

## Das Reagenz • The Reagent

Cyclopentadienyldicarbonylferrates ( $[\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}]\text{M}$ ,  $\text{M} = \text{Na}, \text{K}$ ):  
Reagents with Various Synthetic Applications

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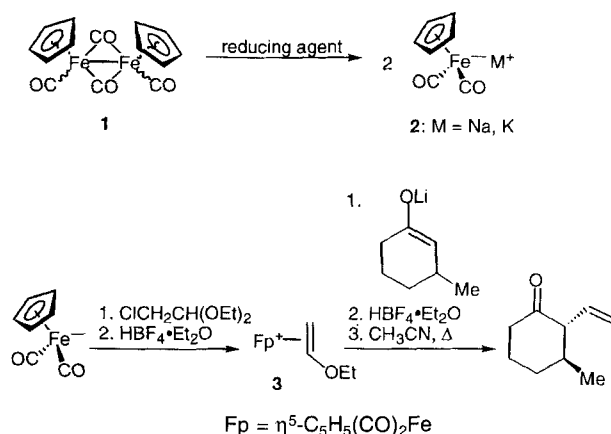
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Transition metal carbonyl anions constitute a useful class of nucleophiles which have been applied for the synthesis of numerous organometallic compounds within the last decades [1–4]. The ferrates **2** are of exceptional nucleophilicity [5]. They are even stronger nucleophiles than bromide, as followed from the kinetics of comparative nucleophilic displacement studies [6]. The reactions of alkali metal cyclopentadienyldicarbonylferrates **2** with a series of organic electrophiles have been thoroughly reviewed in the past. [3, 4, 7, 8]. Thus, the cyclopentadienyl(dicarbonyl)iron moiety ( $[\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}]$ ) proved to be one of the most useful and versatile transition metal fragments. The chemistry of *e.g.* coordinated  $\eta^1$ -alkyl,  $\eta^1$ -acyl or carbene ligands as well as of  $\eta^2$ -alkene complexes opens up new routes and possibilities for the development of synthetic methodologies for organic synthesis. Recent results in this area will be reported here.

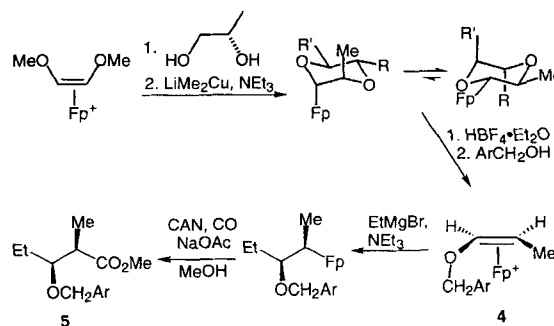
Transition metal monoanions are readily available starting from the corresponding metal-metal dimers and reducing agents [1, 2]. As heterogenous metal reductants sodium-potassium alloy [9] and mercury-sodium amalgam (1–2% sodium) [10] are commonly applied, particularly for large scale preparations and despite the hazards in their application. Sonochemically activated potassium metal was published to be a powerful stoichiometric reducing reagent for rapid one-pot generation of the potassium ferrate from **1**, too [11]. Gladysz and coworkers reported the application of commercially available trialkylboronhydrides as effective homogenous reductants. Thereby, K-Selectride<sup>®</sup> [(*sec*- $\text{C}_4\text{H}_9$ )<sub>3</sub>BH<sup>-</sup> K<sup>+</sup>] was found to be a useful alternative for a convenient one-pot preparation of potassium ferrate. However, on large scale preparations the amount of (*sec*- $\text{C}_4\text{H}_9$ )<sub>3</sub>B formed from K-Selectride has to be considered because of its flammability upon exposure to air [12, 13]. Other procedures, employing for example alkali metal silicides, [14] potassium benzophenone ketyl [15, 16] or naphthalene-sodium, [17] have been reported and applied in a few cases.

Cationic ( $\eta^2$ -olefine)iron complexes **3**, prepared from ferrates and alkyl halogenides, were shown to be valuable vinyl cation equivalents which have been applied *e.g.* for the vinylation of cyclohexanone enolates [8, 18, 19]. Optically active complexes were obtained starting for example from



Scheme 1

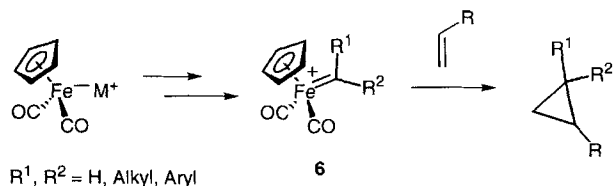
optically active epoxides [8]. Chiral 3-hydroxypropionate-2,3-dication equivalents were converted to (*2R,3S*)-configured 3-hydroxypentanoates **5** by the addition of C-nucleophiles and subsequent redox-promoted carboxylation [20, 21].



Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>  
Fp =  $\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}$

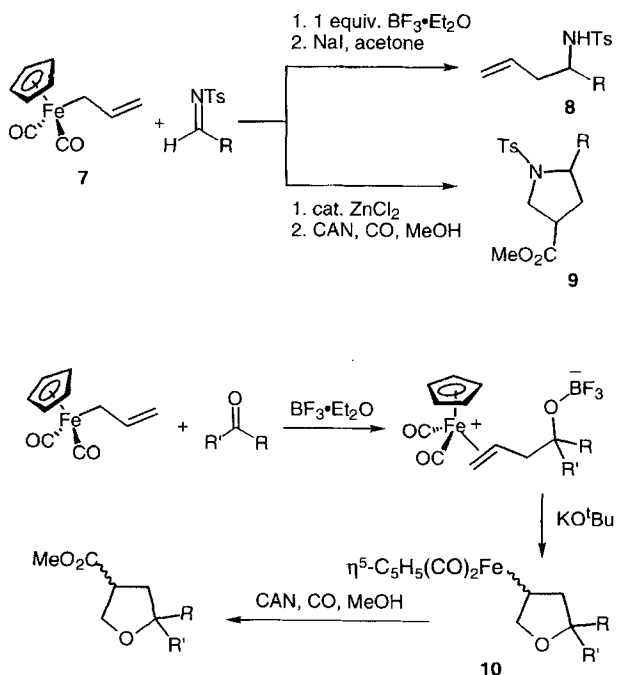
Scheme 2

In the past cationic nonheteroatom-stabilized carbene complexes **6** proved to be useful tools in metal-carbene-transfer chemistry [22, 24]. These complexes can be synthesized starting from ferrates and various electrophiles and were found to react with a variety of alkyl- and aryl-substituted alkenes at low temperature to yield cyclopropanes.



Scheme 3

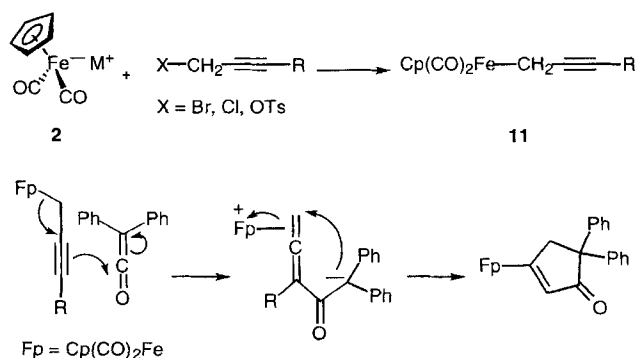
The potential and chemistry of allyl iron complexes **7** in metal-assisted [3+2] cycloaddition reactions with electrophilic olefins was explored by Rosenblum *et al.* [25]. Complex **7** was first prepared in 1963 by treatment of allyl chloride with ferrate **2**. Recently E. Turos *et al.* reported on reactions of *N*-tosylimines with **7** furnishing the allylation products **8** or pyrrolidines **9**, as [3+2] cycloaddition products, depending on the Lewis-acid applied and the work-up procedure employed. Analogously in  $\text{ZnCl}_2$ -catalyzed reactions of carbonyl compounds tetrahydropyranyl adducts **10** were obtained [26, 27]. Ceric ammonium nitrate oxidation allows the mild and efficient cleavage of the metal carbon bond [28].



Scheme 4

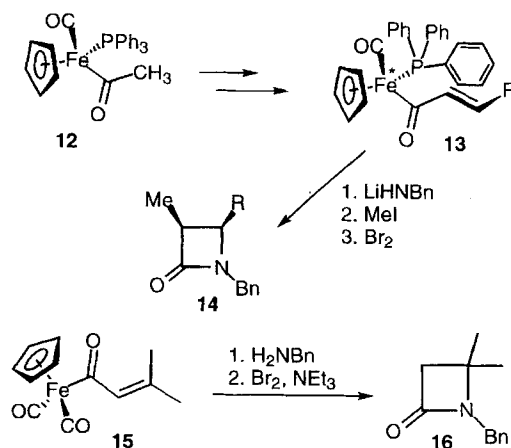
Additionally, reactions of iron propargyl complexes **11** with ketenes were studied, furnishing cyclopentenone derivatives [29, 30].

Transition metal acyl complexes have found many applications in organic synthesis. Cyclopentadienyl(dicarbo-



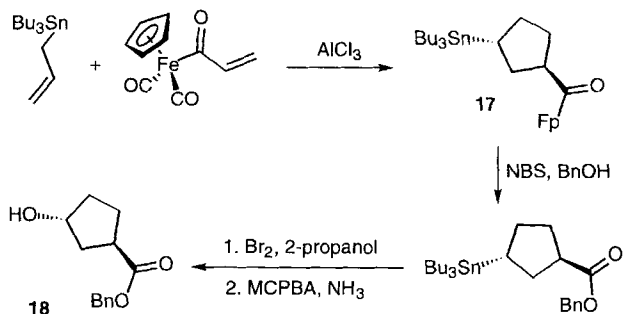
Scheme 5

nyl)acyl iron complexes are accessible from acid chlorides [10] or mixed anhydrides [31] and ferrates. Especially Davies *et al.* developed chiral acyl iron compounds derived from the well-known iron chiral auxiliary  $[\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)]$  for asymmetric synthesis [4, 32]. Treatment of the ferrate **2** with methyl iodide and subsequent reaction with  $\text{PPh}_3$  does furnish **12** as a racemic mixture [33]. The latter has been kinetically resolved *e.g.* via aldol reaction employing camphor [34]. Besides stereoselective enolate reactions, especially addition reactions to  $\alpha,\beta$ -unsaturated compounds and cycloadditions, *e.g.* Simmons–Smith reactions, have been utilized. Michael-type additions of amines and thiols to enoyl iron complexes **15** were carried out by Ojima *et al.* to afford the corresponding  $\beta$ -aminoalkanoyl and  $\beta$ -thioalkanoyl iron compounds in 51–98% yield [35]. The primary amine adducts formed can be treated with bromine in the presence of triethylamine to yield the  $\beta$ -lactams **14** and **16**, respectively. Additionally,  $\alpha,\beta$ -unsaturated acyl iron complexes [36] and alkynyl-substituted compounds [37] were investigated in Lewis acid catalyzed Diels–Alder reactions.



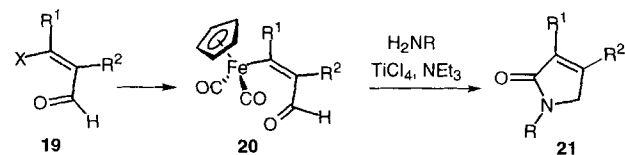
Scheme 6

Lewis acid mediated cycloaddition reactions of  $\alpha,\beta$ -unsaturated acyl iron complexes with allylstannanes were found to give five-membered rings **17** in high stereoselectivity [38, 39]. Upon demetallation the ester obtained was treated with bromine and by subsequent oxidation with *m*-chloroperoxybenzoic acid the cyclopentane alcohol **18**.



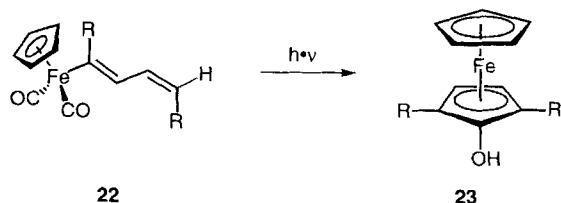
Scheme 7

(*E*)-Configured  $\beta$ -cyclopentadienyl(dicarbonyl)iron-substituted alkenones have been reported in the literature, but scarcely applied in synthesis [40, 41]. Recently (*Z*)-configured iron vinyl aldehydes proved to be useful starting materials in Domino processes furnishing  $\alpha,\beta$ -unsaturated  $\gamma$ -lactams [42]. The iron compounds **20** were prepared regio- and stereoselectively starting from ferrates and  $\beta$ -halogen vinyl aldehydes **19**. The  $\gamma$ -lactams **21** are formed from **20** and donor-substituted primary amines in a  $\text{TiCl}_4$ -mediated reaction in the presence of triethylamine. Thus, the reaction proceeds by the initial attack of the amine at the aldehyde functionality,



Scheme 8

carbonylation as well as intra- or intermolecular hydrogen transfer and ring closure, without further application of additional reagents being necessary.



Scheme 9

The photoexcitation of simple cyclopentadienyl(dicarbonyl)iron-substituted organic compounds has been intensively examined. Interestingly, photolytic studies of cyclopentadienyl (dicarbonyl)iron-substituted dienes **22** were reported by Allison *et al.* leading to otherwise rarely accessible hydroxy-

ferrocenes **23** [43]. Recently, the formation of carbon centered radicals generated photochemically from either alkyl- or acyl complexes in the presence of *e.g.* acrylonitrile was studied and reported in the literature [44].

At room temperature the potassium ferrate can be utilized as efficient catalyst for the dimerization of aromatic aldehydes to carboxylic esters as demonstrated by the studies of Yamashita *et al.* [45]. The ferrates serve as precursors for the synthesis of various iron Lewis acids, too. These have been applied successfully *e.g.* in reactions of ethyldiazoacetate with olefins furnishing cyclopropanes [46] or for example in asymmetric Diels–Alder reactions [47].

Increasing interest in application of organometallic compounds is observed in material science and molecular electronics, because of the expected physical characteristics *e.g.* non-linear optical properties [48, 49]. The cyclopentadienyl(dicarbonyl)iron fragment for example caused attention as terminal part of polyene segments [50] or polyalkyne moieties [51]. Diiron mixed valence complexes with phosphor ligands were found to have delocalized structures with interesting physical properties [52].

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