a known procedure (Scheme 68) and then hydrosilated the compound either in the presence or absence of a catalyst.

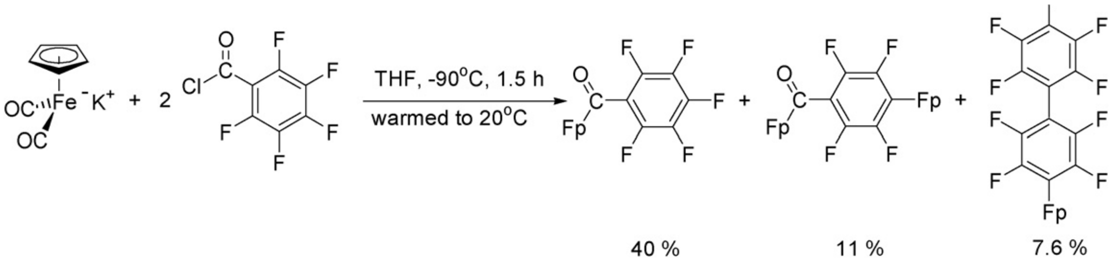
Gibson and coworkers reacted [128] ethylchloroformate with the Fp anion by a known procedure to form the acyl complex (Scheme 69) as a precursor to the Lewis acid catalyst, $CpFe(CO)_3^+$ PF_6^-. This Lewis acid was then reacted with



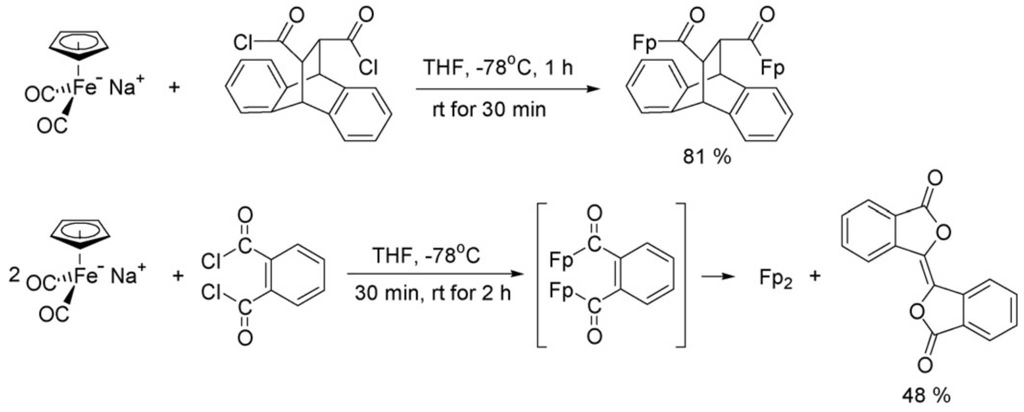
Scheme 60.



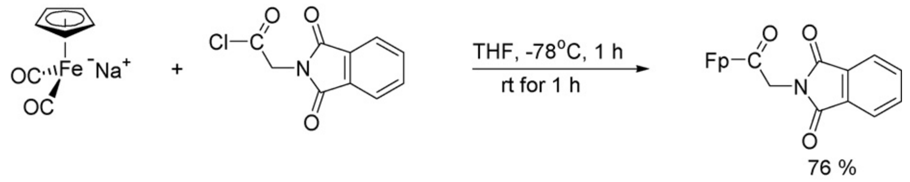
Scheme 63.



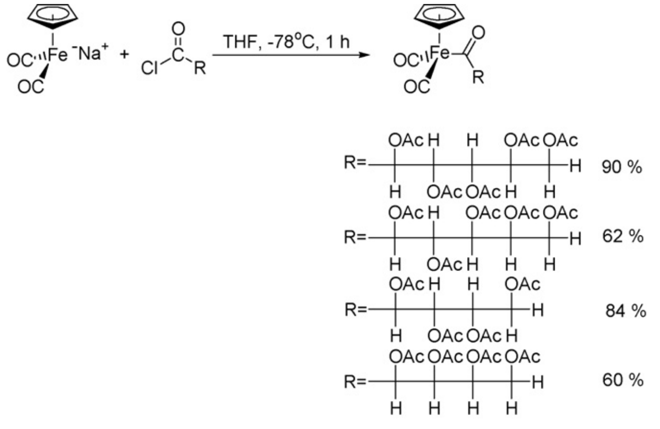
Scheme 64.



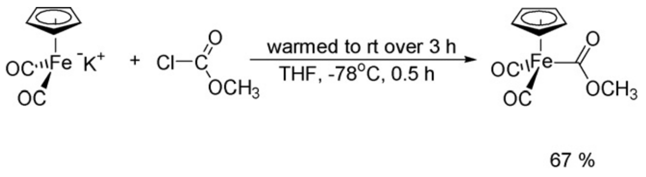
Scheme 65.



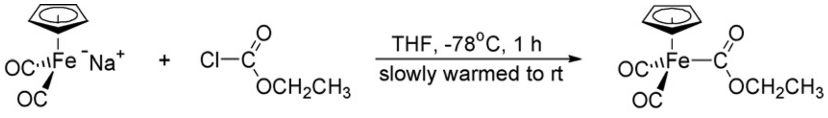
Scheme 66.



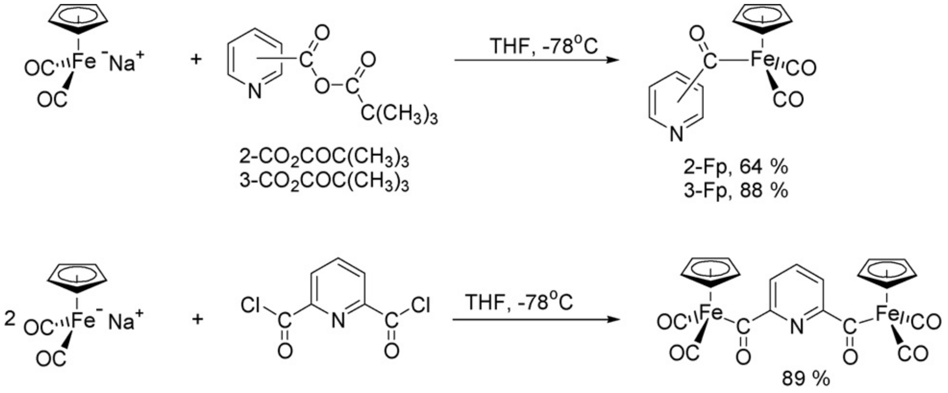
Scheme 67.



Scheme 68.



Scheme 69.

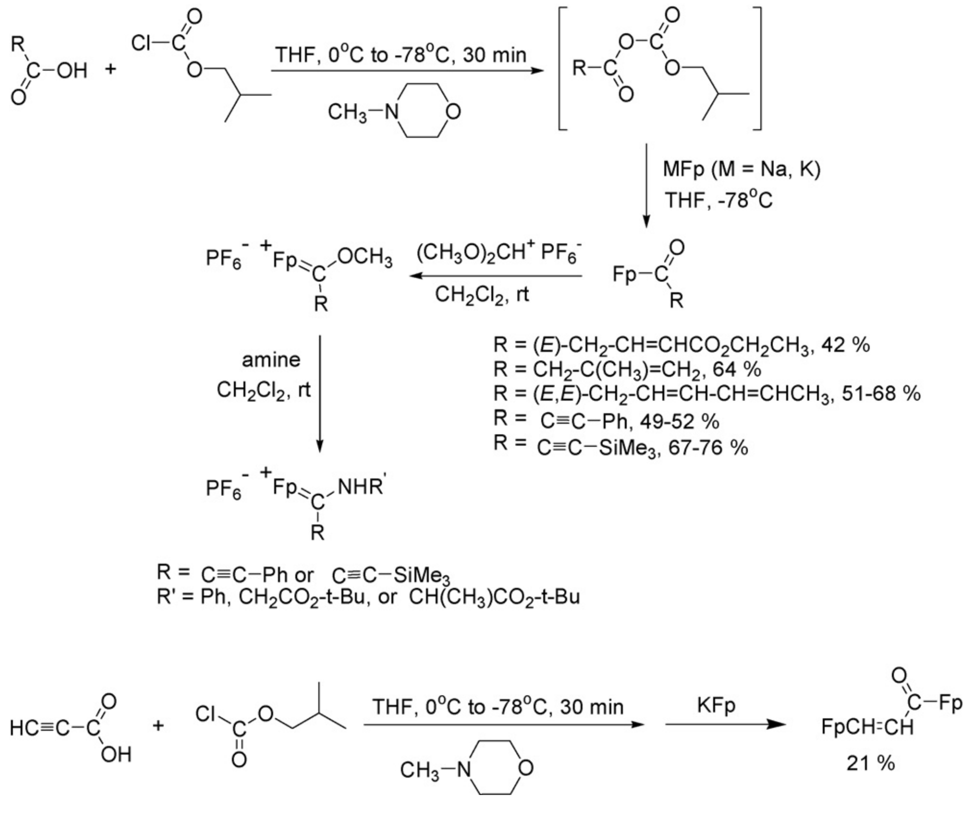


Scheme 70.

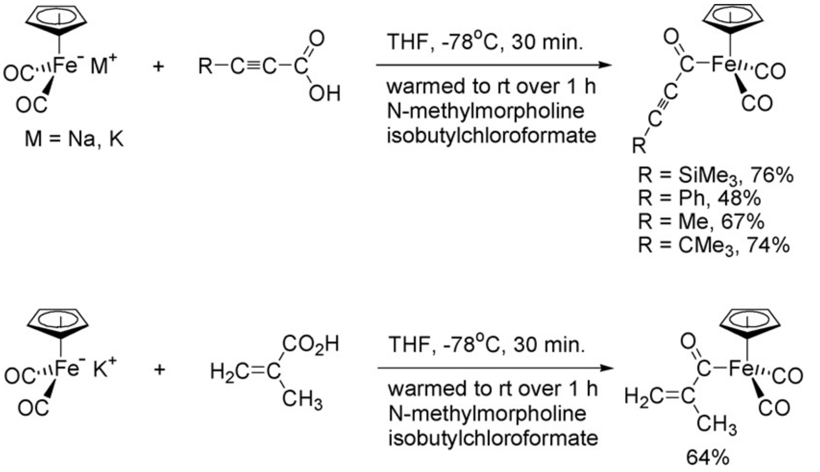
anions of chiral phosphoramides to give chiral isocyanide ligated complexes.

Beck et al. prepared [129] several Fp pyridoyl complexes to serve as ligands to palladium. Reactions between the Fp anion and anhydrides or acid halides produced the 2- and 3-pyridoyl Fp complexes in very good yields (Scheme 70).

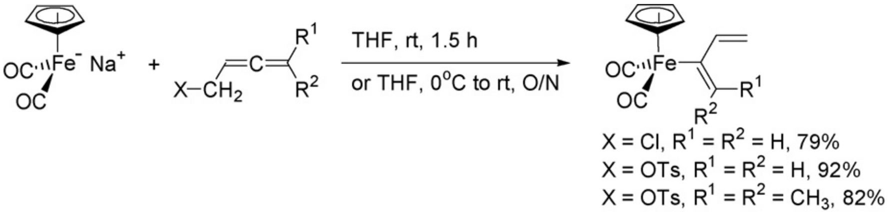
Rück-Braun and Kühn reported [130] an efficient, one-pot procedure for preparation of Fp-acyl complexes *via* a mixed anhydride formed *in situ* from carboxylic acid. The mixed anhydride is generated *in situ* from the carboxylic acid and isobutylchloroformate in the presence of *N*-methylmorpholine. The *N*-methylmorpholine hydrochloride must be separated before the solution of the mixed anhydride is treated with the Fp anion. Two of the acyl complexes were converted to the corresponding cationic (alkynyl) methoxy carbene iron complexes and treated with amines to form aminocarbene Fp complexes



Scheme 71.



Scheme 72.



Scheme 73.

(Scheme 71). Rück-Braun et al. extended [46,131] their procedure to other mixed anhydrides (Scheme 72) and reacted them with primary amines affording [(2-aminoethenyl)carbene]iron complexes.

4.1.3. Fe–C (sp) bond formation (Table 6)

In this section, electrophiles with the reactive carbon having sp hybridization will be studied, that is, alkynes and allenes. There are far fewer examples of reactions in which the Fp anion attacks a sp-hybridized carbon than either of the previous sections which featured attack at sp^3 or sp^2 carbons. Perhaps this is an area for future work.

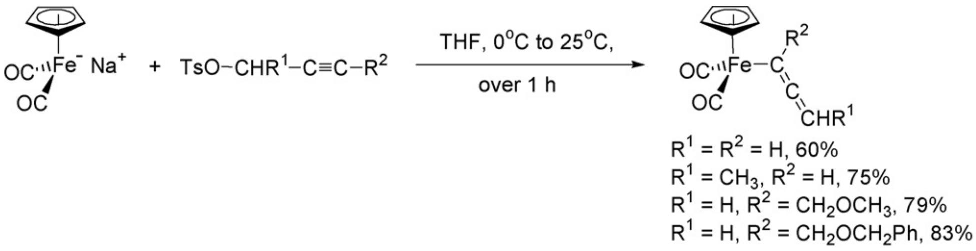
Welker and coworkers reacted [132] allene halides and tosylates with the Fp anion. Fp η^1-1,3-dienyl complexes were prepared, characterized, and their reactivity explored (Scheme 73). The compounds were found to be somewhat air and temperature sensitive so Welker attempted to form more stable complexes by photolysis and thermolysis in the presence of PR_3 or $P(OR)_3$. Instead of substitution, decarbonylation occurred with formation of CpFe(CO) η^3-butadiene.

Welker et al. also synthesized [82] Fp-containing allenyl complexes from alkynes (Scheme 74) in order to perform 3 + 2 cycloaddition reactions with sulfur dioxide. The sulfenate esters produced have potential as inhibitors of HIV type 1 replication.

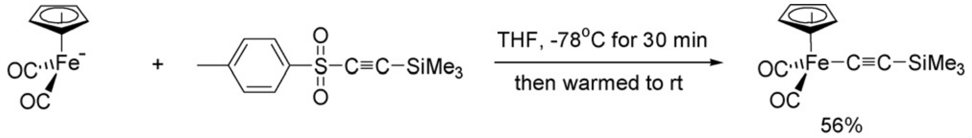
Beck and coworkers synthesized and characterized [133] an Fp-containing alkynyl complex from Fp anion and p-tolyl(trimethylsilylethynyl)sulfone (Scheme 75). The authors reported that such monometalated alkynes have potential as building blocks for metal clusters and as π-ligands.

4.1.4. Fe–Si bond formation (Table 7)

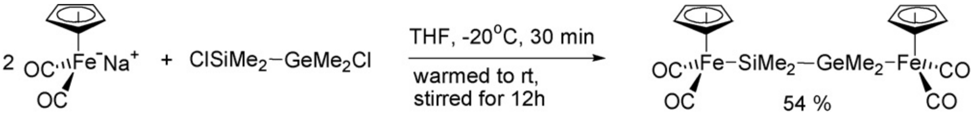
Based on the shear number of publications, the second most studied element involved in substitution reactions with the Fp anion is silicon. As a group 14 element, similar type reactions are expected to occur and indeed do occur that mimic the reactions of carbon-containing electrophiles. However, unlike carbon where electrophiles had sp^3, sp^2, and sp hybridization at the reactive carbon, only electrophiles with sp^3 hybridization at the reactive silicon have been reported. Thus, this section will be organized according to the work of individual research groups.



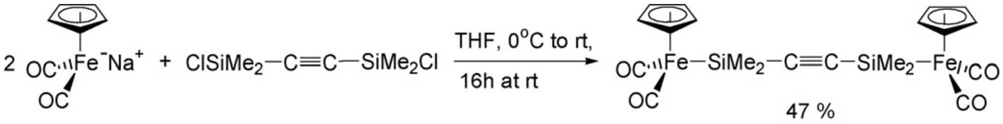
Scheme 74.



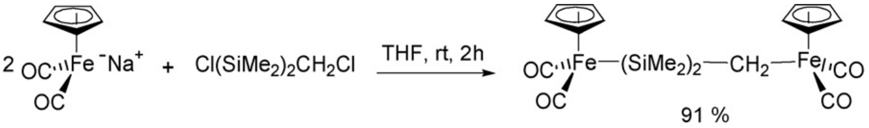
Scheme 75.



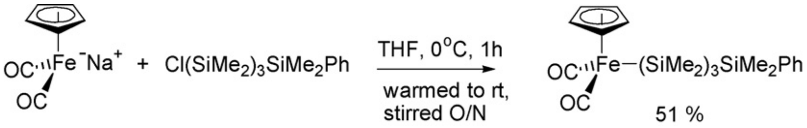
Scheme 76.



Scheme 77.



Scheme 78.



Scheme 79.

Often, the Fp–silicon complexes that are formed readily undergo photochemical and thermochemical-induced rearrangements and eliminations. These complexes have interesting mechanistic implications and downstream synthetic uses. As such, many research groups have studied their reactive pathways. Some of the iron–silicon complexes have direct or indirect applications as semiconductors, silicon carbide precursors, heat resistant materials, precursors for chemical vapor deposition, and optical filters, among others.

In order to understand the photochemical rearrangement of the bimetallic disilyl complex $FpSiMe_2SiMe_2Fp$, Sharma and Pannell prepared [134] analogs of this complex containing mixed group 14 elements. These researchers reasoned that they could then compare the relative stabilities of the coordinated silylenes. The new Fe–Si bond was formed from Fp anion and $ClSiMe_2GeMe_2Cl$ (Scheme 76).

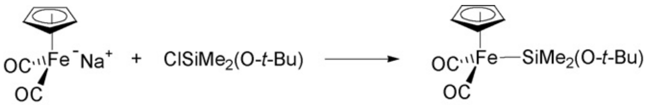
Pannell et al. prepared and characterized [135] diFp-substituted silylacetylene. Silylacetylenes have utility as ligands to various transition metals (Scheme 77). To investigate their potential as ligands these researchers complexed them with $Co_2(CO)_8$.

Pannell and coworkers prepared [136] the complex $FpSiMe_2SiMe_2CH_2Fp$ to study the possibility of photochemical-induced γ- and/or β-elimination (Scheme 78). Experimental evidence indicated that only β-elimination occurred to afford $FpSiMe_2CH_2SiMe_2Fp$.

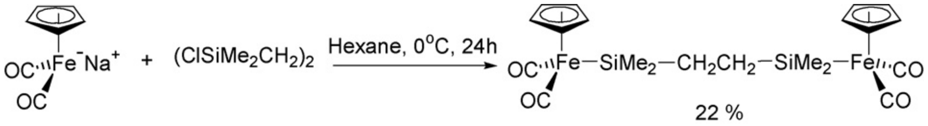
To understand more about the mechanistic aspects of photochemical-induced rearrangement of the tetrasilane complex, $Fp(SiMe_2)_3SiMe_3$, Sharma and Pannell prepared [137] the tetrasilane complex, $Fp(SiMe_2)_3SiMe_2Ph$ (Scheme 79). Photolysis of the latter resulted in the rearranged product, $FpSi(SiMe_3)_2SiMe_2Ph$.

Sharma and Pannell prepared [138] the dimethyl silyl *tert*-butoxy Fp complex in order to characterize a decomposition product against an authentic sample (Scheme 80). While studying the reactivity of the base-stabilized CpFe(CO)(η^2-$SiMe_2$-O-*t*-Bu-$SiMe_2$) under photolytic and subsequent thermolytic conditions, $FpSiMe_2O$-*t*-Bu was generated along with various other decomposition products.

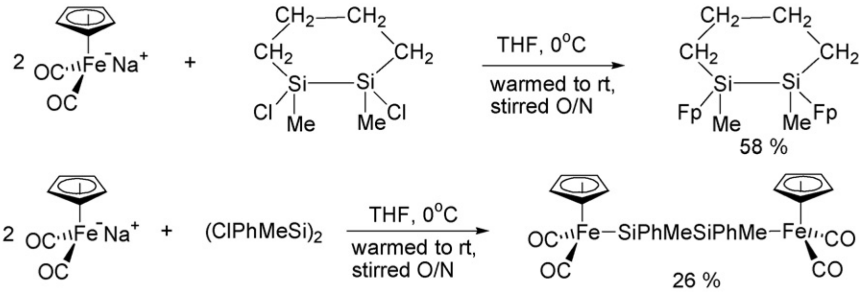
Pannell and coworkers synthesized [86] complexes with two terminal Fp moieties at opposite ends bonded directly to either a silicon or a carbon atom (Scheme 81, also see



Scheme 80.



Scheme 81.

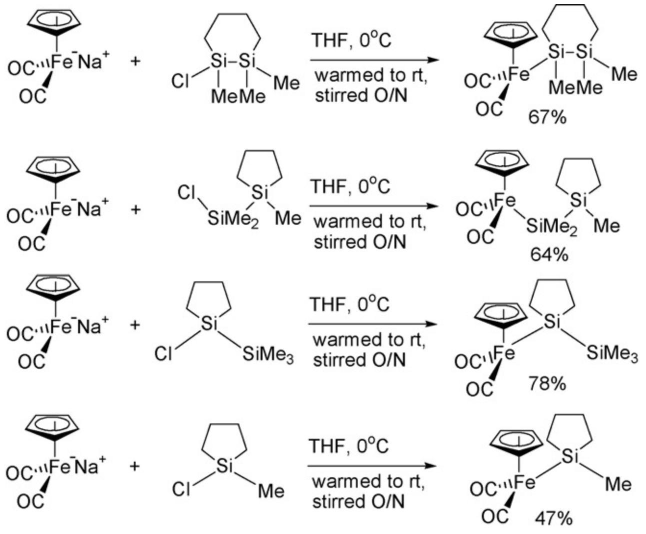


Scheme 82.

Scheme 21). These oligosilyl Fp derivatives were prepared to study their photochemical-induced rearrangements and eliminations to form stereospecific 1,3-disilacyclobutanes.

To examine the photochemical reactivity potential of rings containing bisFp oligosilyl systems, Pannell and coworkers synthesized, characterized, and studied [139] the photochemical reactivity of $\mathrm{Fp\overline{SiMe(CH_2)_4MeSi}Fp}$. The related FpSiMePh-SiMePhFp complex was also prepared and studied (Scheme 82).

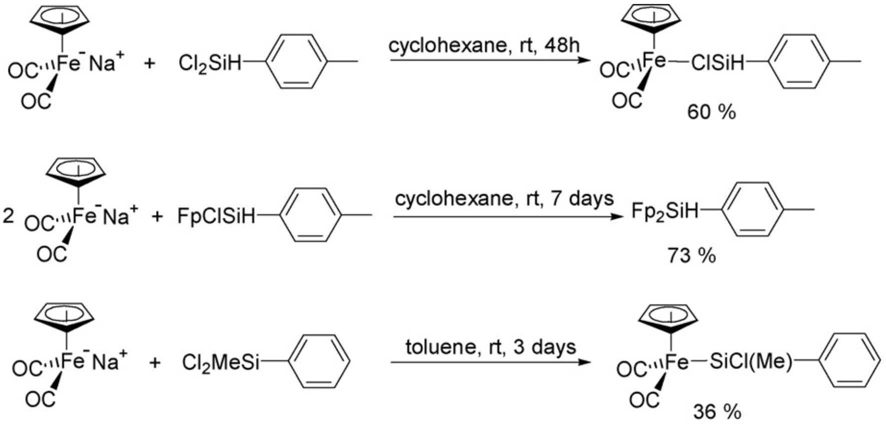
Zhang and Pannell prepared [140] three cyclic disilyl-iron complexes to understand more about the nature of photochemical-induced 1,3-migrations (Scheme 83). Each was proposed to proceed through silyl(silylene)iron intermediates to form $\mathrm{FpSiMe_3}$ and $\mathrm{Fp\overline{SiMe(CH_2)_3CH_2}}$ in the same ratio 34:66 via silylene eliminations. Irradiation of each in the presence of HMPA led to silylene intermediates, $\mathrm{CpFe(CO)({=}SiMe_2{\cdot}HMPA)(SiR_3)}$. A fourth Fp compound was prepared to compare one of the products to an authentic sample.



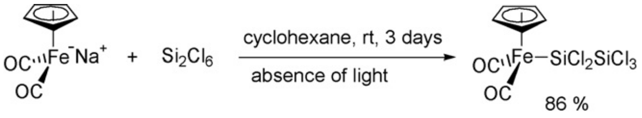
Scheme 83.

Malisch and coworkers prepared [141] a bisFp-substituted silane (Scheme 84) to use as a precursor for oxygenation with dimethyldioxirane. The subsequent bisFp-substituted silanol complex was produced in 95% yield. In a similar manner, an Fp-substituted methylphenylchlorosilane complex was prepared [142] (Scheme 84) as a precursor to its corresponding triphenylphosphine hydrosilane then subsequently converted to a silanol via reaction with dimethyldioxirane.

The same research group synthesized [143,144] an Fp pentachlorodisilane $\mathrm{FpSiCl_2SiCl_3}$ (Scheme 85) along with



Scheme 84.



Scheme 85.

other transition metal derivatives to study its reactivity with $LiAlH_4$ and the corresponding pentahydridodisilane product from dimethyldioxirane treatment. These investigations were motivated by a desire to understand the electronic effect of various transition metal centers on the reactivity of the α- and β-silicon in disilanyl complexes. Both the pentachloro- and the pentahydridodisilane were separately photolyzed in order to study their reactivity.

Malisch et al. produced the first hetero-bismetalated silanol from its functional silane precursor. The precursor was prepared [145] by reacting the Fp anion with a tungsten-substituted chlorosilane (Scheme 86). Treatment of the precursor with dimethyldioxirane resulted in oxygenation of the SiH group to form the silanol. This silanol and other similar silanol complexes underwent facile condensation reactions with chlorodimethylsilane to afford the corresponding siloxanes.

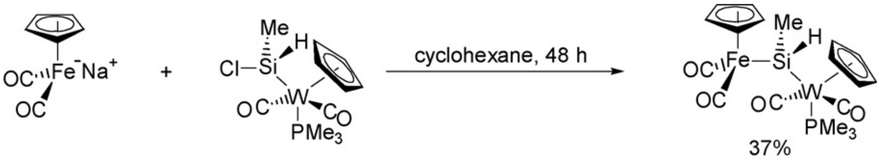
Malisch et al. synthesized [146] Fp substituted polychlorosiloxanes *via* metalation with Fp anion of perchlorinated siloxanes (Scheme 87). Further functionalization was achieved *via* methanolysis of selected complexes to form methoxy-substituted analogs.

Hengge and coworkers prepared and characterized cyclopenta- [147] and cyclohexasilanyl [148] Fp complexes from the Fp anion and their corresponding halides or triflate (Scheme 88). The implied interest in these and other similar transition metal complexes is due to their use as precursors in metal silicide CVD processes.

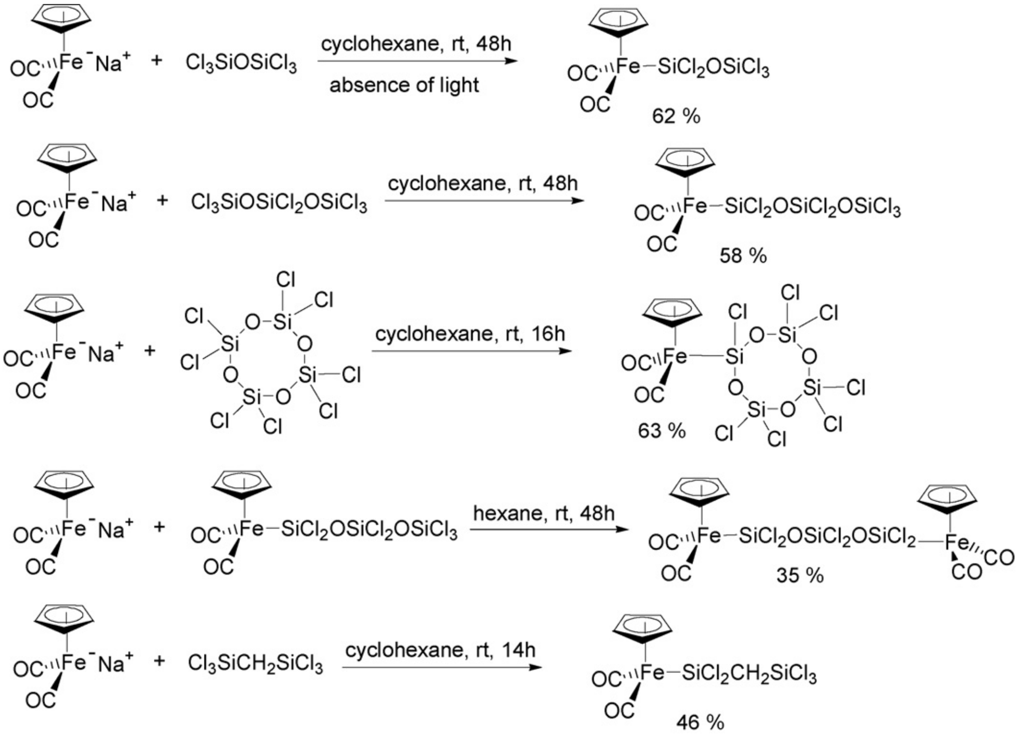
Hengge et al. synthesized [149] two Fp-substituted silanes from one or two equivalents of Fp anion and $Cl_3SiSiCl_3$ (Scheme 89). Using the hydrosilanes, $Br(SiH_2)_nBr$, they generated the diFp-substituted dihydrosilanes.

This same research group used an unconventional phenylthio leaving group to prepare [150] Fp silanes (Scheme 90). Both mono- and di-substituted Fp complexes were formed.

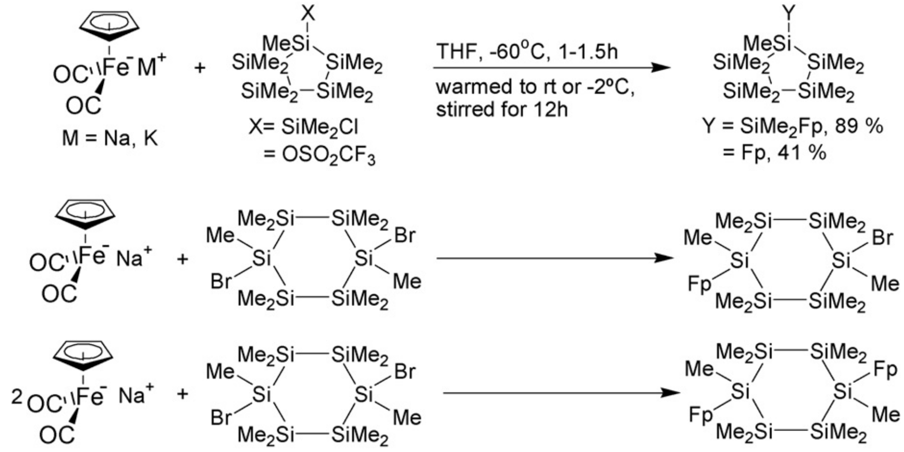
Ogino and coworkers prepared [151] several (silyl)Fp complexes to study their reactivity with hydride reducing reagents (Scheme 91). The Fp silyl complexes react with $LiAlH_4$ to give the hydrosilane $HSiR_3$ and the methylsilane CH_3SiR_3, the latter via reduction of a carbonyl ligand and subsequent migration.



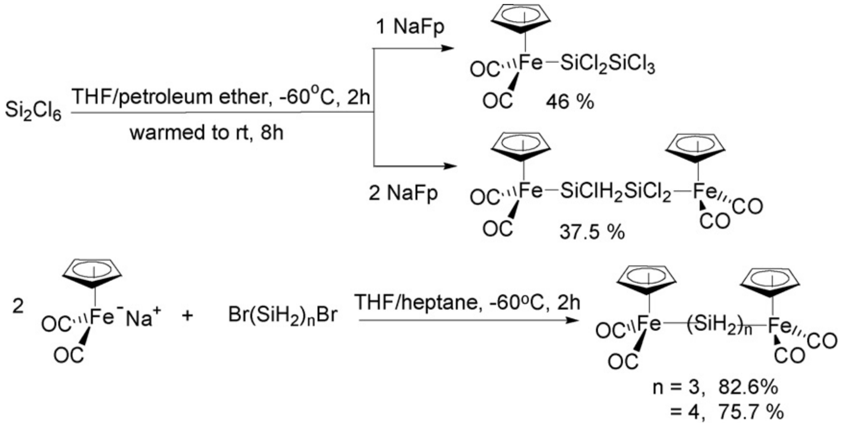
Scheme 86.



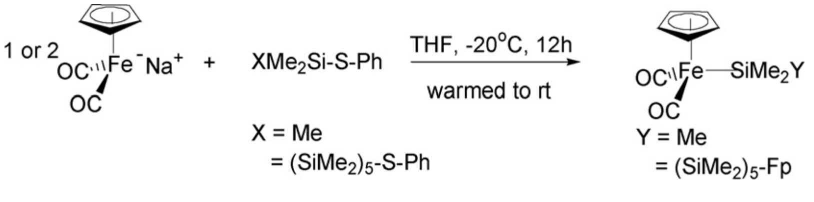
Scheme 87.



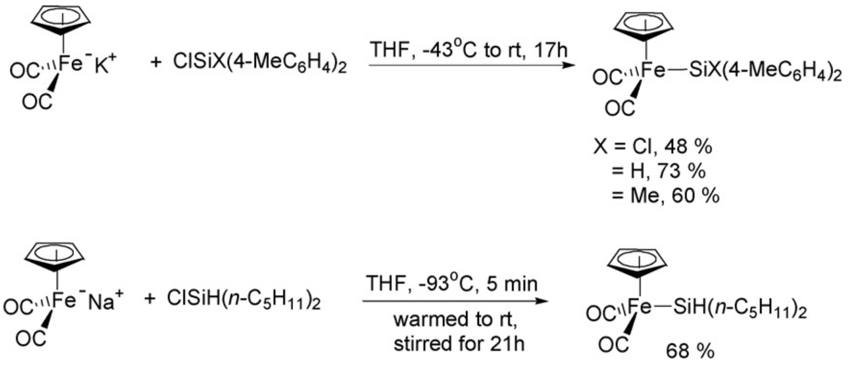
Scheme 88.



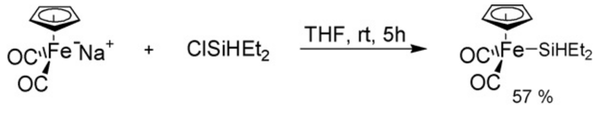
Scheme 89.



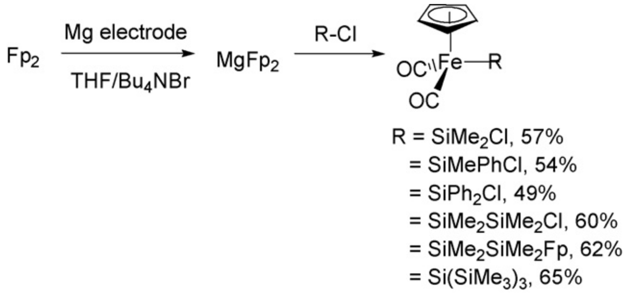
Scheme 90.



Scheme 91.



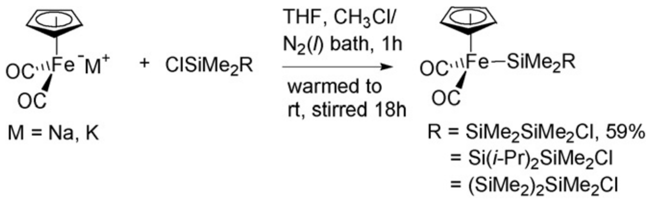
Scheme 92.



Scheme 93.

To understand the origin of the alkyl group in phosphite-induced insertion reactions to acetyl iron complexes of silanes, Ogino and coworkers prepared [152] (Scheme 92) and subsequently reacted $FpSiHEt_2$ with trimethyl phosphite. The results showed that the alkyl group originated from the phosphite.

With an aim to developing electrochemical methods for forming functionalized silanes of the general formula $X(SiR_2)_nR'$, Gogger and coworkers prepared [153] a range of Fp-substituted silanes via electrolysis of Fp_2 in the presence of chlorosilanes (Scheme 93). This research group extended [154] the electrochemical method of generating Fp anion and its use in the preparation of Fp-substituted silyl complexes (Scheme 94). The electronic interactions of one of the complexes ($FpSi_2Me_4C_6H_4CH{=}C(CN)_2$), made via conventional substitution, was studied using UV–vis absorption spectroscopy and cyclic voltammetry.

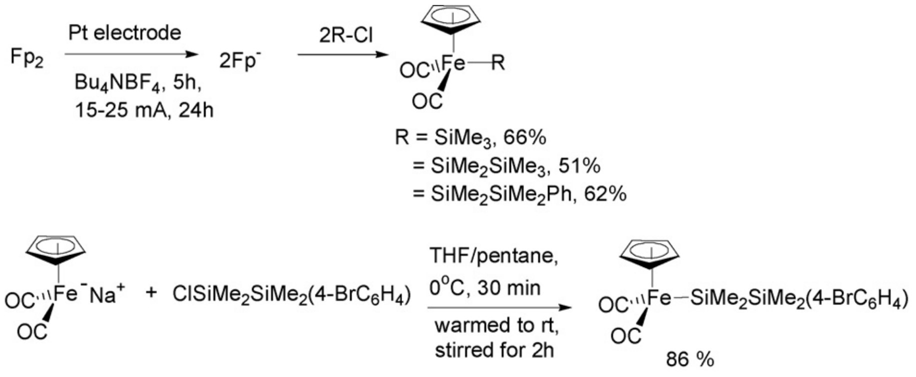


Scheme 96.

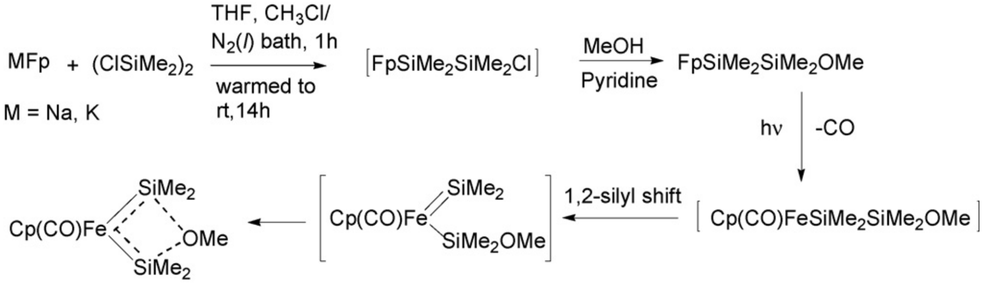
Tobita et al. synthesized [155] a (chlorodisilanyl)Fp complex to study its methoxy analog for photochemical-induced reactivity (Scheme 95). Irradiation of the methoxy complex afforded the methoxy-stabilized bis(silylene) complex $Cp(CO)Fe[SiMe_2\cdots O(Me)\cdots SiMe_2]$ via a proposed CO dissociation followed by a 1,2-shift of the terminal silyl group and cyclization. Irradiation of the (methoxydisilanyl)Fp complex $FeSiMe_2SiMe_2OMe$ in the presence of $(SiMe_2)_6$ was also studied.

These researchers also prepared [156] (chloropolysilanyl)Fp complexes (Scheme 96) to convert them to the methoxy analogs for photochemical reactivity studies. Photolysis gave intramolecular base-stabilized (disilanyl-silylene) iron complexes.

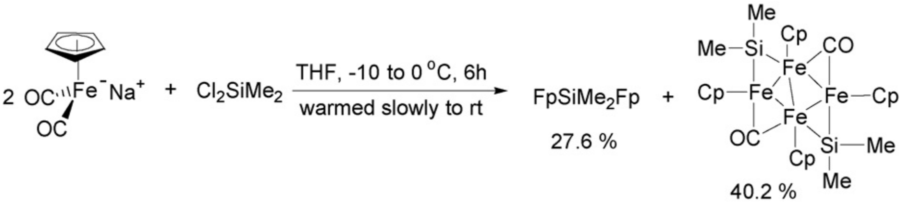
Several groups prepared Fp trialkyl- or triarylsilanes from the corresponding trialkyl- or triarylsilane chlorides for varied reasons. Brookhart and coworkers generated [157] the Fp-substituted triethylsilane ($FpSiEt_3$) as a precursor to its triphenyl- and triethylphosphine derivatives. The phosphine



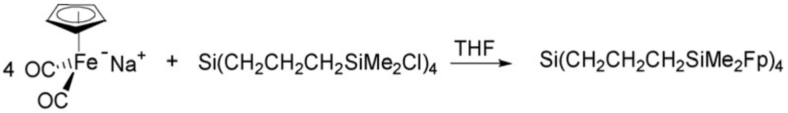
Scheme 94.



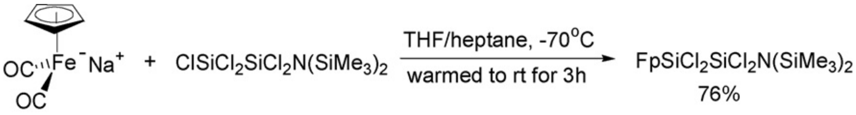
Scheme 95.



Scheme 97.



Scheme 98.



Scheme 99.

complexes were then converted to cationic η^2-silanes and cationic η^2-H_2 complexes.

Ruiz et al. prepared [158] $FpSiMe_3$ to demonstrate the potential of replacing mercury amalgams and alkali metals with electrolytic generation of the Fp anion. The less hazardous and environmentally friendlier means of generating the Fp anion used a consumable Mg anode, a n-Bu_4NBr supporting electrolyte solution in THF, and a constant current of 50 mA.

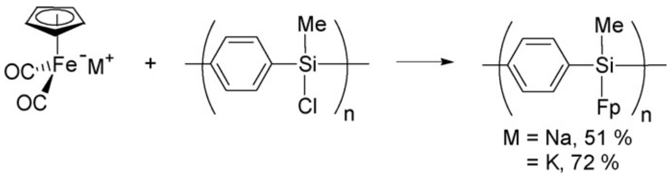
McQuire et al. at the UK Ministry of Defense prepared [159] Fp triphenylsilane as one example of an organometallic complex that, when coated onto a transparent container, acts as a photochromically active optical filter to protect optical equipment against laser attack.

To extend previous work, Safiullah et al. reacted [160] the Fp anion with $ClSiMe_2Cl$. Two products resulted, the major product consisted of a bridged tetrairon complex and the minor product was the disubstituted Fp complex (Scheme 97).

Cuadrado and coworkers attached [161] four Fp groups by substitution of chlorides to a tetrachloropolysilyl dendrimer (Scheme 98). Dendrimers such as these have been employed on electrode surfaces. In addition, the authors cite potential use in catalysis and multi-electron redox and photochemical processes.

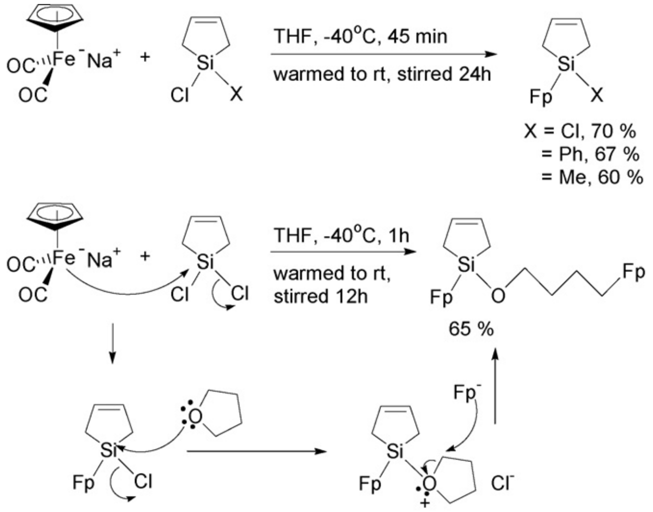
The ease with which Si–N bonds can be made and broken coupled with the stability of aminosilanes toward various nucleophiles provided the motivation for Stüger and coworkers to investigate aminochlorodisilanes as precursors to multi-functionalized disilanes. To study the chemical properties of bis(trimethylsilyl)aminopentachloro disilane, these researchers reacted the Fp anion with it to afford [162] the corresponding chloride substitution product (Scheme 99). The tetrachloride underwent reduction in the presence of $LiAlH_4$ to afford the tetrahydrosilane.

Ohshita et al. prepared [163] an Fp-functionalized polymer of (methylsilylene)phenylene (Scheme 100) to study its electrochemical activity. A thin solid film of the polymer proved to be active within the −0.2 to +0.7 V range versus SCE. Polymers such as this one having a regular alternating arrangement of a π-electron system and an organosilicon moiety in the backbone have shown promise as semiconductors, silicon carbide precursors, and heat resistant materials.

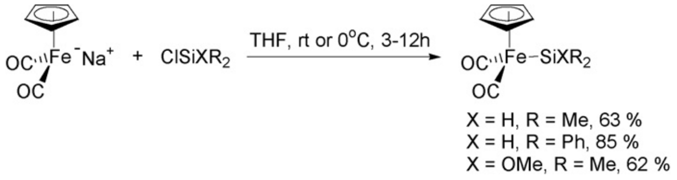


Scheme 100.

Dartiguenave and coworkers prepared [164] and characterized three silacyclopentene complexes and an unusual THF insertion compound, all in good yields (Scheme 101). The pro-



Scheme 101.



Scheme 102.

posed mechanism for the THF incorporated product involved substitution of one Cl by Fp and the second Cl by THF. A second equivalent of the Fp anion, when added to the THF, resulted in a ring-opened adduct.

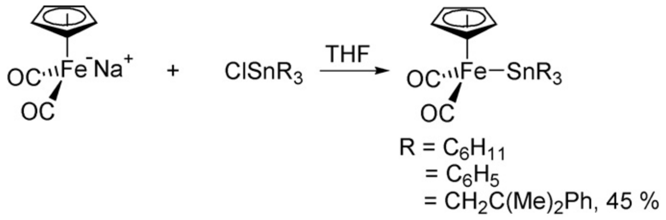
Goldman et al. synthesized [165] a series of Fp silyl compounds from reaction of the Fp anion with chlorosilanes (Scheme 102). The Fp silyl compounds were subsequently reacted using various reagents to afford substitution at silicon.

McIndoe and Nicholson prepared [166] Fp silane complexes (Scheme 103) to characterize and study their structural relationship and tendency to undergo 1,2-migration of the X-containing aryl group from silicon to the iron center. There was no tendency for the X-group on silicon to migrate to iron, thus elimination of silylene was not observed.

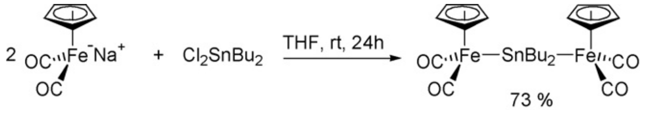
4.1.5. Fe–Ge, Fe–Sn, and Fe–Pb bond formation (Table 8)

The most widely studied electrophiles in substitution reactions with the Fp anion have been the group 14 elements of carbon and silicon. A few reactions with other group 14 elements have also been investigated. The recent substitution reactions of germanium, tin, and lead will be reviewed here in order of the element's position in the periodic table.

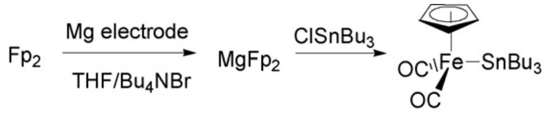
In order to understand the effects of the different group 14 elements on the relative stabilities of the coordinated silylenes, germylenes, and stannylenes, Sharma and Pannell prepared [134] and performed photochemical reactions with them. One of the complexes formed by a known procedure was a compound containing a Fe–Ge bond (FpGeMe$_2$Cl). Irradiation of the derivative Fp–GeMe$_2$SnMe$_3$ resulted in formation of FpGeMe$_3$ and FpSnMe$_3$ as a 60:40 mixture. In this same report, these researchers also prepared a disubstituted Fp complex of germanium and silicon (see Scheme 76).



Scheme 105.



Scheme 106.

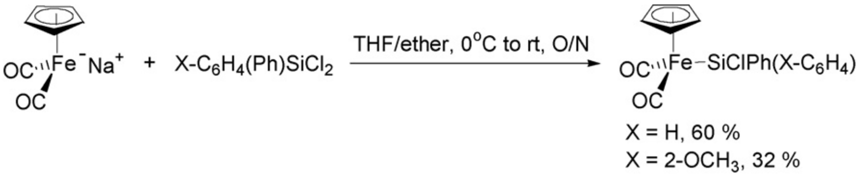


Scheme 107.

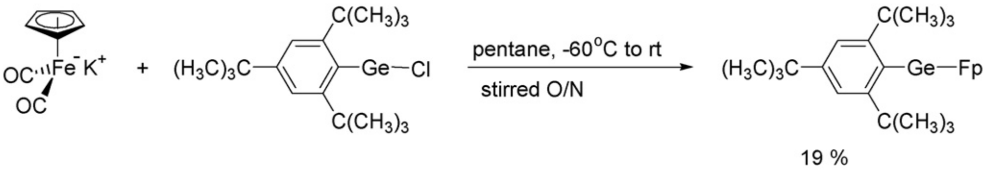
Jutzi and Leue prepared [167] a (supermesityl)ferriogermylene by reacting KFp with (supermesityl)chlorogermylene (Scheme 104). This germylene complex, along with its C$_5$Me$_5$Fe(CO)$_2$ analog, represented the first well-characterized members of this novel class of germanium compounds.

Gao and coworkers reacted Fp anion with trialkyl and triaryltin chlorides to form [168] new Fp complexes (Scheme 105). To explore the relationship between the structure of bimetallic complexes and their properties, Gao extended [169] tin halide reactions with Fp anion to give Fp-Sn(CH$_2$CMe$_2$Ph)$_3$ (Scheme 105). Similar types of complexes have shown potential as polymerization catalysts and in antiviral activity. These researchers showed that an Fe–Sn bond existed based on the X-ray crystal structure.

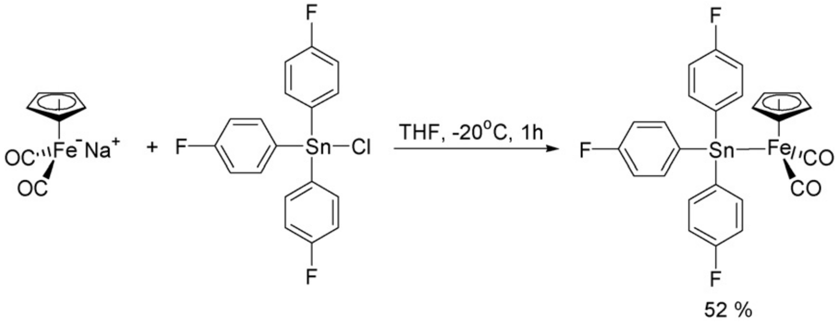
Kang et al. investigated [170] reactions of triorganotin halides containing intramolecular Sn–P coordination. One such reaction was chloro substitution on tin in 1-PPh$_2$-2-SnClMe$_2$-1,2-C$_2$B$_{10}$H$_{10}$ by the Fp moiety.



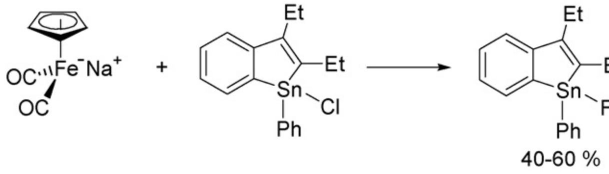
Scheme 103.



Scheme 104.



Scheme 108.



Scheme 109.

Butyl substituted tin chlorides were used as electrophiles by two research groups to prepare Fp derivatives. Kundu and coworkers prepared [171] a diFp-substituted dibutyltin compound (Scheme 106). Ruiz et al. synthesized [158] $FpSnBu_3$ (Scheme 107) along with other complexes to demonstrate the potential of replacing mercury amalgams and alkali metals with electrolytic generation of Fp anion. The method is reported to be safer to handle and better for the environment.

Kravtsov and coworkers prepared [172] the tris(4-fluorophenyl) Fp-substituted complex to study bond polarity between tin and iron (Scheme 108). Meunier et al. isolated [173] an Fp-substituted benzostannole by replacement of a chloro group by the Fp moiety (Scheme 109).

Continuing their study of metallodendrimers, Schumann and coworkers prepared [56] several Fp dendrimers. One of the dendrimers studied had four peripheral Fp moieties after substitution of the four chloro groups (Scheme 110).

In the only example of a lead compound bonded to the Fp group, Herberhold et al. prepared [174] a number of complexes with Fe–Pb bonds (Scheme 111). The Fp–lead complexes were fully characterized by ^1H, ^{13}C, and ^{207}Pb NMR.

4.1.6. Fe–P, Fe–Sb, Fe–Bi, and Fe–Te bond formation (Table 9)

Very little work has been done during the last twelve years with either group 15 or group 16 electrophiles via Fp anion substitution reactions. Of the reactions that formed new Fe–X bonds (X = groups 15 and 16 element) only electrophiles of phosphorus, antimony, bismuth, and tellurium have been reported.

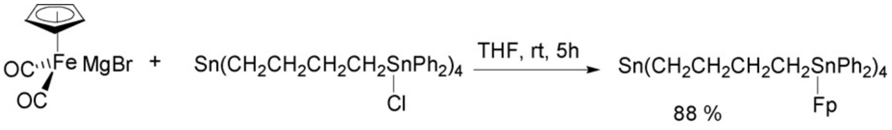
Three research groups reported substitution reactions with Fp anion and phosphorus electrophiles. To investigate the reactivity of $CpMnCo(CO)_5PPhH$, De and Bhar reacted [175] this complex with various metal carbonyl salts (Scheme 112). One of those salts was KFp.

Schrödel and Schmidpeter reacted 1,3-dihalo-2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetane with a wide range of nucleophiles to investigate the reactivity of this unusual synthon. One nucleophile that underwent a chloro substitution was NaFp (Scheme 113) [176].

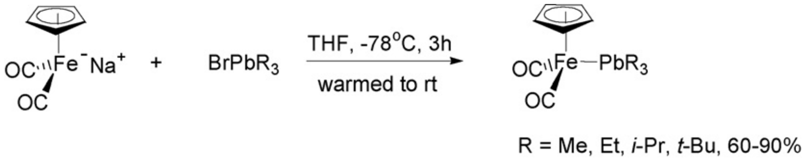
To study the bond character between Fe-P in complexes, Nakazawa and coworkers prepared [177] an Fp-substituted thiophosphonate complex (Scheme 114). These researchers concluded based on Mössbauer spectroscopy that the Fe–P bond in $Fp[P(S)(OEt)_2]$ is as covalent as the Fe–C bond in FpMe.

Only two publications mention antimony electrophiles in substitution reactions. To extend their systematic investigation of phosphorus–metal bonds to group 15 elements other than phosphorus, Lorenz and coworkers studied [178] the substitution reactions of $SbCl_3$ and $SbCl_5$ with Fp anion (Scheme 115).

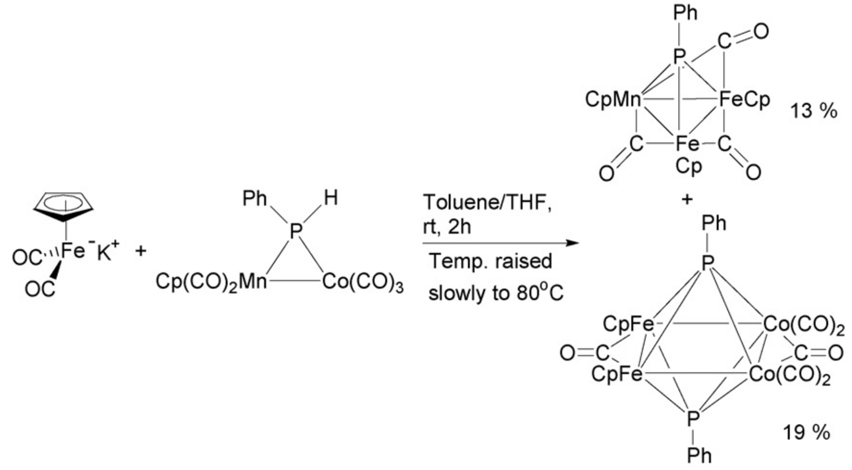
To investigate reactions of higher oxidation state antimony fragments with low oxidation state transition metal complexes, Gibbons and Sowerby reacted [179] Fp anion with $SbPh_2Cl$



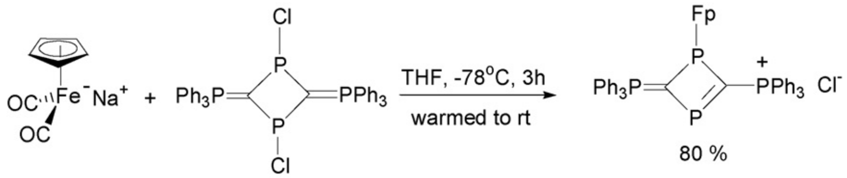
Scheme 110.



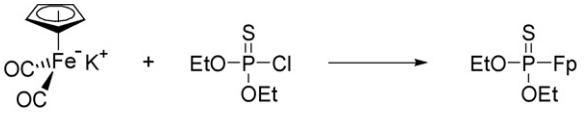
Scheme 111.



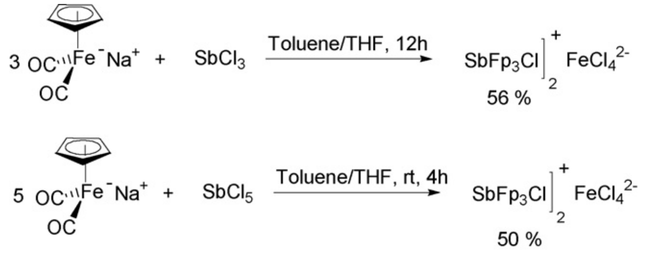
Scheme 112.



Scheme 113.



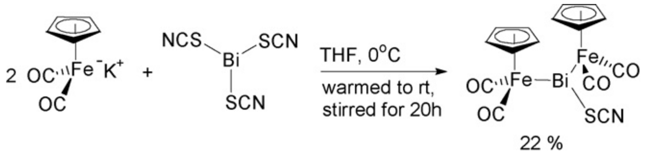
Scheme 114.



Scheme 115.

(Scheme 116). An inseparable mixture of $FpSbPh_2$ and Fp_2SbPh was observed.

Norman and coworkers reported [180] on synthetic and structural studies of some organotransition-metal bismuth thiocyanate complexes. One of those complexes was formed by reaction of Fp anion with $Bi(SCN)_3$ (Scheme 117). These thiocyanate substituents act much like halides in substitution reactions.



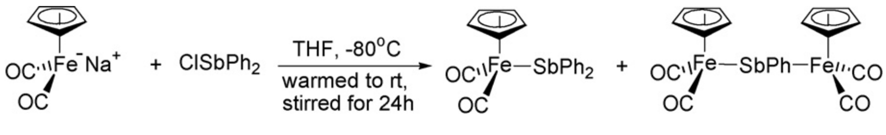
Scheme 117.

Kundu and coworkers prepared [181] and spectroscopically characterized a new complex containing a tellurium–iron bond via a metal halide substitution reaction with Fp anion (Scheme 118). This represented the only reported Fp–tellurium complex over the past 12 years and the only group 16 element involved in a new bond to iron via substitution.

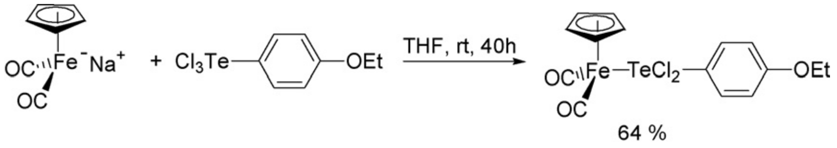
4.1.7. *Fe–H bond formation (Table 9)*

Although not a major area of focus, protonation of Fp anion has been used as a means to study or prepare other transition metal complexes. Nakazawa and coworkers generated [177,182] FpH *in situ* (Scheme 119) as an intermediate to $CpFe(CO)(PMe_3)Cl$. Their target molecule was an Fp-substituted phosphonate.

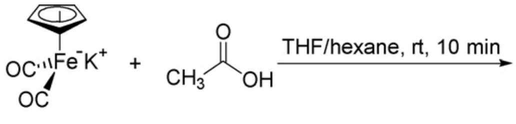
In their study of the reactivity of transition metal hydrides, D'Alfonso and coworkers reacted [27] a mixed-metal hydride with the Fp anion to form the FpH molecule (Scheme 120). These



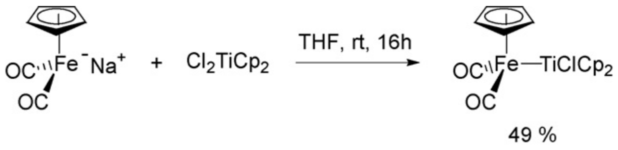
Scheme 116.



Scheme 118.



Scheme 119.



Scheme 121.

researchers found that although the Fp anion is a very strong nucleophile in S_N2 reactions with alkyl halides, it abstracted a proton from the mixed metal hydride despite being classified as a weaker Brønsted base than $Re(CO_5)^-$ (see Scheme 2).

Dahlenburg and Hache studied reactions between transition metal hydrides and $M(PMe_3)_3CH_3$ (M = Ir, Rh) to form ionic and covalent mixed-metal heterobimetallic complexes. Oxidative addition occurred between the metal hydrides and the metal methyl complexes. One of the hydrides studied was FpH, thus, it was prepared [183] from FpK in a mixture of acetic acid and thiophenol.

4.1.8. Fe–Ti, Fe–Zr, Fe–Hf bond formation (Table 10)

There were no reports for reactions with Fp anion and the group 3 elements (M = Sc, Y, Lu) to form new Fe–M bonds via substitution. However, many examples of reactions with other transition metals and the Fp anion exist. Often, the authors cited the potential for catalysis or to simply activate an organic bond. The breaking of a metal–metal bond can be thought of as a facile way to form a nucleophile and an electrophile. These fragments may then react further with organic molecules for downstream functionalization.

Electrophiles of the group 4 elements have been shown to react with the Fp anion via substitution. To explore the structural relationship of bimetallic complexes to their properties, Gao and coworkers prepared [169] an Fp–titanium complex (Scheme 121). Similar type complexes have shown potential as catalysts and antiviral agents.

Ullah and Khanal prepared [184] several new Fp-substituted titanium mixed cluster complexes (Scheme 122). All of the complexes were tested for bioactivity using the brine shrimp lethality test. The $FpTiCl_3$ complex had the lowest LD_{50} at 7 ppm.

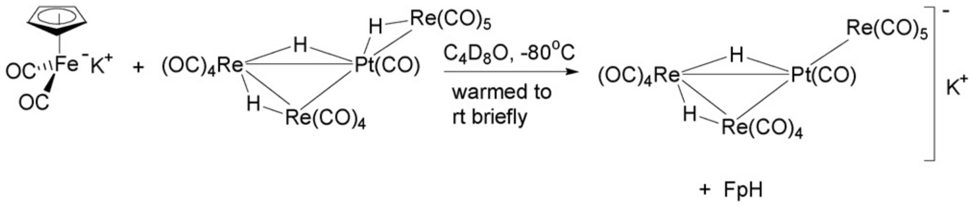
To study heterobimetallic complexes of transition metals with unsupported metal–metal bonds, Gade and coworkers have worked with and developed stable Ti–amidohalide complexes containing tripodal amido ligands. These ligands are the key to generation of these stable Ti–M heterobimetallics. Several complexes containing the Fe–Ti bond were prepared [185,186] from Fp anion (Scheme 123).

A titanium tri-*tert*-butoxy Fp complex was prepared [187] by Selent and coworkers from KFp and titanium tri-*tert*-butoxy chloride (Scheme 124).

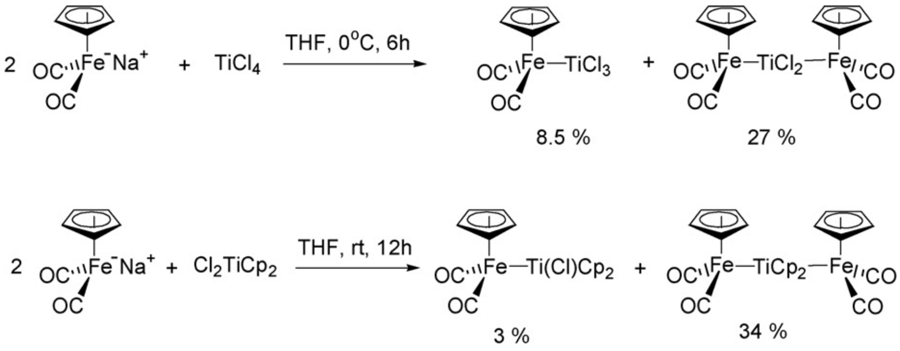
Bimetallic activation of molecules using complementary metal centers has been the interest of many research groups. Cleaving the metal–metal bond could generate complementary pairs of reactive complex fragments which may react in a cooperative manner with organic molecules. The instability of these systems had hampered the development of such systems. With these stability issues in mind, Gade and coworkers prepared [188,189] a range of group 4 elements and other transition metal complexes that contain stable metal–metal bonds (Scheme 125). Complexes with Fp–Ti, Fp–Zr, and Fp–Hf bonds among other complexes were synthesized.

As part of their continued study of tripodal amido ligands containing an “active” ligand periphery, Gade et al. prepared [190,191] two other Fp-substituted tripodal amido zirconium complexes (Scheme 126). These partially fluorinated complexes when substituted with Fp were prepared and then reacted with a wide variety of polarized organic substrates, most of which contained unsaturated functional groups.

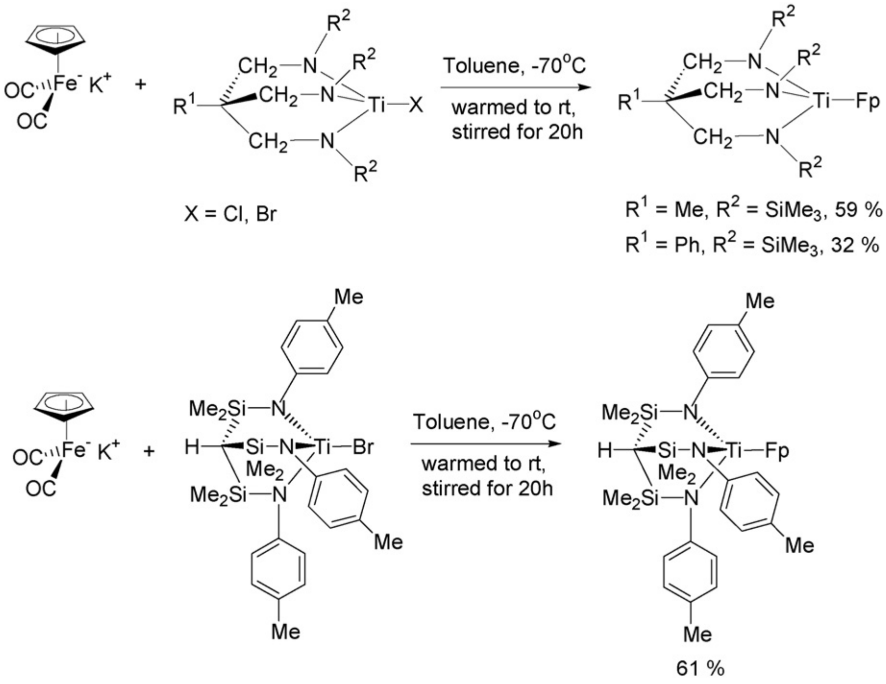
With the understanding that heterobimetallic complexes generate two reactive fragments upon cleavage of the metal–metal bond and that these complexes could be reactive toward unsaturated hydrocarbons, Gade and coworkers prepared a number of



Scheme 120.



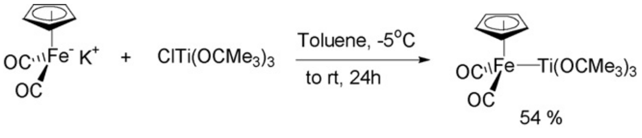
Scheme 122.



Scheme 123.

zirconium–metal heterobimetallic complexes for investigation. One such complex was an Fp-functionalized zirconium complex (Scheme 127) [192]. Replacing the Cp ligand with a chloro group allowed Gade to prepare a similar diFp amidozirconium complex [193,194] and a monochloro Fp-substituted version [194] by treating the electrophile with one or two equivalents of the Fp anion, respectively (Scheme 128).

Cutler and coworkers reacted [195] Fp anion separately with $Cp_2ZrCl(OMe)$ and Cp_2ZrCl_2 in an attempt to generate Fp-substituted products (Scheme 129). The Cp_2ZrCl_2 did not produce the desired chloro replacement product.



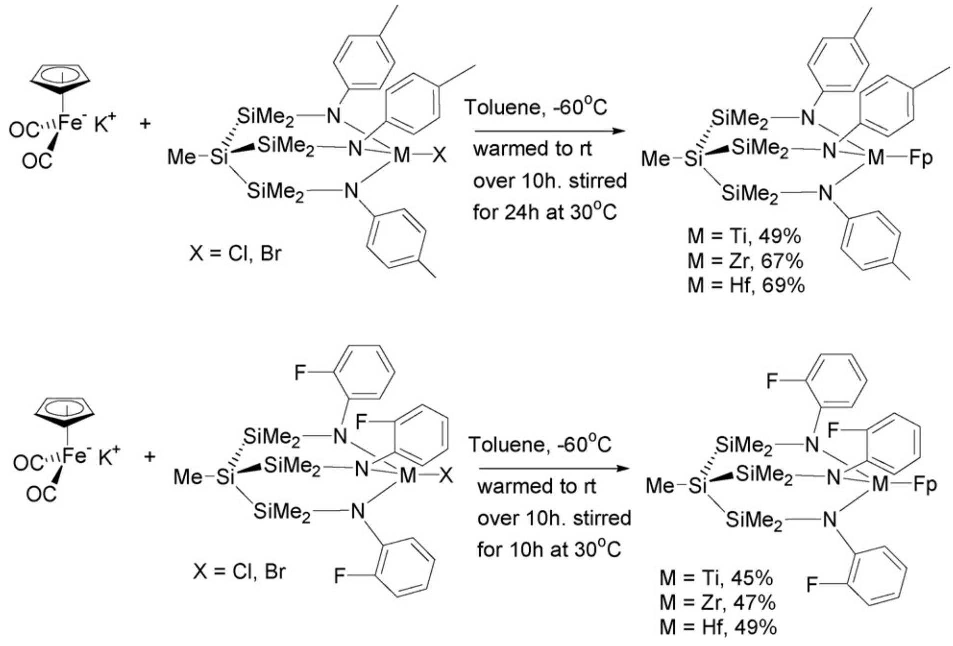
Scheme 124.

4.1.9. *Fe–Cr and Fe–Mo bond formation (Table 11)*

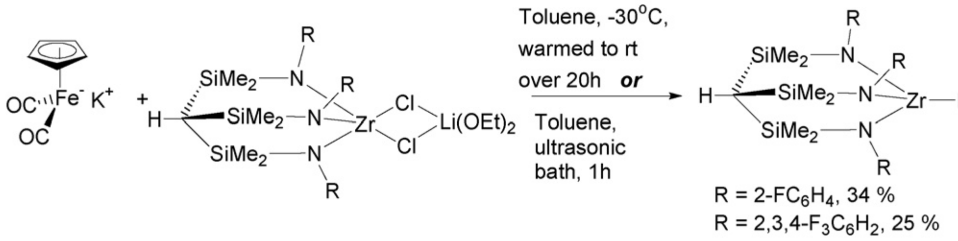
Of the group 6 elements, only examples of chromium and molybdenum electrophiles were found in the recent literature to react with the Fp anion. Three examples were cited. Ullah and coworkers prepared two Fp-substituted chromium complexes to study the reactivity of chromyl chloride. At room temperature, chromyl chloride may react explosively with organometallic and organic reagents. To test the reactivity of this strong oxidizing agent, these researchers reacted [196] the Fp anion with chromyl chloride at low temperature (Scheme 130).

To prepare and study the chemistry of iron–chromium carbynes in which the (η^6-benzene)Cr(CO) moiety was substituted for the CpCr(NO) moiety, Hersh and coworkers reacted [197] the Fp anion with $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CH_3CN)$ (Scheme 131). An interesting heterobimetallic bridging carbonyl anion was produced.

Maslennikov and coworkers studied the reactivity of FpMgCl to prove that it is stable in DMF. Reaction of magnesium metal with FpCl in DMF was believed to form FpMgCl *in situ*. By



Scheme 125.



Scheme 126.

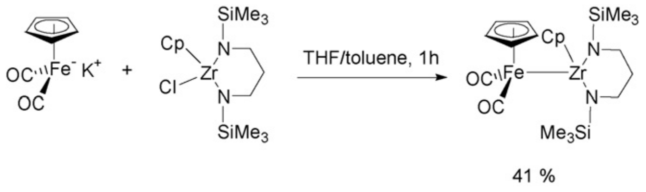
reacting the *in situ* generated FpMgCl with $Cp(CO)_3MoCl$, the chloro substituted adduct was isolated [57] lending proof to the proposed *in situ* generation of FpMgCl (Scheme 132).

4.1.10. Fe–Mn bond formation (see Table 9)

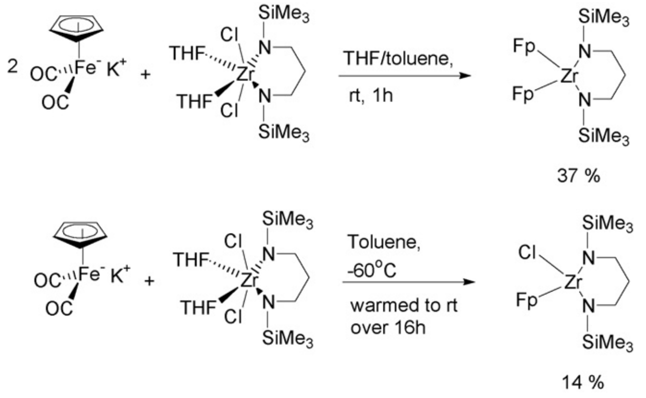
The only mention of a group 7 element in a reaction with the Fp anion was manganese. As was mentioned previously, the mixed-metal $CpMnCo(CO)_5PPhH$ was reacted [175] with various metal carbonyl salts by De and Bhar. One of the nucleophiles used was the Fp anion (see Scheme 112).

4.1.11. Fe–Ru bond formation (Table 11)

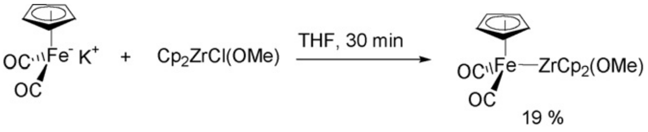
Only the group 8 element, ruthenium showed any definitive reactions with the Fp anion. Stone and coworkers prepared [198] some novel di- and trinuclear metal complexes to extend their



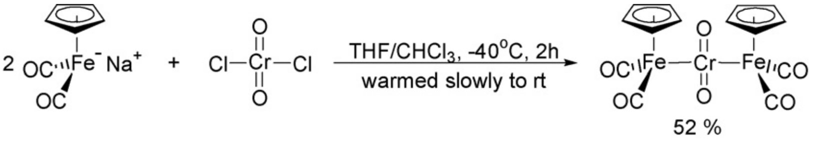
Scheme 127.



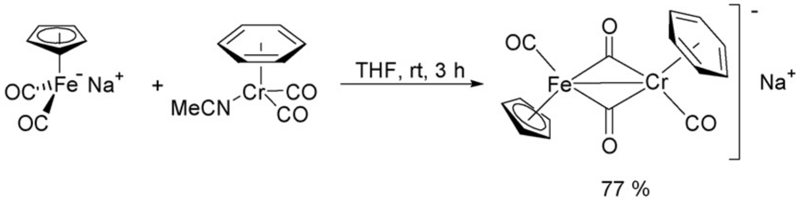
Scheme 128.



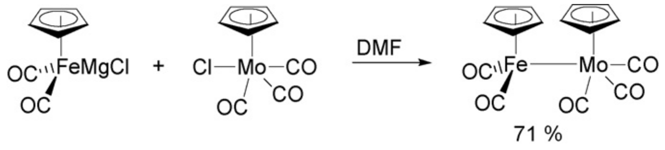
Scheme 129.



Scheme 130.



Scheme 131.



Scheme 132.

study of ruthenium complexes containing the η^5-7,8-$C_2B_9H_{11}$ ligand (Scheme 133).

Knox and coworkers prepared [199] a mixed iron–ruthenium complex by reaction with Fp anion (Scheme 134). In this way they were able to study and extend reactions to produce bimetallic complexes. The mixed metal complex was subsequently subjected to irradiation in the presence of unsaturated organic substrates.

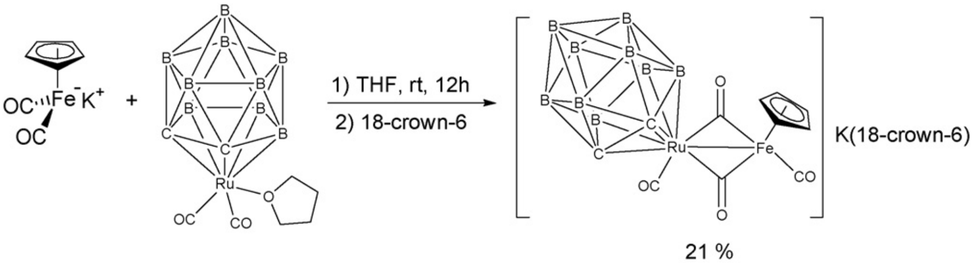
4.1.12. Fe–Co, Fe–Rh, and Fe–Ir bond formation (Table 11)

As was mentioned previously, the mixed-metal $CpMnCo(CO)_5PPhH$ was reacted [175] with various metal carbonyl salts by De and Bhar (see Scheme 112).

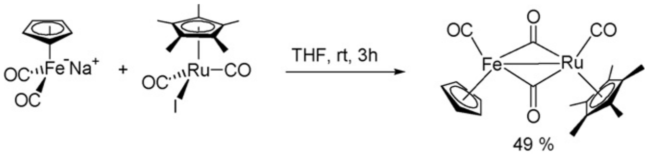
In studying the reactions with $M(PMe_3)_4Cl$ (M = metal) and the Fp anion, Dahlenburg and Hache produced [183] heterobimetallic complexes as a result of phosphine loss and partial transfer of PMe_3 from a group 9 element to iron (Scheme 135).

4.1.13. Fe–Hg bond formation (Table 11)

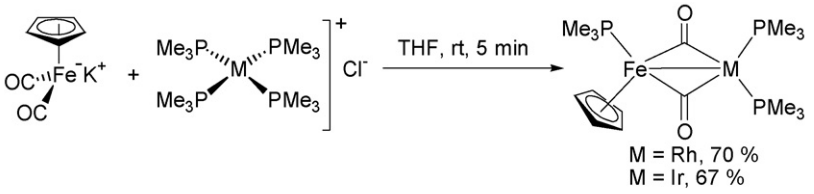
As was mentioned earlier, Maslennikov and coworkers studied the reactivity of FpMgCl in DMF. Reaction of magnesium metal with FpCl in DMF was believed to form FpMgCl *in situ*. By reacting the *in situ* generated FpMgCl with $HgCl_2$, the chloro substituted adduct was isolated [57]



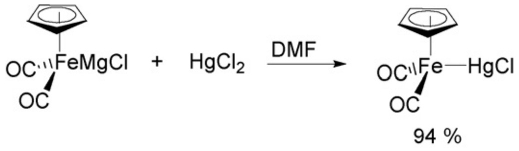
Scheme 133.



Scheme 134.



Scheme 135.



Scheme 136.

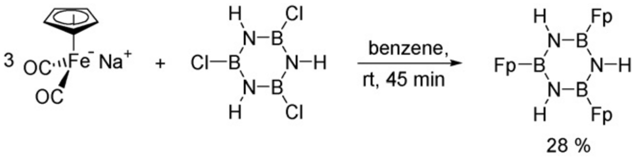
lending proof to the proposed *in situ* generation of FpMgCl (Scheme 136).

4.1.14. *Fe–B, Fe–Al, Fe–Ga, Fe–In, and Fe–Tl bond formation (Table 12)*

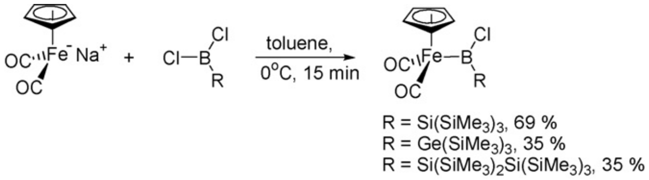
Apart from the group 14 elements of carbon and silicon, the group 13 elements have been the second most studied group of elements associated with Fp anion reactions via substitution. Substitution reactions with boron have exhibited some of the most interesting complexes and serve as precursors to other boryl complexes. Additionally, some of these compounds have been shown to functionalize alkanes under photolytic conditions. Several groups have been at the forefront of these recent developments.

Braunschweig and coworkers prepared [200] and characterized the first Fp-substituted diborane(4) compound. Reaction of the Fp anion with $B_2(NMe_2)_2Cl_2$ resulted in substitution of one chloro ligand although dinuclear substitution failed under refluxing conditions, apparently due to steric reasons. Braunschweig and Koster extended [201] their reactions between Fp anion and other 1,2-diaminodichlorodiboranes to afford Fp diborane(4)yl complexes (Scheme 137).

This same research group prepared [202] amino-substituted boryl complexes of Fp by reacting dimethyl aminodichloroborane and di(trimethylsilyl)aminodiborane with the Fp anion (Scheme 138). Similar boryl complexes have been employed in the hydroboration and functionalization of alkanes.



Scheme 140.

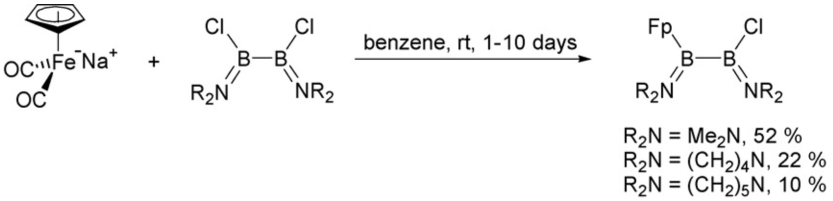


Scheme 141.

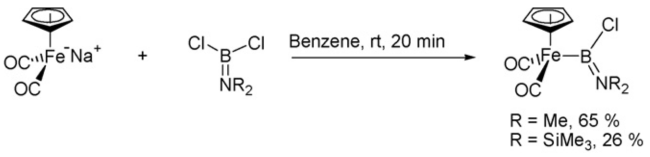
To develop a more general pathway to bridged borylene complexes, Braunschweig et al. reacted [203] the Fp anion with dimethylaminodibromoborane (Scheme 139). A 1:1 mixture of boryl and bridged borylene products resulted from reaction with one to two moles of Fp anion.

Braunschweig et al. reported the preparation and characterization [204] of the first η^1-coordinated borazine complex of Fp having boron–iron σ bonds. Reaction of trichloroborazine with Fp anion afforded an η^1-borazine complex (Scheme 140).

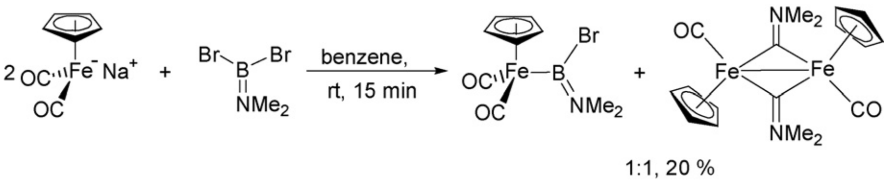
A range of new Fp boryl complexes was prepared [205] by Braunschweig and coworkers (Scheme 141). The authors cite the potential importance of such complexes for functionalization of hydrocarbons by metal-catalyzed hydroboration of olefins and photochemically induced selective α-borylation of alkanes by C–H activation.



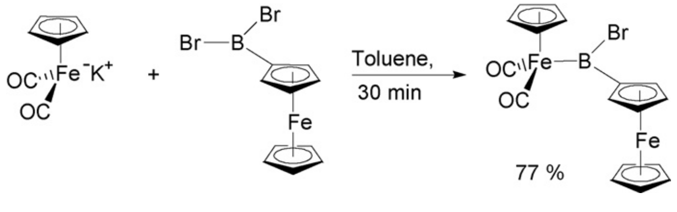
Scheme 137.



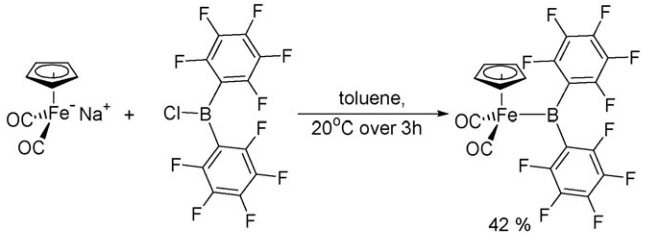
Scheme 138.



Scheme 139.



Scheme 142.

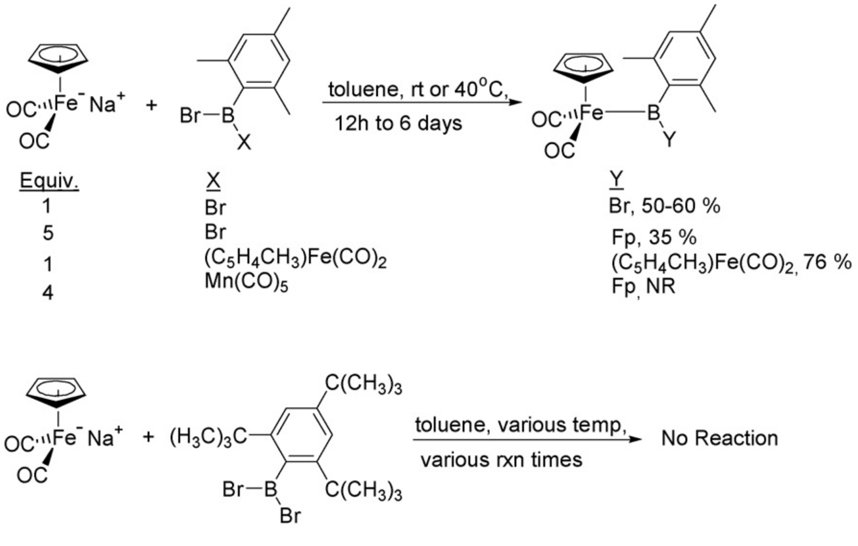


Scheme 143.

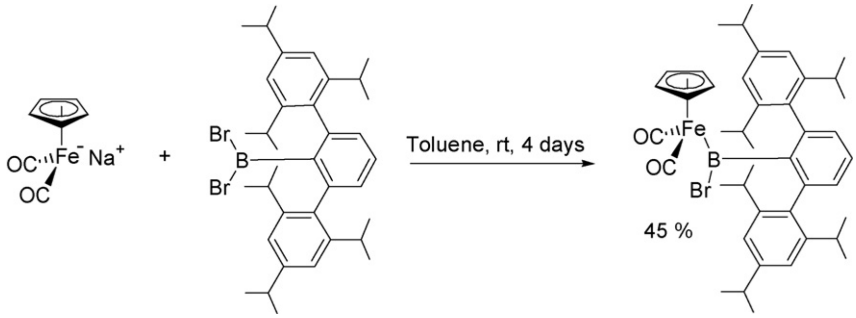
To study if the ferrocenyl(bromo)boryl group could serve as a probe for the presence of any significant Fe–B π-bonding, Braunschweig and coworkers synthesized and characterized Fp[B(Fc)Br] (Scheme 142) [206]. By comparing the crystal structure of this complex and its Fp* ($C_5Me_5Fe(CO)_2$) analog, these researchers concluded that the differences in steric bulk of the η^5-C_5R_5 (R = H or Me) in the Fp ligands, affects the orientation and thus its π-bonding.

Another group of researchers that has extensively studied boron complexes of the Fp moiety is the Aldridge group. In an effort to develop synthetic routes to metal complexes containing the $B(C_6F_5)_2$ ligand, Aldridge and coworkers synthesized [207] $FpB(C_6F_5)_2$ (Scheme 143). Complexes containing C_6H_5-like moieties show potential as highly acidic Lewis acids at the boron centers and thus may serve as useful probes for possible boryl ligands to act as π-acids. With this in mind, Aldridge et al. investigated π-back bonding of $FpB(C_6F_5)_2$. Although the role of π-back bonding in the Fe–B linkage was expected to be strong due to the strong withdrawing effect of the perfluorobenzenes, the role of π-back bonding was found [208] to be minor.

Aldridge and coworkers prepared [209,210] a range of Fp-substituted asymmetric mesitylboron complexes (Scheme 144). The facial photolytic conversion potential of these complexes was demonstrated by irradiation of the diFp mesitylboron complex, affording a bridged complex.

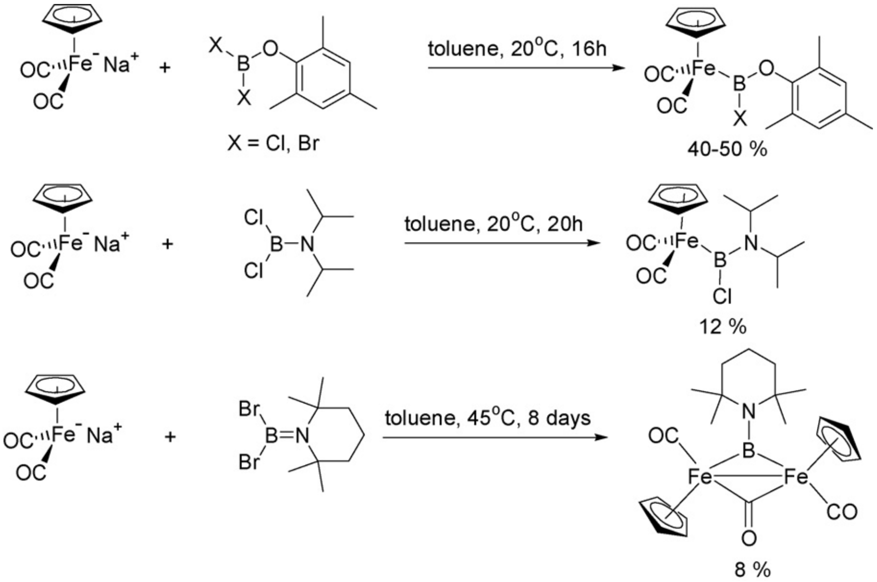


Scheme 144.

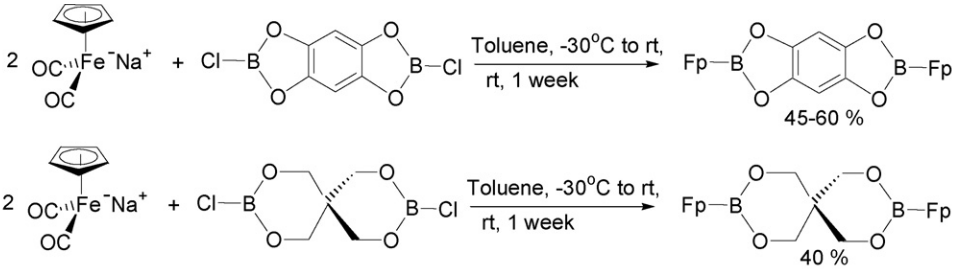


Scheme 145.

As a means to a range of boryl complexes through boron-centered substitution chemistry, Aldridge and coworkers prepared [211] asymmetric (bromo)boryl Fp complexes (Scheme 145) to serve as potential precursors to other boryl complexes. To that end, these researchers probed the reactiv-



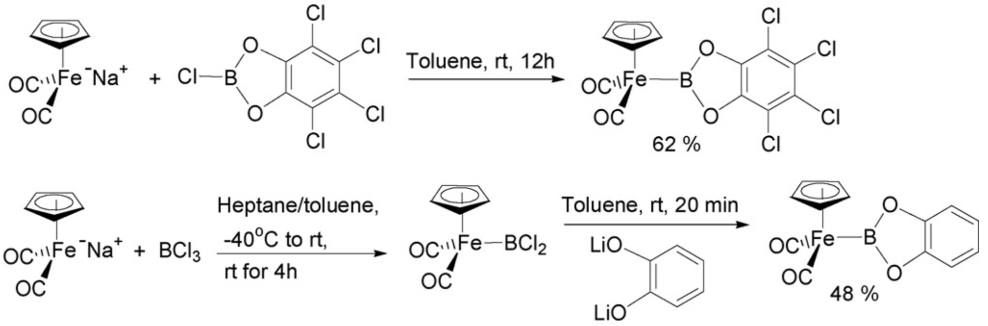
Scheme 146.



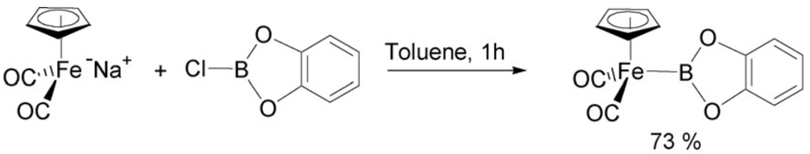
Scheme 147.

ity of these precursors with a variety of nucleophiles, including alkoxides, sulfides, amides, and hydrides.

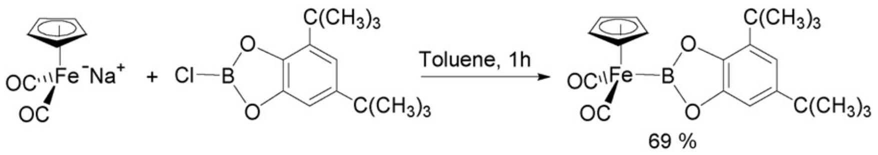
Aldridge and coworkers extended [212] the preparation of heteroatom stabilized haloboranediyl complexes to the Fp moiety (Scheme 146). These complexes serve as precursors to a range of other boron-containing complexes. The halide of these Fp-boryl complexes was substituted for by various groups, for example, –OC_6H_4-4-*t*-Bu, –SPh, and –F groups through nucleophilic substitution. Chloride abstraction of the diisopropylaminoborylene chloro Fp complex (Fp[B(N(*i*-Pr)$_2$)Cl])



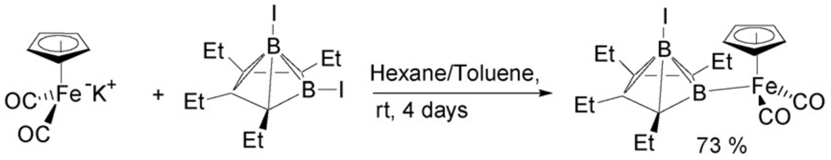
Scheme 148.



Scheme 149.



Scheme 150.



Scheme 151.

by Na(B(3,5-$(CF_3)_2C_6H_3)_4$ afforded [213] the cationic B/N vinylidene which underwent M=B metathesis reactions with E=O and E=S bonds (E = P and As-containing fragments).

To expand their understanding of ligand properties of boryl systems, Aldridge et al. synthesized and characterized diFp systems featuring bridging boryl ligands (Scheme 147) [214,215]. These researchers asserted that this new methodology could be applied to unsaturated bridging "spacer" groups such as those based around benzene and also saturated aliphatic systems such as the spiro spacer. Comparative structural studies of the two diFp boryl compounds revealed the importance of the chelating alkoxo backbone of the boryl ligand in determining its electronic properties.

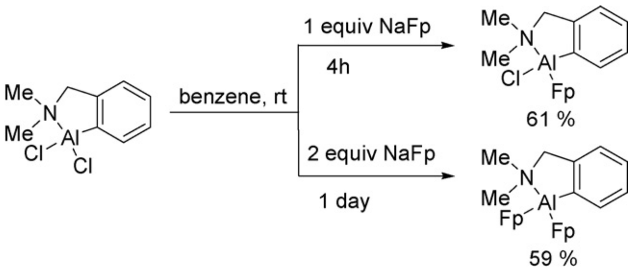
Aldridge and coworkers also prepared [216] two Fp-substituted boryl complexes containing a perchlorocatechol and a catechol fragment (Scheme 148). The catechol-containing complex was prepared by an indirect route from $FpBCl_2$. Both the catechol and perchlorocatechol Fp-containing compounds were prepared to study their reactivity and conversion to other metal boryl complexes.

Hartwig and coworkers prepared [217] an Fp boryl catechol complex via a direct route (Scheme 149) to demonstrate its functionalization capabilities in C–H activation reactions with arenes and alkenes. Aryl- and vinylboronate esters were produced which can be converted to a variety of functionalized organic molecules.

Waltz and Hartwig prepared, characterized, and performed photochemical functionalizations of alkanes by isolated transition metal boryl complexes. One of the Fp complexes prepared [218] (Scheme 150) was subjected to photochemical reaction with pentane but was found to be inert.

To study the reactivity of a diiodohexaborane toward a variety of nucleophiles, Siebert et al. reacted [219] the Fp anion and characterized the iodo substitution product (Scheme 151). Although two possible substitutions could have occurred, Fp replaced the basal iodo group regiospecifically.

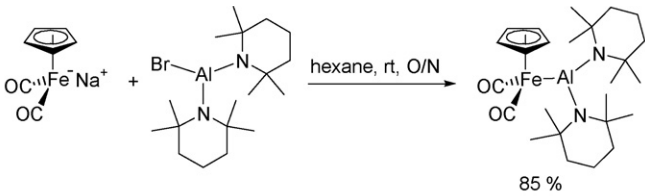
Many groups have studied other group 13 elements. However, in these complexes the elements are metals and formation of a new metal–metal bond often defines the reactivity of these compounds. Besides their work with boron, the Braunschweig group also prepared and spectroscopically characterized aluminum compounds. Two alanes were prepared [220] having one and two Fp moieties (Scheme 152).



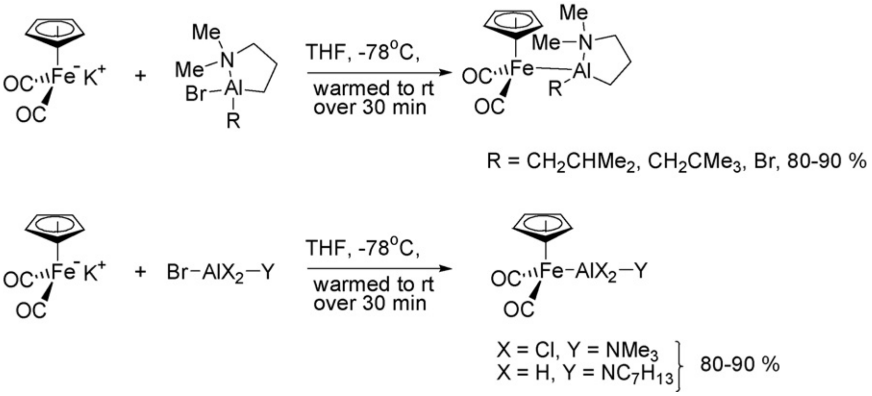
Scheme 152.

To expand the understanding of compounds that contain the Fe–Al bond, Nöth et al. synthesized and fully characterized a tricoordinated alanyl containing the Fp group (Scheme 153) [221].

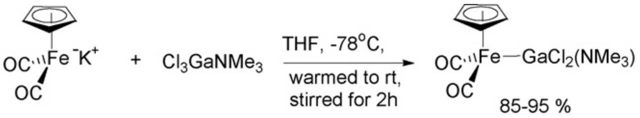
Fischer and Priermeier prepared [222] Fp-substituted alanes via halide substitution by Fp anion (Scheme 154). Previous attempts by other researchers to generate Fe–Al bonds via salt elimination using aluminum halides and Fp anion had failed. Success was achieved in part as a result of ion-pairing through controlling the reactivity between the aluminum halides and transition metal carbonylates. The amido group helped to stabilize the aluminum to substitution. These researchers were attracted to organoaluminum chemistry because of the potential for deposition of mixed-metal thin films via metal organic chemical vapor deposition (MOCVD). Some low-pressure MOCVD preliminary screenings were carried out to evaluate some of the compounds. These researchers concluded that using the alanes reported in their publication resulted in much more difficult deposition of pure metal/Al thin films than with metal/Ga or In compounds. They attributed the difficulty to higher Al–C



Scheme 153.



Scheme 154.



Scheme 155.

and Al–N bond strengths and the stronger affinity of aluminum centers for carbonyl oxygen atoms, which may impact the decomposition process.

Fischer and Priermeier synthesized new metal–Ga bonded compounds and studied their properties and structural aspects. One of those compounds prepared was the result of chloride substitution by the Fp anion on Cl_3GaNMe_3 (Scheme 155) [223]. A select few of the cobalt-gallium compounds that were prepared were tested for their potential as single source precursors to deposit binary intermetallic materials using low-pressure MOCVD.

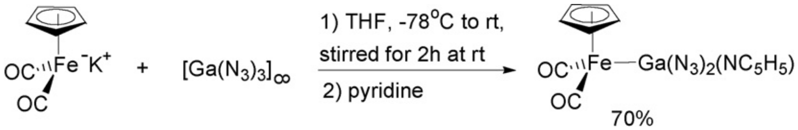
To explore reactions and applications of triazidogallium and its derivatives, Fischer and coworkers prepared [41] an Fp-substituted diazidogallium compound (Scheme 156). Again, these researchers had interest in gallium compounds as MOCVD precursors and as sources for nanoparticles of GaN.

Power and coworkers synthesized and characterized [224,225] new organogallium Fp-containing compounds through substitution of chloro groups by the Fp moiety (Scheme 157). The authors mentioned possible applications of derivatives of organogallium as single source precursors for binary intermetallic phases and their isolobal relationship to cationic carbene transition metal species.

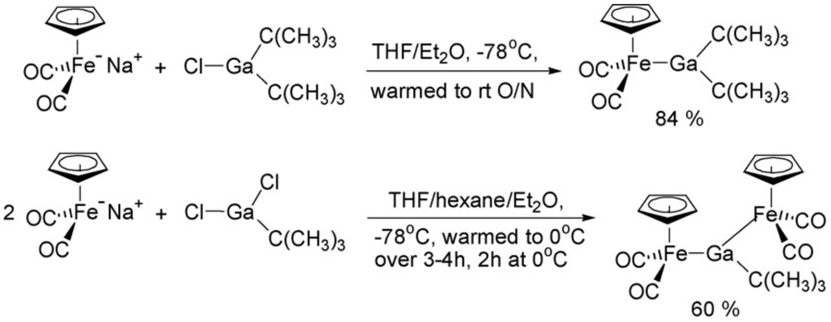
Bott and coworkers synthesized and characterized [226] Fp-containing gallium compounds (Scheme 158). Volatile derivatives of group 13 elements and transition metals have been used as MOCVD precursors to give thin film alloys.

Leiner and Scheer had previously shown that a Cp*(C_5Me_5) σ-bonded to a phosphorus underwent migration to a tungsten to form η^5-Cp* bonding. To extend the study of Cp* migration to group 13 elements, these researchers prepared gallium complexes. One such complex was formed from two Fp anions and Cp^*GaCl_2 (Scheme 159) [227].

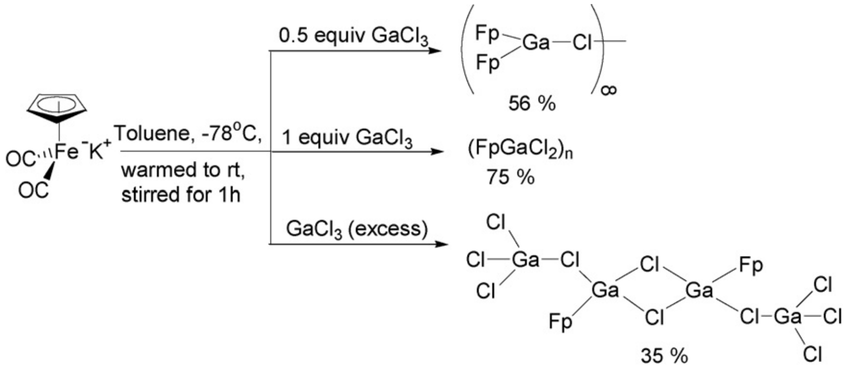
Ueno and coworkers prepared [228] a diFp substituted gallium complex (Scheme 160) as a precursor to a bridged derivative via irradiation and loss of a carbonyl ligand.



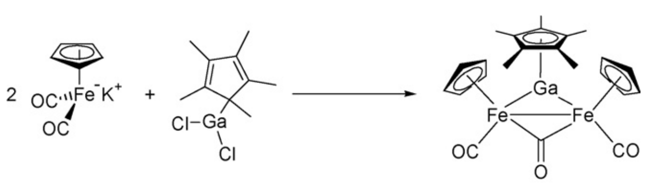
Scheme 156.



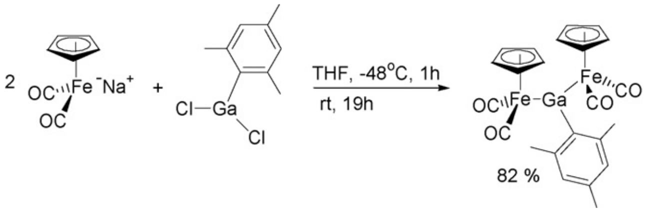
Scheme 157.



Scheme 158.



Scheme 159.



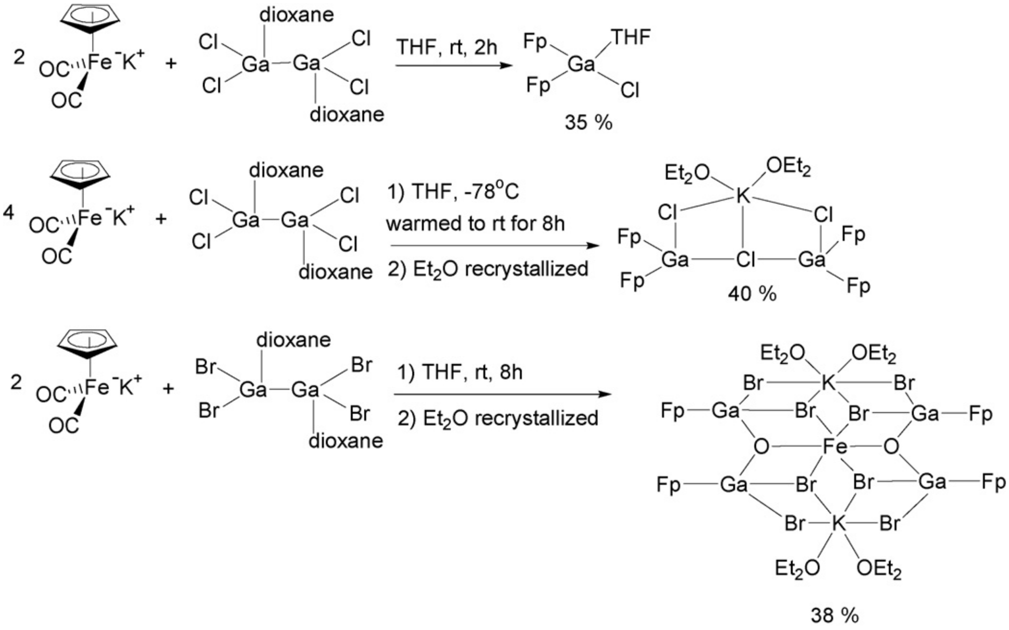
Scheme 160.

In an effort to prepare and characterize new complexes having Ga–Fe bonds, Linti and coworkers reacted [229] KFp with $Ga_2X_2 \cdot 2$dioxane (X = Cl, Br) (Scheme 161).

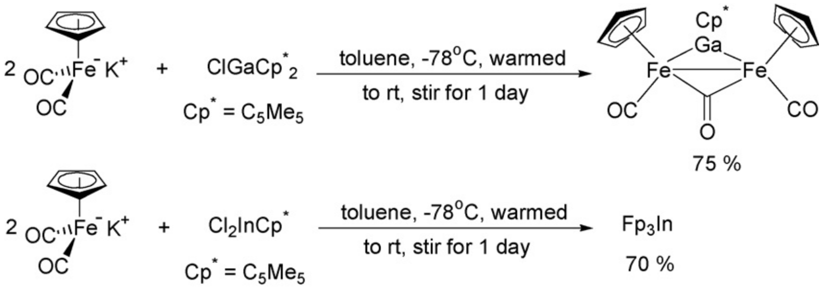
As part of their efforts to synthesize gallium complexes and extend that methodology to indium compounds, Leiner and Scheer prepared [230] a dinuclear iron–gallium-bridged complex. Unlike gallium, the indium did not form a bridged complex but instead generated a triFp-substituted indium compound (Scheme 162).

Investigation into various organoindium complexes because of their potential as precursors to organometallic chemical vapor deposition of intermetallic thin films, led Fischer and coworkers to make a range of metal–indium complexes. One of the complexes they investigated was an Fp-substituted indium complex (Scheme 163) [231].

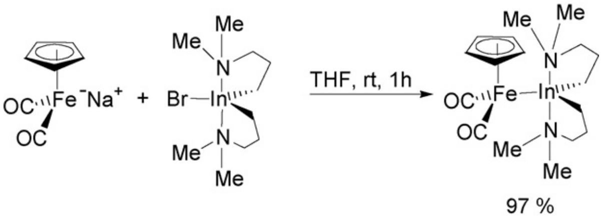
Norman and coworkers extended their studies of organotransition metal–indium complexes by preparing [232] Fp-indium thiocyanate complexes (Scheme 164) as part of a more general study on pseudo halide complexes of the heavier p-block



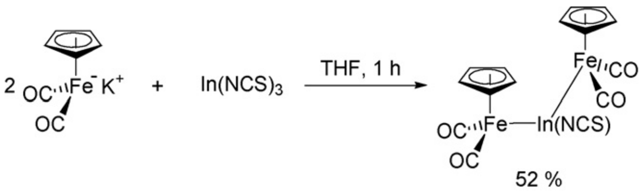
Scheme 161.



Scheme 162.



Scheme 163.

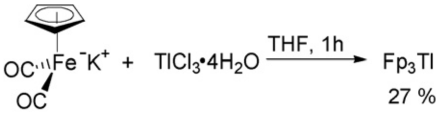


Scheme 164.

elements. The $Fp_2In(CNS)$ complex was subsequently reacted with 4-picoline to form the adduct, $Fp_2In(NCS)(4\text{-pic})$.

In an effort to expand halide abstraction methodology for the synthesis of base-free cationic group 13 diyl systems, Aldridge and coworkers prepared [233] a range of Fp– and Fp*–indium precursors. Two Fp-substituted indium complexes were formed by Fp substitution for one or two bromo groups (Scheme 165).

In conjunction with their study on the solution dynamics of thallium–metal compounds using [205] Tl NMR spectroscopy, Whitmire and coworkers prepared [234] an Fp_3Tl complex (Scheme 166). The Lewis acid character of the various compounds was probed by NMR. The Fp_3Tl complex did not form a Lewis base adduct.



Scheme 166.

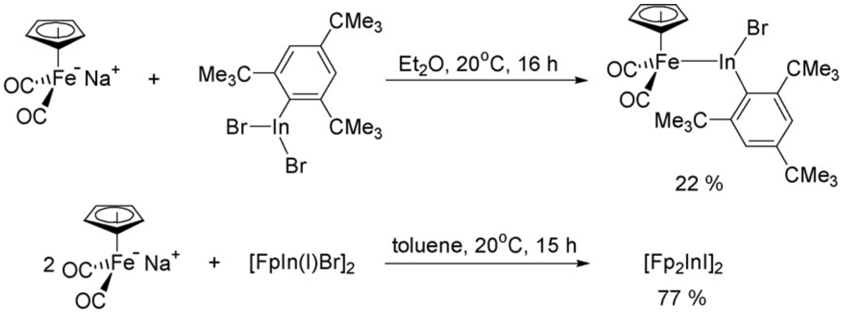
4.2. Addition reactions of the (η^5-C_5H_5)$(CO)_2$Fe anion

Since the Fp anion has been shown to form new iron bonds by substitution, likewise it can alternatively undergo addition with a suitable electrophilic substrate. Most of the addition reactions involve iron–carbon bond formation. While electrophilic substrates for addition reactions can also be viewed as either neutral or cationic, they will be treated according to hybridization at the electrophilic carbon. As mentioned earlier, complexes that do not involve an Fe–C bond will be discussed in a separate section under Section 4.2.4.

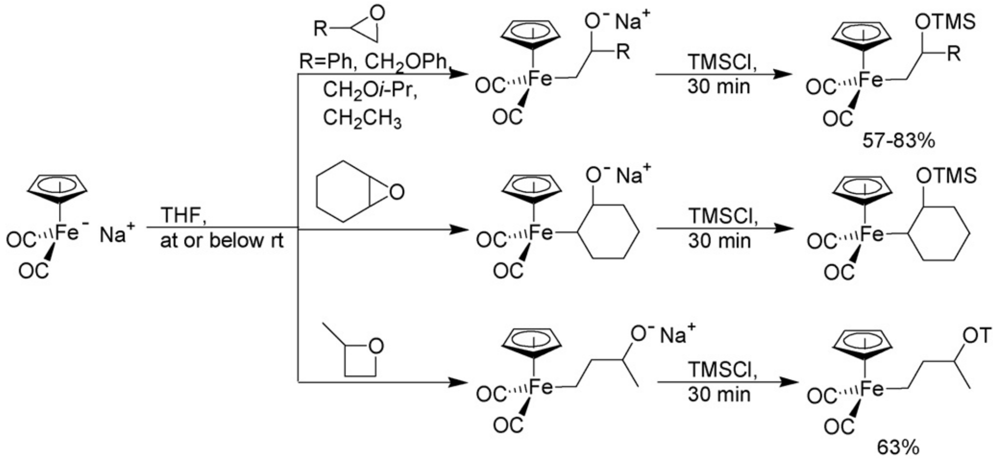
It should be mentioned that these reactions often involve the use of $ClSiMe_3$ or a similar trapping agent since the initial anionic addition product formed from a neutral electrophile is usually not isolated. The use of $ClSiMe_3$ and similar trapping agents provides a method of determining the yield from initial addition. Chlorotrimethylsilane is a popular trapping reagent with oxygen-containing electrophiles because of the inherent strength of the resulting Si–O bond.

4.2.1. Reactions with sp^3-hybridized carbon electrophiles (*Table 13*)

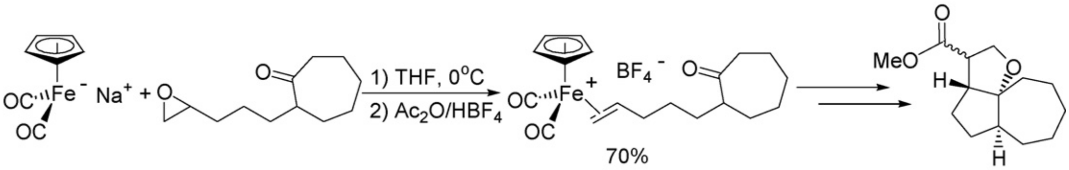
Epoxides are representative of this class. Saidi et al. have successfully added NaFp to a range of epoxides and an oxetane in order to form various substituted β- and γ-hydroxy esters, respectively. These strained 3- and 4-membered cyclic ethers



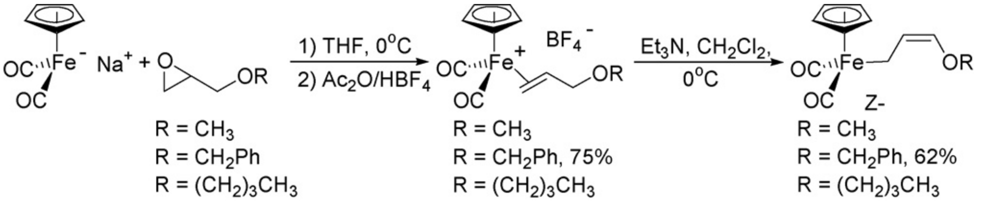
Scheme 165.



Scheme 167.



Scheme 168.



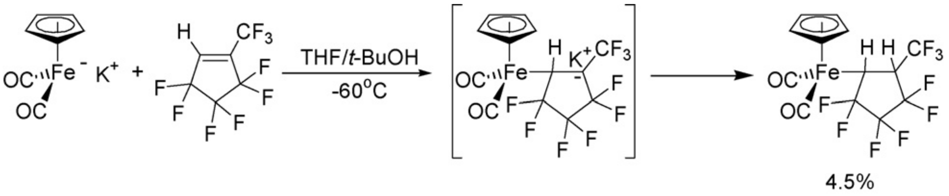
Scheme 169.

show exclusive addition of Fp anion to the least sterically hindered α-carbon with resultant ring-opening (Scheme 167) [95]. According to Rück-Braun and Kühn, optically active complexes can also be obtained from achiral epoxides [39]. Addition to epoxy ketones was also reported to be useful for the preparation of Fp complexes of α,β-unsaturated ketones [235]. Turos and coworkers have employed the Fp anion addition to various epoxides in the synthesis of substituted tetrahydrofurans [75,236] and homoallylic alcohols [74,237]. An example of their work involving a substituted tetrahydrofuran is presented in Scheme 168. In the formation of homoallylic alcohols, metalation of the epoxide followed by acidification and dehydration also gives the stable cationic Fp–olefin π-complex, which is subsequently treated with triethylamine to give exclusively the *Z*-isomer (Scheme 169).

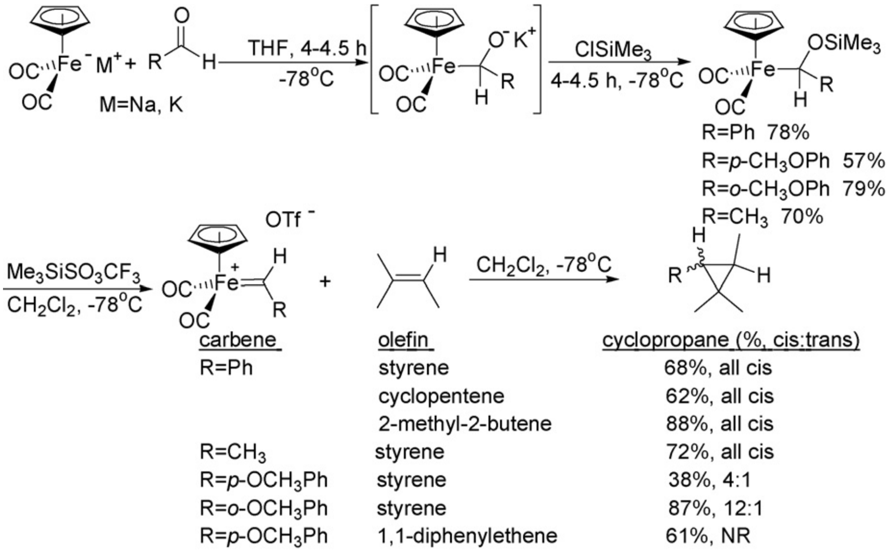
4.2.2. Reactions with sp^2-hybridized carbon electrophiles (Table 14)

Complexed and uncomplexed alkenes as well as aldehydes are the most common among the electrophilic substrates that undergo addition of the Fp moiety to a carbon within the substrate. The resulting complexes have newly formed carbon–iron bonds that undergo sp^2 to sp^3 hybridization changes at the reactive carbon.

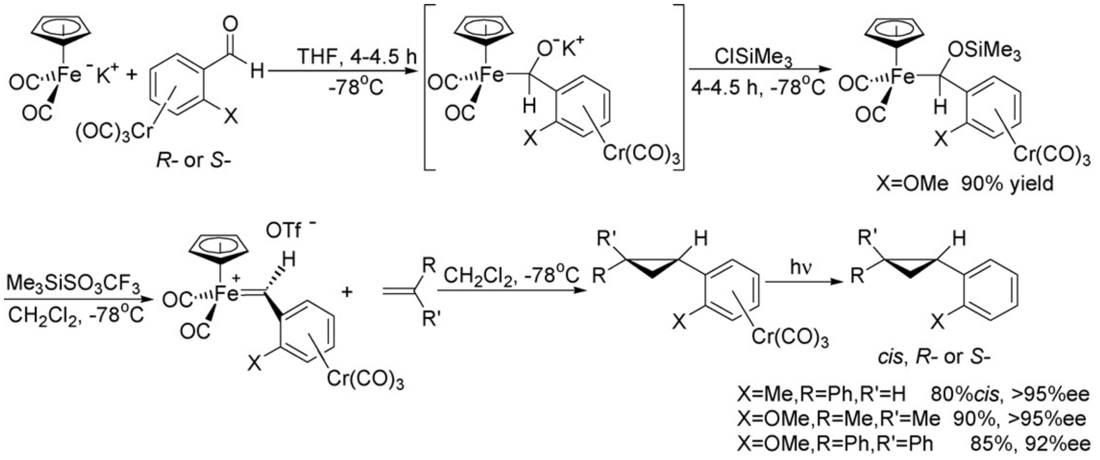
There has been one report by researchers Sazonov, Artamkina, and Beletskaya regarding apparent Fp anion addition to



Scheme 170.



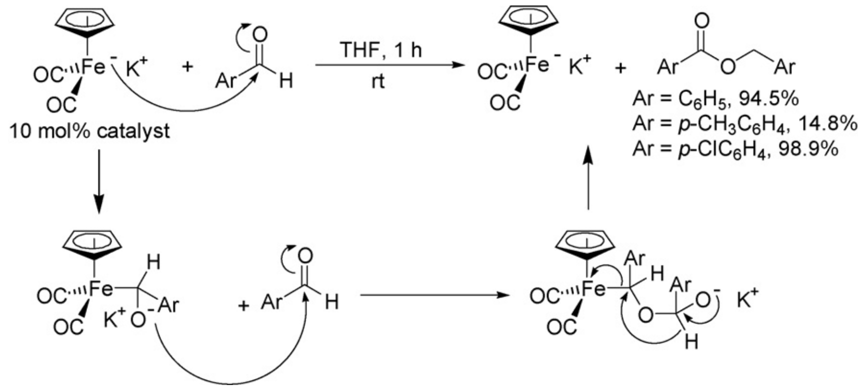
Scheme 171.



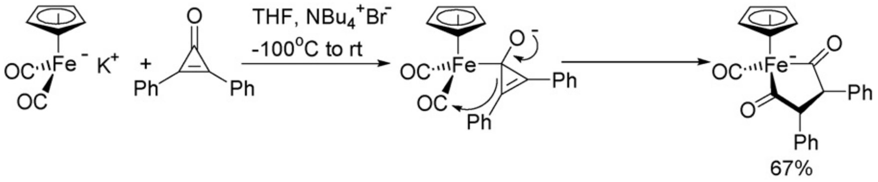
Scheme 172.

the alkene hexafluoro-2-hydro-1-trifluoromethyl)cyclopent-1-ene (Scheme 170) [106].

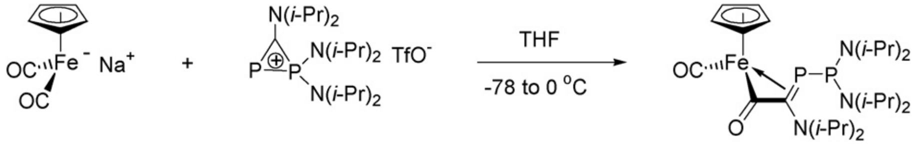
The Hossain group has been quite productive concerning addition of Fp anion to aryl and alkyl aldehydes to form silyl ether complexes and subsequently the cationic Fp carbene complexes (Scheme 171). These cationic carbene complexes are useful in the downstream synthesis of *cis* cyclopropanes by reaction with various substituted olefins [12]. A hallmark of the Hossain procedure uses the aforementioned $ClSiMe_3$ to trap the resultant alkoxide complex followed by addition of TMSOTf *in situ* to generate the cationic Fp^+ carbene. Their method has been employed toward the synthesis of enantiospecific cyclopropanes



Scheme 173.



Scheme 174.



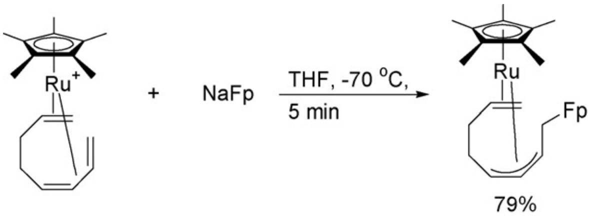
Scheme 175.

using Fp anion addition to various chiral η^6-$Cr(CO)_3$ aryl aldehydes [12,238–241]. This asymmetric method has resulted in various chiral *cis* cyclopropanes in high ee and overall yield. The method has been applied in the synthesis of a precursor for cilastatin [242]. The resultant chiral Fp^+ carbene is reacted in the presence of a suitable substituted olefin to generate the desired chiral *cis* cyclopropane [243,244]. An example of this asymmetric procedure is given in Scheme 172.

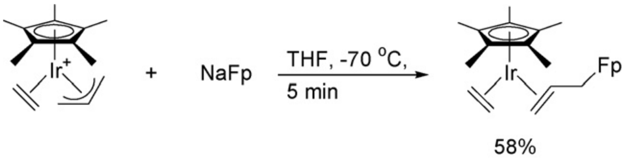
In 1994, Yamashita discovered that the Fp anion catalyzes the dimerization of aromatic aldehydes to carboxylic esters at room temperature (Scheme 173). Borrowing from work by the Hossain group concerning initial addition of Fp anion to aldehydes and resultant trapping of the alkoxide by $ClSiMe_3$, these researchers were able to arrive at a tentative mechanism for this interesting catalytic process [245].

Gade et al. have been able to successfully add Fp anion to diphenylcyclopropenone to form a metallacyclopenta-2,5-dione. It is interesting to note that, in this addition reaction, intramolecular CO insertion takes place (Scheme 174). The final structure of this dione was confirmed by X-ray crystallography [191].

The group of Bertrand discovered an unexpected result when a diphosphirenium salt was reacted with the Fp anion. Following CO insertion, an η^2-phosphaalkene forms in high yield as shown in Scheme 175 [246]. The structure of the complex was confirmed by X-ray crystallography and fully characterized by ^{31}P, ^1H, and ^{13}C NMR. These researchers found the resulting complex was interesting in that reaction with Fp anion did not break the P–P bond, whereas with more sterically hindered nucleophiles such as diphenylphosphide, bis(trimethylsilyl)phosphide, bis(trimethylsilyl)mesitylsilylphosphide, and trimethylstannyl anions, the P–P bond was broken. The authors suggested that the Fp anion follows a different pathway than other nucleophiles, leading them to propose a SET mechanism (see Section 2.1, Scheme 1), whereby one-electron transfer occurs from the Fp anion to the diphosphirenium cation.



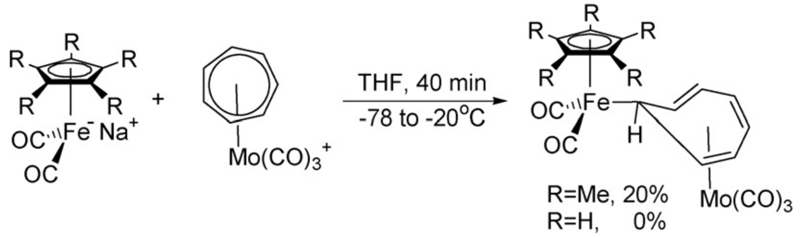
Scheme 176.



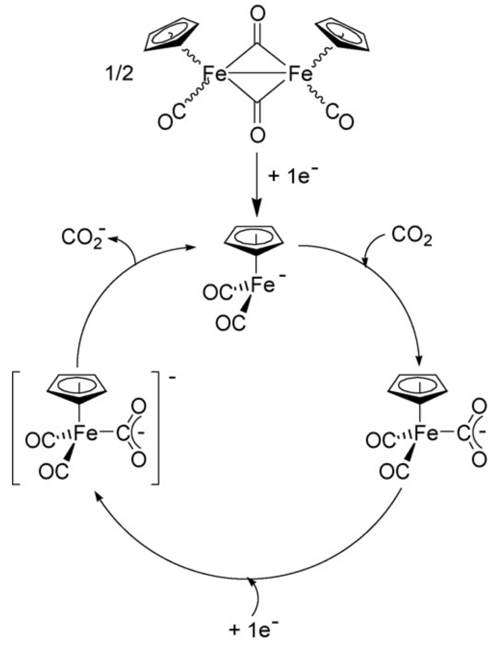
Scheme 177.

Researchers Beck et al. were able to add the Fp anion to the organometallic cation complexes $[Cp^*Ru(\mu\text{-}\eta^2\text{:}\eta^4\text{-}C_8H_{12})]^+$ and $[Cp^*Ir(\eta^2\text{-}C_2H_4)(\eta^3\text{-}C_3H_5)]^+$ in 79% [247] and 58% [248] yields, respectively (Schemes 176 and 177). In all cases, addition occurred at the terminal portion of the unsaturated ligand.

Davies and Whitely have been able to synthesize the cycloheptatrienyl-bridged heterobimetallic complex $Mo(CO)_3(\mu\text{-}\eta^6\text{:}\eta^1\text{-}C_7H_7)Fe(CO)_2(Cp^*)$ shown in Scheme 178. The

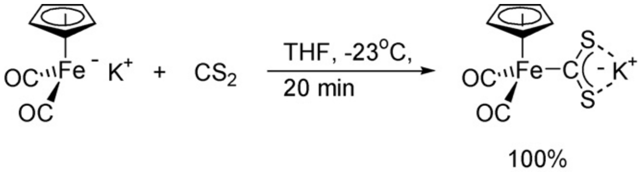


Scheme 178.



Scheme 179.

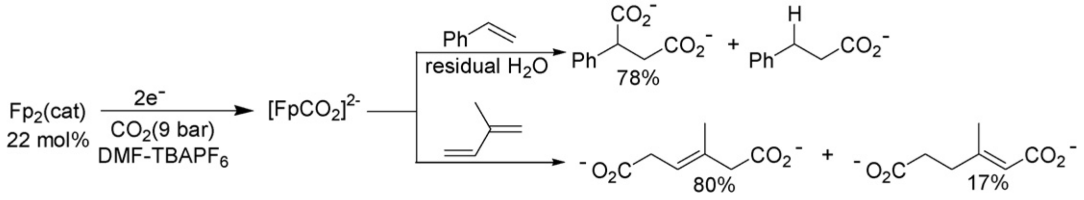
synthesis was performed at low temperature using NaFp* in the presence of the metal cation salt $[Mo(CO)_3(\eta\text{-}C_7H_7)]^+PF_6^-$. This complex rapidly decomposes into separate Mo and Fe dimers at higher temperatures. Interestingly, despite all efforts, substituting NaFp for NaFp*produced only the dimers $Mo_2(CO)_6(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_{14}H_{14})$ and $Fe(CO)_2Cp_2$. Although no Fp heterobimetallic could be isolated, the authors did note its intermediacy by IR and ^1H NMR. On the other hand, the stability of the Fp* heterobimetallic complex was attributed to the increased stability of the Cp* ligand on iron. There is evidence of migration of Fp* around the cycloheptatrienyl ring. The authors noted [249] this heterobimetallic is a unique example of a “first row transition metal bonded η^1 to the cycloheptatrienyl ligand.”



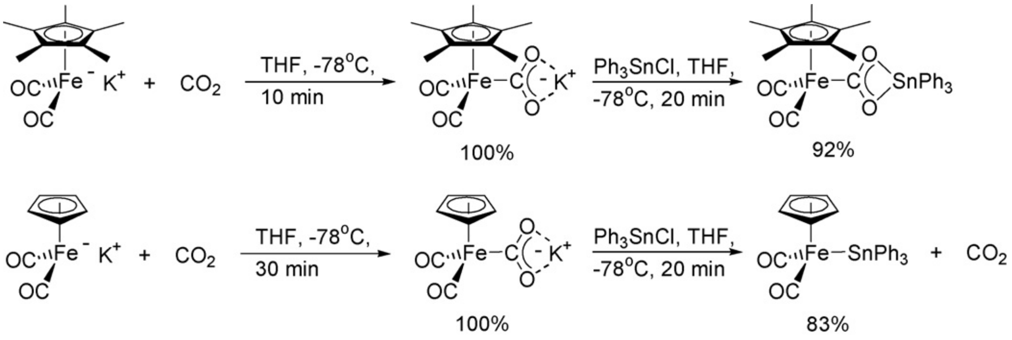
Scheme 182.

4.2.3. *Reactions with sp-hybridized carbon electrophiles (Table 15)*

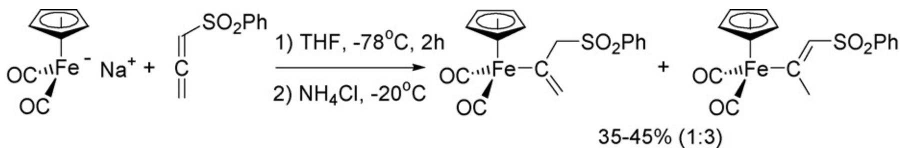
Carbon dioxide, carbon disulfide, and an allenic sulfone all undergo direct addition of the Fp anion to a sp-hybridized carbon within the electrophile. While the addition of CO_2 to Fp anion is not new, at least two interesting methods have evolved in this area in the recent literature. Electrocatalytic reduction has been performed using Fp anion for the selective carboxylation of isoprene and styrene. A catalytic amount of Fp dimer generates the Fp anion under controlled potential electrolysis (Scheme 179). Addition of CO_2 to an *N*,*N*-dimethylformamide-tetrabutylammonium hexafluorophosphate solution of Fp dimer and substrate allowed for carboxylation at a lower negative potential. The presence of Fp anion resulted in an increased yield and greater regioselectivity in dicarboxylation of isoprene. In the absence of Fp anion, the reaction was not selective. Styrene also gave an increased yield and favored dicarboxylation in the presence of Fp anion, whereas in its absence only the monocarboxylated product was observed. This monocarboxylated product undergoes addition of one hydrogen at the alpha carbon of styrene due to the presence of residual water (Scheme 180) [51].



Scheme 180.



Scheme 181.



Scheme 183.

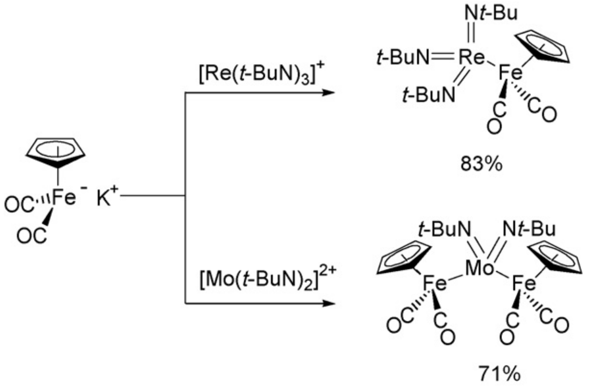
The Fp anion is well known to form the salts $FpCS_2^-$ or $FpCO_2^-$ in the presence of carbon dioxide or carbon disulfide. Researchers Pinkes and Cutler have been active in this area and were able to note the quantitative conversion of $[C_5Me_5(CO)_2Fe]^-$ (i.e., Fp* anion) to its carboxylate salt $Fp^*CO_2^-K^+$. This salt was efficiently trapped with Ph_3SnCl to give $C_5Me_5(CO)_2Fe$-CO_2SnPh_3 in 92% yield. The less nucleophilic Fp anion also reacted quantitatively with CO_2 to its carboxylate salt according to IR spectroscopy, although subsequent trapping with Ph_3SnCl gave only $C_5H_5(CO)_2Fe$-$SnPh_3$, apparently due to dissociation of CO_2 from the carboxylate salt and subsequent trapping of the Fp anion itself (Scheme 181) [250]. In a later study, reaction of 1 equivalent of CS_2 with Fp anion gave $FpCS_2^-K^+$ in quantitative yield as determined by IR spectroscopy (Scheme 182) [195]. The authors have used these compounds to rigorously study the reaction of CS_2 and CO_2 insertions into the Fe–Zr bond of $FpZrClCp_2$ compared to addition of $FpCS_2K$ or $FpCO_2K$ to $ZrCl_2Cp_2$ itself.

Welker and coworkers were able to show that the Fp anion adds to the central sp-hybridized carbon of allenic sulfones to give Fp-substituted allyl or vinyl sulfones as shown in Scheme 183. The temperature at which the reaction was quenched affected the ratio of the two sulfones, whereby the ratio of vinyl to allyl sulfone increases with increasing temperature. Ultimately, the kinetic product was found to be the allyl sulfone, which subsequently rearranges to the vinyl sulfone on standing. Furthermore, an appreciable amount of Fp dimer is produced in these reactions leading the authors to propose that the reaction may involve acid/base or redox side reactions. The authors were able to apply this method toward formation of chiral organoiron complexes [251].

4.2.4. *Reactions with other electrophiles (Table 16)*

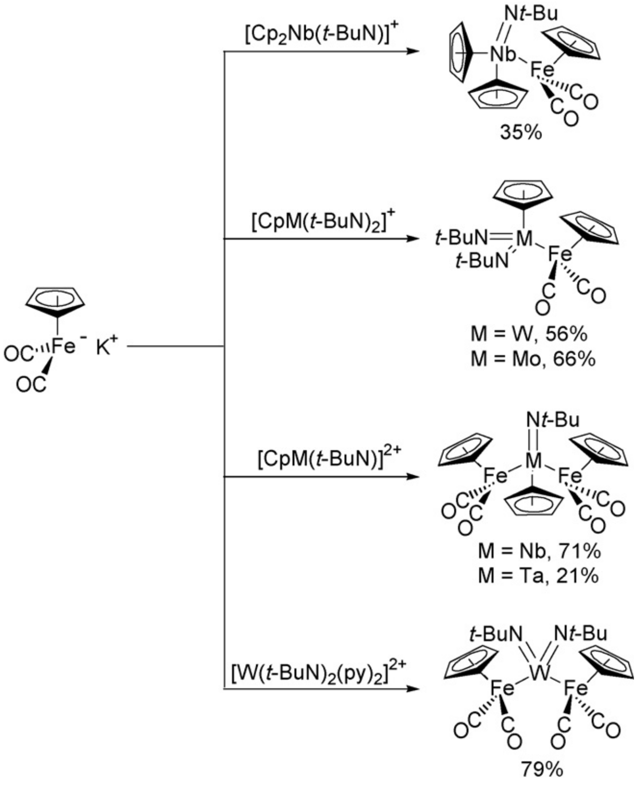
Since 1994, there has been a significant amount of research regarding Fp anion addition to non-carbon centers in various electrophiles. These electrophiles can be regarded as neutral or cationic Lewis acids.

Researchers Sundermeyer and Runge have added the Fp anion to a number of cationic metal (groups 5–7) imido complexes. These researchers were able to form bonded complexes of the types Fe–M–Fe and Fe–M (M = metal moiety) [252,253]. Their first report, incorporated nucleophilic carbonyl metalates of groups 6–8 including the Fp anion in reactions with $[Re(Nt\text{-}Bu)_3]^+$ and $[Mo(Nt\text{-}Bu)_2]^{2+}$ (Scheme 184). The authors noted that the volatile Re–Fe complex has promising potential as a starting material for the deposition of thin layers from the gas phase in metal organic chemical vapor deposition. The trimetallic Fe–Mo–Fe complex has potential application as a starting material to give isocyanates or mixed metal carbonyl-oxo complexes. Later work by these researchers involved exclusively the Fp anion in reactions with other groups 5–7 metal imino cations (Scheme 185). Each of the complexes illustrated in Schemes 184 and 185 was characterized by ^{13}C NMR, IR, elemental analysis, and melting point.

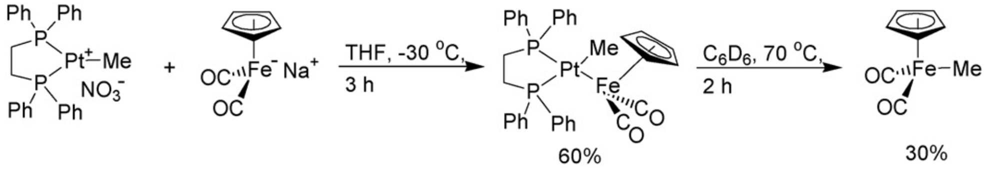


Scheme 184.

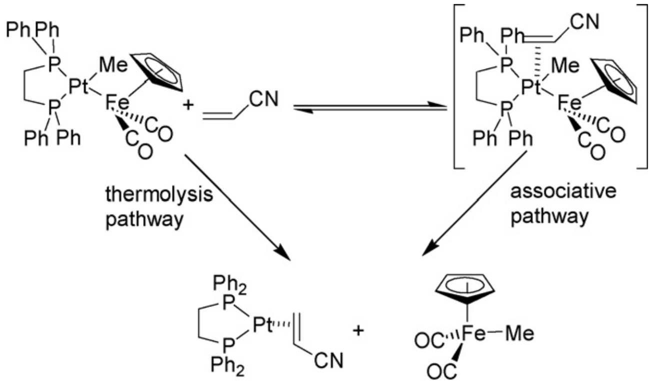
Komiya et al. have been able to form the air stable complex (dpe)MePt-$FeCp(CO)_2$ by reaction of NaFp with $[(dppe)MePt]^+NO_3^-$ in 60% yield (Scheme 186) [254]. The



Scheme 185.



Scheme 186.



Scheme 187.

structure of the resulting complex was confirmed by X-ray crystallography and exhibited square planar geometry about Pt and tetrahedral geometry about Fe. Interestingly, at 70 °C for 2 h (thermolysis) the complex was found to undergo methyl migration to form $MeFp(CO)_2$. Carbon monoxide and electron deficient olefins such as acrylonitrile were found to accelerate the rate of methyl migration. A kinetic investigation found the methyl migration to be dependent on the electron deficiency of the olefin. Using acrylonitrile as an electron deficient olefin in kinetic studies, the authors proposed that acceleration of methyl migration could be explained by rapid formation of the olefin π-complex as an intermediate and subsequent reductive elimination. The methyl migration could follow two possible pathways, either by the aforementioned thermolysis or by an associative path involving the acrylonitrile intermediate (Scheme 187).

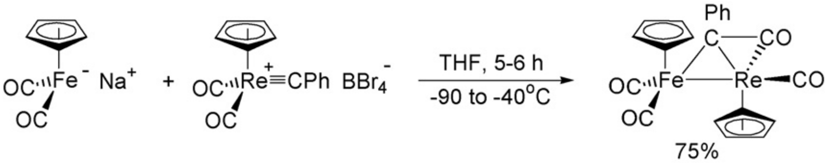
The research group of Chen has produced an interesting η^1,η^2-ketene complex from the reaction of NaFp with the cationic carbyne complex $[\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}CC_6H_5]^+BBr_4^-$ [255]. The product (Scheme 188) was characterized by IR, ^{1}H NMR, elemental analysis, and melting point.

Paetzold and coworkers have reacted NaFp with the aza-*closo*-dodecaborane $MeNB_{11}H_{11}$ in THF to give two isomeric products as sodium salts [256]. The Fp anion was the only anionic base in the study to produce two isomeric products. The ratio of isomer 1 to isomer 2 was 2:3 by ^{11}B and ^{1}H NMR (Scheme 189) after 12 h and 1:3 after 3 days. Eventually, isomer 1 completely disappears as the amount of the isomer 2 increases.

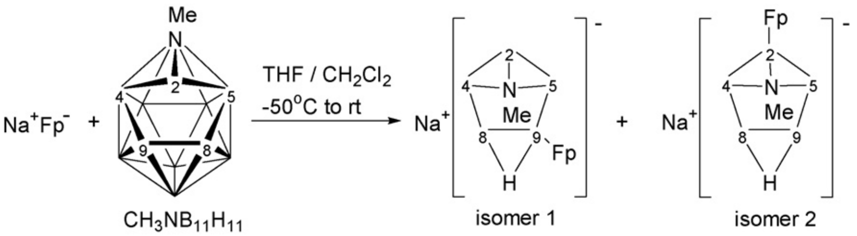
5. Conclusion

As one of the most widely studied species, the Fp anion has been investigated in substitution and addition reactions for both mechanistic understanding and synthetic applications. In this review we report the breadth and depth of the chemistry of the Fp anion and its "supernucleophilicity" with carbon-centered and noncarbon-centered electrophiles. The Fp anion has been employed as a starting material or precursor to activate a remarkably large number of molecules, from alkyl halides to aryl halides, from silyl triflates to stannyl halides, from epoxides to aldehydes and beyond.

Not only have researchers found mechanistic studies to be intriguing but also applications of their newly formed complexes. A variety of reactive cationic and carbene precursors have been prepared with wide-spread utility as catalysts for Diels–Alder reactions, cyclopropanations, epoxidations, and aziridinations. Stoichiometric auxiliaries have been prepared



Scheme 188.



Scheme 189.

for a wide range of organic and inorganic species. Some of the more recent advances using Fp anion as a reagent now involve such diverse fields as materials science where application of its analogs in vapor deposition methods has shown promise. A host of organometallic compounds have been prepared for such applications as MOCVD, photochromically active optical filters, semiconducting polymers, and heat resistant polymers.

In addition, the Fp anion has been applied toward an even broader range of asymmetric and regiospecific reactions than ever before. This review explores the wealth of research that has been done since 1994 involving reactions with the Fp anion but in so doing exposes the opportunities for yet to be discovered reactions and applications. We envision that this review will continue to advance the development of the Fp anion as a unique reagent in organic and inorganic synthesis and motivate others to explore areas that have been underdeveloped.

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Appendix A. Supplementary data (Tables 3–16)

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ccr.2007.12.022.

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