

# 1

## Monodentate Ferrocene Donor Ligands

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### 1.1 Introduction and Scope

Even though it was first discovered over 50 years ago, research into ferrocene-containing compounds continues apace, largely due to applications within catalysis and materials science.<sup>1, 2</sup> In coordination chemistry, the ferrocene moiety has played a significant role as a backbone or a substituent in ancillary ligands due to: the specific and unique geometries that the ferrocene provides; and its electronic (redox) properties, whereby the possibility of switching the redox state of the ferrocene backbone gives potential access to control of reactivity at a metal centre. The gamut of ligands formed via substitution of ferrocenes by various donor heteroatoms have found wide application.<sup>3, 4</sup>

This chapter focuses on the synthesis and coordination chemistry of monofunctional or monodentate ferrocene ligands, along with a survey of the applications of these ligands, particularly in homogeneous catalysis. Our scope has been those monofunctional ferrocene ligands in which the donor groups are bonded to the ferrocene unit either directly or via a simple methylene spacer, the classification being (i) nitrogen donors, (ii) oxygen donors, (iii) phosphorus donors and (iv) chalcogen donors. We have detailed those examples where there has been an application of the ligand or at least extensive coordination chemistry, rather than solely a ligand synthesis. There is also a short section on general synthetic routes to monosubstituted ferrocenes.

The chapter concentrates on monofunctional ligands synthesised up to December 2006. It should be noted that, in some cases, the coordination mode of the ligand to

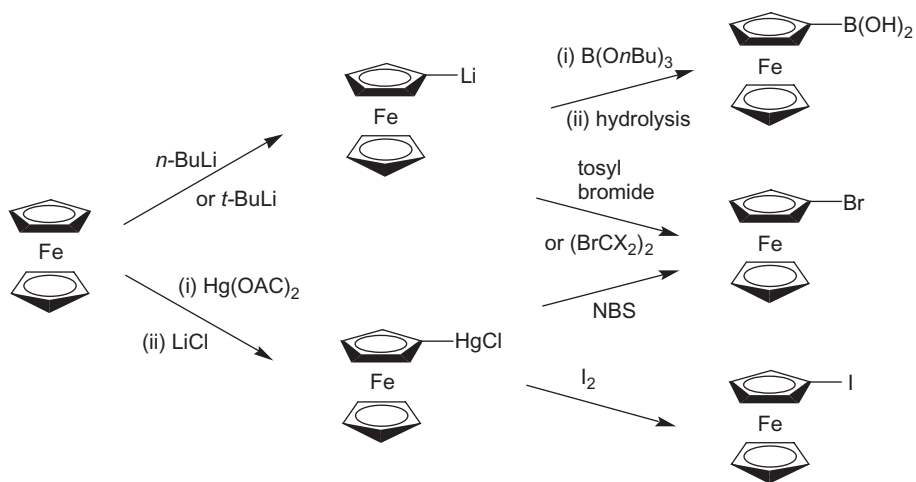
the metal centre in a catalytic system has been established through the synthesis and characterisation of model metal complexes which may provide mechanistic information about the catalytic process under study. However, in other cases, the catalytic efficacy of the ligand has been determined with little evidence for the manner in which the ligand actually interacts with the catalytic metal centre – these ligands are also considered herein, however.

There is an excellent summary by Max Herberhold of ‘ferrocene compounds containing heteroelements’ that appeared in the original ‘Ferrocenes’ book of 1995.<sup>5</sup> Our aim is not to duplicate the information contained there as much of it is still relevant, especially the more historical synthetic methods and heteroatom derivatives of ferrocene – but rather to bring the field up to date, with more recent synthetic methodology and applications of monosubstituted ferrocenes being discussed. Herberhold’s article also contains material on disubstituted ferrocenes, which is not our remit here. In fact, the various di- or tri-substituted heteroatom ferrocenes are covered in Chapters 2–6 of this book. The monofunctional ligands have tended to be overshadowed by the wealth of information and catalytic application of the disubstituted ferrocenes. With more facile and reproducible synthetic routes now available however, the monosubstituted species are undergoing something of a renaissance, especially for applications in catalysis. The ligands are of interest as the substituents may be designed to electronically and/or sterically alter the environment around the catalytic metal centre in such a way as to increase the turnover or, in some cases, to allow the catalysis to happen at all. Enantiomerically pure versions of chiral ligands may favour the formation of a product with a particular configuration so allowing asymmetric catalysis.

## 1.2 General Synthetic Routes to Monosubstituted Ferrocenes

The isolation of monosubstituted ferrocene derivatives is often not a trivial exercise due to the lack of suitable synthetic routes and difficulties in their separation from disubstituted analogues. Although ferrocene undergoes facile electrophilic substitution and mercuration, it is sensitive to oxidation and thus reactions such as halogenation and nitration cannot be used for the synthesis of substituted ferrocenes. In fact, only radical substitution and electrophilic substitution under nonoxidising conditions, i.e. Friedel–Crafts acylation, Mannich reactions, borylation,<sup>6</sup> lithiation and mercuration, can be used in the formation of substituted ferrocenes. To incorporate just one heteroatom directly onto a cyclopentadienyl ring can really only be carried out via lithiation and mercuration.

Metallation of ferrocene has long been the best method to obtain halogenated derivatives and these species are vital intermediates in the synthesis of heteroatom-substituted ferrocenes. The useful intermediates for the synthesis of monosubstituted ferrocenes are briefly summarised in Scheme 1.1. Lithiation is possibly the most convenient entry into the preparation of ferrocene derivatives. Lithiation with *n*-butyllithium (*n*-BuLi) generally leads to a mixture of mono- and 1,1′-dilithiated species (Scheme 1.2), though dilithioferrocene can be formed exclusively when *n*-BuLi is used along with *N,N,N′,N′*-tetramethylethylenediamine (tmeda) in hexane.<sup>7, 8</sup> To obtain exclusively monolithioferrocene, *t*-BuLi has to be used in Et<sub>2</sub>O solution. Kagan and co-workers



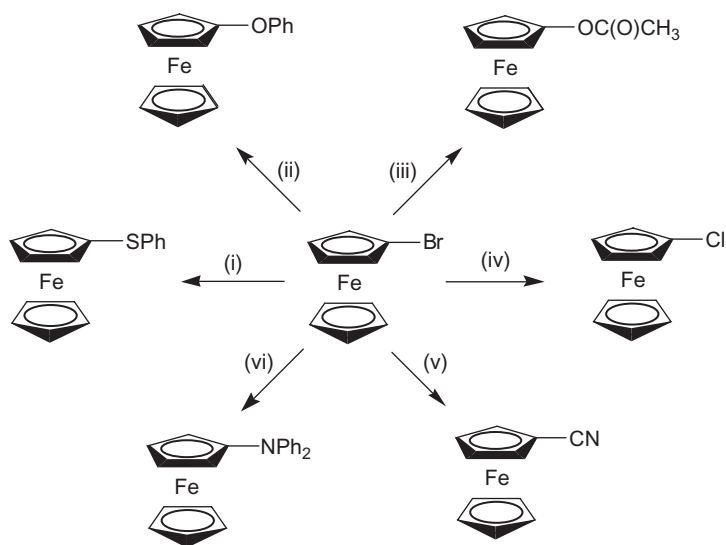
**Scheme 1.1** Ferrocene intermediates used for the incorporation of heteroatoms



**Scheme 1.2** Formation of lithioferrocenes using  $n$ - or  $t$ -BuLi

have made exhaustive investigations into the best conditions for the lithiation of ferrocene and subsequent monosubstituted ferrocene derivatives. The lithiation agent, reaction time, temperature and solvent each play an important role and they used tri- $n$ -butylstannyl derivatives for purification purposes and as precursors for reaction with electrophiles giving monosubstituted ferrocenes in nearly quantitative yields.<sup>9, 10</sup>

The mercuration of ferrocene to give chloromercurio-ferrocenes is normally facilitated via a one-pot reaction of firstly  $\text{Hg(OAc)}_2$  followed by addition of a chloride salt such as potassium chloride or lithium chloride.<sup>11</sup> The mixture of mono- and di-substituted ferrocene- $\text{HgCl}$  species formed can be purified by Soxhlet extraction and sublimation.<sup>12</sup> The  $\text{HgCl}$  substituent can be easily exchanged via halogenating agents to give mono-halogenated ferrocenes – along with the lithio-species, the most versatile precursors towards ferrocenes bearing heteroelements. For instance, as shown in



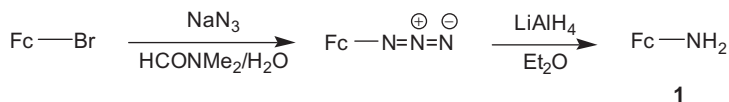
**Scheme 1.3** Some examples of copper-assisted substitution reactions of FcBr; (i) CuSPh, pyridine; (ii) KOPh/Cu, xylene, 160 °C; (iii) Cu(OAc)<sub>2</sub>, 135–140 °C; (iv) CuCl, pyridine; (v) CuCN, pyridine, 135–140 °C; (vi) NaNPh<sub>2</sub>, CuBr, 120 °C

Scheme 1.3, the halogen group in FcX (generally bromine and iodine, and to a lesser extent chlorine) can be replaced with other anionic groups via nucleophilic substitution in the presence of copper(I) salts and polar solvents such as pyridine.<sup>13, 14</sup> Using this methodology, chloro-<sup>15</sup> and cyano-<sup>16</sup> substituents can be incorporated, as well as derivatives featuring nitrogen, oxygen and sulfur, and these are discussed in the following sections.

### 1.3 Nitrogen-Substituted Ferrocenes

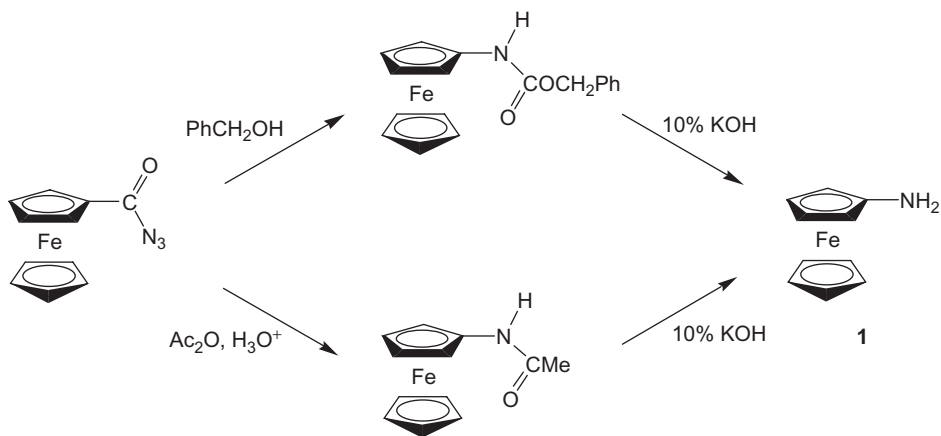
Aminoferrocene (FcNH<sub>2</sub>, **1**) has long been a ‘holy grail’ for ferrocene chemists and coordination chemists in general and although substituted ferrocene amines are known, the formation of N-substituted ferrocene species has been hampered by the lack of good synthetic routes. However, in recent years more efficient routes to the synthesis of the primary amine (FcNH<sub>2</sub>), and indeed the diamine fc(NH<sub>2</sub>)<sub>2</sub>, have opened up the area. It remains the most reliable and versatile route into appending a nitrogen substituent directly onto the ferrocene cyclopentadienyl rings.

The first report on **1** came from Nesmeyanov *et al.* in 1955<sup>17</sup> who reacted FcLi with the *O*-benzyl ether of hydroxylamine (H<sub>2</sub>NOCH<sub>2</sub>Ph). Yields though were disappointing (25%) so the same group devised routes to aminoferrocene from (i) the reaction of *N*-ferrocenylphthalimide and hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>•H<sub>2</sub>O) in boiling ethanol<sup>18, 19</sup> and (ii) FcN<sub>3</sub>, and its reduction by lithium aluminium hydride (LiAlH<sub>4</sub>)<sup>20</sup> (Scheme 1.4). Both routes produced aminoferrocene in yields of ca. 70–80%, though



**Scheme 1.4** The azide route to amine **1**

the preparations were not straightforward due to difficulties in handling the air- and moisture-sensitive material. The azide of ferrocenyl carboxylic acid ( $\text{FcC}(\text{O})\text{N}_3$ ) could also be gainfully used either to form a urethane<sup>21, 22</sup> or an acetamide.<sup>23</sup> The amine is formed via hydrolysis (Scheme 1.5) and Herberhold *et al.* were able to isolate the product in high yield after purification as the crystalline hydrochloride salt.



**Scheme 1.5** Synthesis of **1** via urethane and acetamide intermediates

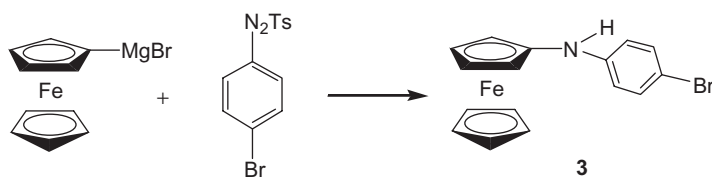
In recent times, a number of these routes have been revisited and improvements made. Bildstein *et al.* have formed **1** in large scale and reasonable yields via the sequence  $\text{FcH} - \text{solid FcLi} - \text{FcI} - N\text{-ferrocenylphthalimide} - \mathbf{1}$ .<sup>24</sup> The main advantage was the selective monometallation of ferrocene and the direct bromination and iodination of lithioferrocene on a large scale (>30 g), along with the avoidance of intermediates such as ferrocene boronic acid and (chloromercurio)ferrocene. Butler and Richards have used a modified Curtius rearrangement to form **1** and its pentaphenylferrocene derivative in improved yields.<sup>25</sup> In the formation of isocyano derivatives, van Leusen and Hessen have perhaps detailed the most convenient and widely used route to **1** – via  $\alpha$ -azidostyrene.<sup>26</sup> The method was based on a procedure developed by Hassner *et al.* for the synthesis of anilines and heteroaromatic amines<sup>27</sup> and involves the reaction of aryllithium reagents with  $\alpha$ -azidostyrene – a reagent that is readily available from styrene in three simple steps.<sup>28</sup> Ferrocene is lithiated in tetrahydrofuran (THF) with 0.9 equiv. of *t*-BuLi, and then reacted with  $\alpha$ -azidostyrene at  $-70^\circ\text{C}$ . Acidification with hydrochloric acid followed by extraction with water and precipitation with base gave crude **1** in ca. 50% yield; vacuum sublimation facilitated further

purification. This attractive route enables the preparation of **1** of good purity in multi-gramme quantities.

The electrochemistry of **1** and other ferrocene amines indicates that the amine substituent acts as an unusually potent activating group for ferrocene oxidation, with **1** oxidising at a potential 0.37 V more negative than ferrocene itself.<sup>29</sup> With the development of better synthetic routes, the chemistry of **1** has been studied in detail, with facile alkylation and acylation and this has led to a wide range of derivatives, some of which are now discussed.

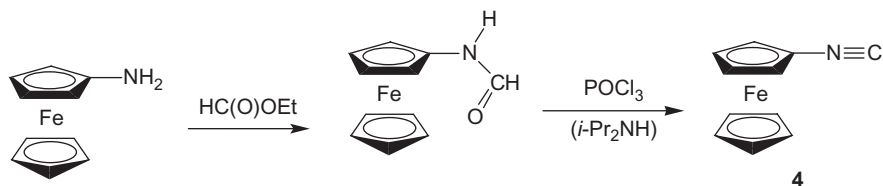
Amine **1** reacts with chlorosilanes in the presence of Et<sub>3</sub>N to give *N*-silylated derivatives **2** such as FcNH(SiMe<sub>3</sub>) (**2a**) and FcNH(SiMe<sub>2</sub>H) (**2b**), whilst *N*-lithiation of **1** followed by reaction with Me<sub>3</sub>SnCl forms *N*-stannyl derivatives, FcNH(SnMe<sub>3</sub>) or FcN(SnMe<sub>3</sub>)<sub>2</sub> (**2c**). These *N*-functionally substituted derivatives can also be extended to the *N*-boryl analogues such as FcN(SiMe<sub>3</sub>)BEt<sub>2</sub> or FcNHBEt<sub>2</sub>.<sup>30</sup>

Carre *et al.* have described the synthesis of 1,1'-bis(*N*-*t*-butyl-*N*-hydroxyamino)ferrocene, where the two hydroxylamino substituents are in eclipsed positions<sup>31</sup> whilst Knochel detailed the synthesis of FcNHAr via the reaction of arylazotosylates with functionalised organomagnesium compounds.<sup>32</sup> This general and elegant amination method features a one-pot reaction sequence consisting of a Grignard reaction, allylation and reduction to give the functionalised diarylamines, e.g. **3**, in good yields (Scheme 1.6). In a 'one-off' but useful reaction, (di-*p*-tolylamino)ferrocene was synthesized using palladium-catalysed C–N bond formation.<sup>33</sup> This route to (diarylamino)ferrocenes was developed as an alternative to the rather unpredictable Ullmann-type coupling reactions. Amine **1** has also featured in the synthesis of a range of 'donor-acceptor' complexes incorporating ferrocene species. The ferrocene unit was linked to a metal–nitrosyl acceptor via a variety of conjugated bridges and the compounds exhibited reasonable second order nonlinear optical (NLO) behaviour that could be redox-switchable.<sup>34, 35</sup>



**Scheme 1.6** Preparation of ferrocenyl aryl amines via arylazo tosylates<sup>32</sup>

Amine **1** is also the parent compound for the important derivative isocyanoferrocene (**4**), formed via the dehydration of formamidoferrocene (Scheme 1.7).<sup>36</sup> The same group also published the synthesis of the analogous isothiocyanatoferrocene (FcNCS). The isocyanides in general, have been extensively employed as ligands in organometallic chemistry since they are analogous to, but more basic than, carbon monoxide. Isocyanide ligands are more versatile than carbon monoxide in the sense that the substituent on nitrogen can be varied to influence the donor/acceptor properties of the ligand and to manipulate the architectures of metal complexes comprising the ligand. Aryl isocyanides are better  $\pi$ -acceptors than alkyl isocyanides and the

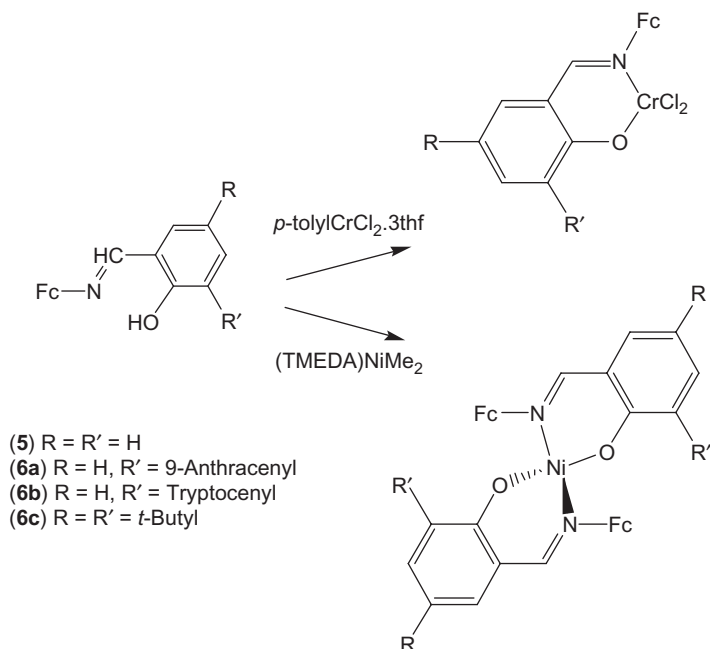


**Scheme 1.7** Synthesis of isocyanoferrrocene (**4**)

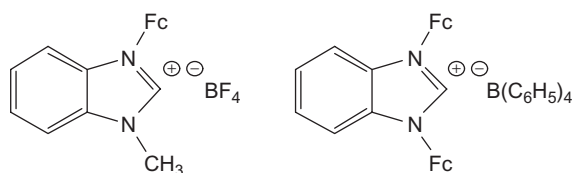
ferrocene derivative is a useful addition – it being a stronger  $\sigma$ -donor but a slightly weaker  $\pi$ -acceptor than isocyanobenzene. The solid state structure of **4** shows an almost undistorted ferrocene-like geometry<sup>37</sup> and it has recently been used in the stabilisation of *ansa*-chromocene derivatives<sup>38</sup> and to form the unusual  $[\text{Cr}(\text{CNFc})_6]$  compound, where there is the incorporation of seven transition metal atoms within the relatively compact  $\text{ML}_6$  motif.<sup>39</sup> The ligands are said to represent a new class of aromatic isocyanides incorporating nonbenzenoid  $\pi$ -systems.

Schiff-base ligands are ubiquitous within coordination chemistry and, in recent years, salicylaldiminato complexes of the early transition metals have played important roles in homogeneous catalysis, in particular as active pre-catalysts for ethylene polymerisation. Within this area, ferrocenyl-substituted Schiff-base ligands and their complexes have been widely explored, largely due to the easily accomplished condensation reactions of amines with acyl- or formyl-ferrocenes. The first such ferrocene ligand,  $\text{FcN}=\text{CH}(\text{C}_6\text{H}_4\text{OH}-2)$  (**5**; Scheme 1.8), was reported in 1977<sup>40</sup> and further investigated 10 years later, it being synthesised by the condensation reaction of **1** with salicylaldehyde. A range of late transition metal complexes have been formed with **5** to study the electrochemical and magnetic properties,<sup>41</sup> but it is the applications within ethylene polymerisation that have brought the ligand motif to the fore. Long and Gibson *et al.* have formed a range of sterically-hindered ligands **6** by the condensation of **1** with a range of salicylaldehydes, which have then been bound to nickel or chromium metal centres (Scheme 1.8).<sup>42</sup> Although very sensitive to air, the chromium complexes were found to act as pre-catalysts for the polymerisation of ethylene. Similar nickel-based complexes featuring pyridyl- and quinoidyl-*N*-substituted ferrocene ligands have proven to be very efficient pre-catalysts for the formation of short chain ethylene oligomers<sup>43</sup> and the same collaborative team is focusing on using the redox-active nature of the ferrocene unit to effect redox-switching within homogeneous catalysis.<sup>44, 45</sup> A series of related magnesium, titanium and zirconium complexes of ferrocenyl-substituted salicylaldiminato species have been recently reported, with the titanium complex exhibiting moderate activity for ethylene polymerisation and the zirconium species being highly active for ethylene oligomerisation.<sup>46</sup>

An interesting set of ligands also derived from **1** have been *N*-heterocyclic carbenes with *N*-ferrocenyl substitution.<sup>24, 47</sup> *N*-Heterocyclic carbenes are of great current interest due to their potential as easily modified ligands for metal complexes with catalytic applications. The ferrocene substituent, with its unique spatial requirements and powerful electron-donating capacity, may offer an additional stabilisation of the electron-deficient carbene moiety. Bildstein and co-workers have reported the synthesis of benzimidazoline-2-ylidenes with one and two *N*-ferrocenyl groups appended (Scheme 1.9).



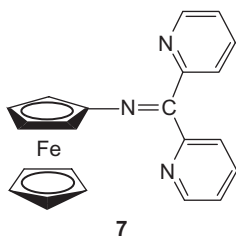
**Scheme 1.8** Sterically-hindered ferrocene Schiff base ligands and their nickel and chromium complexes



**Scheme 1.9** Examples of precursors to *N*-ferrocenyl *N*-heterocyclic carbenes<sup>24, 47</sup>

Electrochemical studies indicate a significant electronic communication between the carbene moiety and the *N*-ferrocenyl substituent. Synthetic routes to these directly attached *N*-ferrocenyl species are not trivial but they do offer some interesting catalytic potential. For example, when bound to palladium(0), they have been used in the efficient telomerisation of 1,3-butadiene with alcohols,<sup>48</sup> showing remarkable catalyst productivities and regioselectivities. The authors hope that the efficiency of the catalyst system, formed *in situ*, as well as the simplicity of the reaction will yield industrial application.

Finally, the FcN= motif has featured in a number of other studies. In 1993, phenylazoferrocene was formed and shown to undergo cyclometallation.<sup>49</sup> Starting from **1**, Imhof has formed a series of heterocyclic imine ligands with a ferrocenyl group

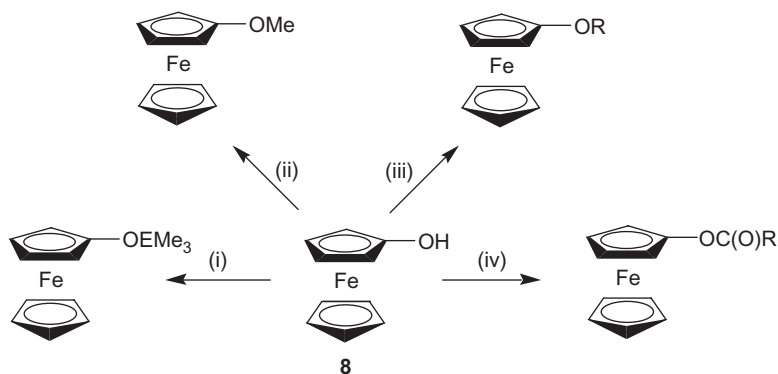


**Scheme 1.10** The fully cyclopentadienyl-conjugated ligand (7)

as the substituent at the imino nitrogen atom.<sup>50</sup> In 2001, Hall described the synthesis of the first ferrocene-functionalised ligand **7** in which all the donor atoms are cyclopentadienyl-conjugated (Scheme 1.10).<sup>51</sup> This ligand was designed to be a responsive metal-binding species, and indeed exhibited enhanced electrochemical response (of the ferrocene moiety) to copper ( $\text{Cu}^+$ ) ion binding relative to similar ligands in which the donor atoms are not conjugated with the cyclopentadienyl (Cp) ring.

#### 1.4 Oxygen-Substituted Ferrocenes

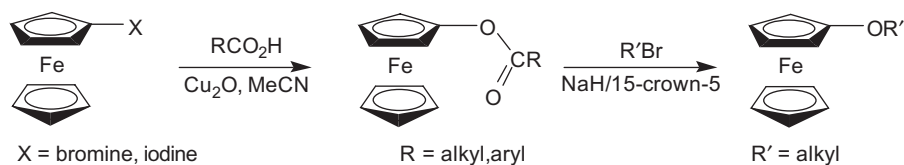
Nesmeyanov and coworkers first reported hydroxyferrocene (FcOH, **8**) in 1959, generating it from either ferrocenylboronic acid  $\text{FcB}(\text{OH})_2$  (via reaction with  $\text{Cu}(\text{OAc})_2$  and then potassium hydroxide) or more conveniently from alkaline hydrolysis (with potassium hydroxide) of the acetate  $\text{FcOAc}$  (the acetate being accessible from  $\text{FcBr}$  and  $\text{Cu}(\text{OAc})_2$  as given above).<sup>52, 53</sup> Alcohol **8** is a yellow, very air-sensitive solid and a slightly weaker acid than phenol. The difficulties in handling **8** mean that its chemistry has not been fully developed though a range of simple derivatives are now known (Scheme 1.11). For example, methoxyferrocene can be formed via methylation



**Scheme 1.11** Some reactions of  $\text{FcOH}$ (**8**); (i)  $\text{Me}_3\text{ECl}$  (E = silicon, tin); (ii)  $\text{Me}_2\text{SO}_4$ ; (iii)  $\text{RX}$  (R =  $\text{CH}_2\text{COOH}$ ,  $\text{CH}_2\text{CH}_2=\text{CH}_2$ ); (iv)  $\text{R}-\text{C}(\text{O})\text{Cl}$  (R = Ph, Fc)

of **8** with dimethyl sulfate ( $\text{Me}_2\text{SO}_4$ ) and alkylation with activated halides  $\text{RX}$  gives ferrocenyl ethers  $\text{FcOR}$ .<sup>54</sup>

The routes to ferrocenyl ethers have been improved upon over the years. Ferrocenyloxy-2-tetrahydrofuran was formed from  $\text{FcB(OH)}_2$ <sup>55</sup> and in 1981, Akabori and co-workers produced a convenient preparation for ferrocenyl esters and ethers (Scheme 1.12). Acylation of a ferrocenylhalide, followed by reduction with sodium hydride ( $\text{NaH}$ ) gives the desired products in reasonable yield.<sup>56, 57</sup> More recently, Plenio *et al.* showed that ferrocenyl aryl ethers could be formed via copper(I)-catalysed routes.<sup>58</sup> For example, the coupling reaction of iodoferrocene with various phenols, a base (such as caesium carbonate or potassium phosphate) and  $\text{CuI}/2,2,6,6\text{-tetramethylheptane-3,5-dione}$  as the catalyst gives the products in excellent yield.

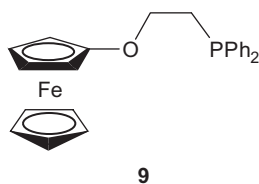


**Scheme 1.12** Synthesis of ferrocenyl ethers

Further derivatives where the oxygen atom is connected directly to the ferrocene unit can be obtained from the reaction of **8** with organoelement chlorides such as  $\text{Me}_3\text{SnCl}$ ,  $t\text{-BuPbCl}_2$ ,  $t\text{-Bu}_2\text{PbCl}$  and  $t\text{-Bu}_2\text{AsCl}$ .<sup>59</sup> Analogous trimethylsiloxy derivative ( $\text{FcOSiMe}_3$ ) can be obtained via the reaction of lithiated ferrocene with bis(trimethylsilyl)peroxide – a route that has also been used in the formation of novel 1,1'-P/O ferrocenediyl ligands (see Chapter 5).<sup>60</sup>

Due the sensitivity of the  $\text{FcO}^-$  species and the difficulty in producing large quantities of ligands, the coordination chemistry is rather limited, though there are a few interesting examples in the literature. *In situ* generation of potassium salts has been used to form crown ether-type polyoxaferrocenophanes.<sup>61</sup> These in turn can bind metal cations so acting as 'chemical sensors'. Reaction of **8** with various chlorides of both three and five valent phosphorus leads to a series of mono- to trinuclear ferrocenolato derivatives  $\text{Ph}_{3-n}\text{P}(\text{OFC})_n$  ( $n = 1-3$ )<sup>62, 63</sup> and organogold compounds of methoxyferrocene are known.<sup>64, 65</sup>

Cyclopalladation is one of the most studied organometallic reactions and usually involves exceptionally high regioselectivity. As an analogue of phenol, hydroxyferrocene **8** has been converted into a phosphite ester with chiral (racemic) butane-1,3-diol, and undergoes cyclopalladation similarly to hydroxyarene phosphites.<sup>66</sup> Planar chirality is present but no diastereoselectivity is observed. An interesting example of a redox-switchable hemilabile ligand (RHL) **9** has been reported, starting from ferrocenylacetate and reacting with  $\text{TsOCH}_2\text{CH}_2\text{Cl}$  followed by  $\text{KPPH}_2$  (Scheme 1.13; see Chapter 4 for 1,1'-analogues to **9**). On complexation to rhodium(I), the authors have demonstrated electrochemical control of the coordination environment around the metal centre.<sup>67</sup> When the ligand chelates, the  $\text{Rh-O}$  (ether) bond is weak and oxidation of the adjacent ferrocenyl group further weakens this bond to dissociation point



**Scheme 1.13** A redox-switchable ferrocenyl ligand **9**

and a  $\eta^6$ -arene-bridged dimer is formed. The oxidation state dependent behaviour of the rhodium chelate complex is proof of the RHL concept: the electrochemical interconversion of the square planar chelate complex and the arene-bridged dimer illustrates the use of RHLs for controlling the electronic and steric environment of transition metal centres, and has potential application in catalysis.

## 1.5 Phosphorus-Substituted Ferrocenes

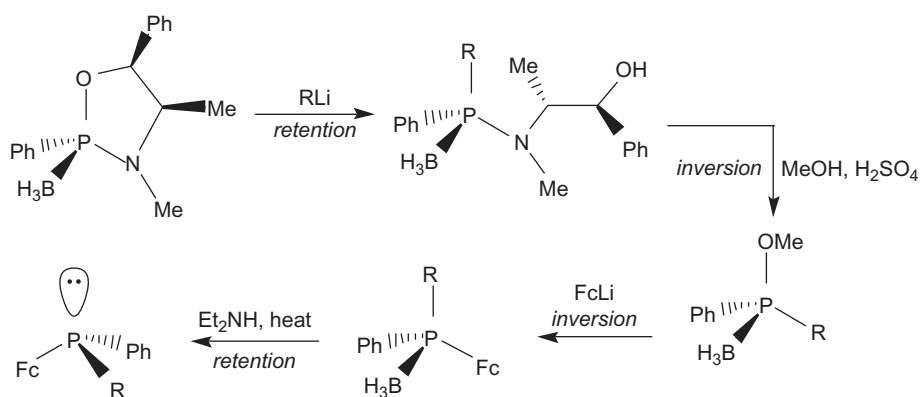
Phosphorus-substituted ferrocenes are the most well-studied class of heteroatom-substituted ferrocenes and whilst much of their interest lies in the disubstituted species, i.e. the applications of 1,1'-bis(diphenylphosphino)ferrocene (dppf) and analogues in catalysis (see Chapter 2), there have also been many interesting investigations into monosubstituted ferrocenylphosphines and their applications within homogeneous catalysis. The possibility of almost limitless variation of the substituent groups has made phosphines extremely popular ligands in organometallic chemistry, in particular chiral phosphines and their complexes for use in asymmetric catalysis. Phosphorus derivatives of ferrocenes were first investigated in 1962 by Sollott and co-workers.<sup>68</sup> Air-stable ferrocenylphenylphosphines were formed by the interaction of ferrocene with phenylphosphonous- and phosphinous chlorides in the presence of anhydrous aluminium(III) chloride ( $\text{AlCl}_3$ ), i.e. under Friedel–Crafts conditions. However, the method has not proven wide-ranging due to derivatives being poorly characterised, obtained as mixtures or relatively inaccessible. Knox and Pauson published an improved synthesis of ferrocenyldimethylphosphine ( $\text{FcPMe}_2$ ) that involved methylation of  $\text{FcPCL}_2$ , sometimes a difficult precursor to reliably obtain.<sup>69</sup> Methanolysis of  $\text{FcPCL}_2$  yields unstable dimethyl ferrocenylphosphonite ( $\text{FcP(OMe)}_2$ ) that can be converted to methyl ferrocenylphosphinite ( $\text{FcPH(O)(OMe)}$ ) on heating or chromatography. An improved synthesis for  $\text{FcPCL}_2$  has been reported<sup>70</sup> and the availability of this species gives access to the other previously unknown members of the halo series – the difluorides, dibromides and diiodides. The general class of ferrocenyldihalophosphines is a valuable synthon for the generation of a large variety of ferrocenylphosphines.

As expected the major application of phosphorus-donor ferrocenes has been in catalysis. For example, Carretero and co-workers<sup>71</sup> have used readily available and air-stable ferrocenylphosphines as new catalysts for Baylis–Hillman reactions between aldehydes and acrylates. In the search for highly nucleophilic yet air-stable phosphines the ferrocenyldialkylphosphines have come to the fore (being impressively more reactive than  $\text{PPh}_3$  and  $\text{PCy}_3$ ), and catalysed the reaction affording adducts in high yields

and short reaction times, with the least hindered diethylphosphine (FcPEt<sub>2</sub>, **10**) giving complete conversion within one hour with 98% adduct yield.

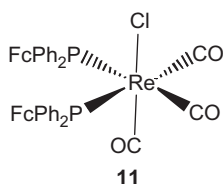
The authors have also tested a range of planar chiral ferrocenyldialkylphosphines in asymmetric Baylis–Hillman reactions. Indeed, planar chiral ferrocenylphosphines have provided countless examples of excellent enantiocontrol in catalytic asymmetric metal-catalysed reactions – see the excellent review articles by Colacot<sup>72</sup> and Richards.<sup>73</sup> Monophosphines containing a ferrocenyl moiety have been particularly effective ligands for catalytic asymmetric metal-catalysed reactions such as dialkyl-zinc additions to aldehydes, allylic alkylations, cross-coupling reactions and aldol reactions. To form enantiomerically pure P-chiral phosphines, PCl<sub>3</sub> is generally used as the starting material with three sequential nucleophilic displacements to introduce alkyl or aryl groups. In 1997, Brown and Laing examined the methods of asymmetric synthesis of P-chiral monophosphines featuring a bulky group.<sup>74</sup> These routes included the arylation of P-chlorooxazaphospholidine, and formation of diarylphosphine boranes, pioneered by Jugé and Genet.<sup>75</sup> The latter route appeared most successful with tertiary phosphines being formed in greater than 92% *ee*. Jamison and co-workers have formed a series of ferrocenylphosphines with high *ee* also by ephedrine-based oxazaphospholidine borane complexes, with primary alkyl, secondary alkyl and substituted aromatic substituents introduced at the P centre.<sup>76</sup> The synthetic route (Scheme 1.14) provides facile access to this underdeveloped class of chiral monophosphines. Examples of their use in catalysis include: the nickel-catalysed reductive coupling of aldehydes,<sup>77</sup> regioselective, asymmetric reductive coupling of 1,3-enynes and ketones,<sup>78</sup> formation of enantiomerically pure primary allylic amines<sup>79</sup> and asymmetric conjugate addition of diethylzinc to enones.<sup>80</sup> Recently, a method involving reaction of a dichlorophosphine with a chiral lithiated ferrocene, followed by a second organometallic reagent has been communicated. The relatively straightforward method gives access to a range of highly stereoselective ferrocene-based P-chiral phosphine ligands.<sup>81</sup>

The coordination chemistry of ferrocenylphosphines is extensive, especially ferrocenyldiphenylphosphine, which is analogous to PPh<sub>3</sub>. Examples of its unidentate



**Scheme 1.14** Formation of chiral ferrocenylmonophosphines via ring-opening of an oxazaphospholidine borane

coordination include: binding to group 10 metal centres to form square planar complexes,<sup>82, 83</sup> with the ferrocenyl ligands taking up a *transoid* orientation, as stabilising ligands in Rh(I) Vaska-type complexes,<sup>84, 85</sup> in formation of transition metal [60]fullerene complexes,<sup>86</sup> within Group 8 metal clusters<sup>87–91</sup> and as a redox-active substituent.<sup>85, 92–96</sup> Wrighton and co-workers showed that the electron density around a metal centre such as rhenium could be achieved via control of the redox state of a ferrocenylphosphine ligand.<sup>97</sup> For example, in **11**, the ferrocenyl units can be reversibly oxidised by one electron each, the oxidation being ferrocenyl-centred (Scheme 1.15). The authors showed that the electron density at the metal centre can be predictably adjusted and tuned by oxidation of a pendant redox centre. Thus examination of the effect of the oxidation state of a pendant redox ligand on the rate of reaction at an affected metal centre could be made.

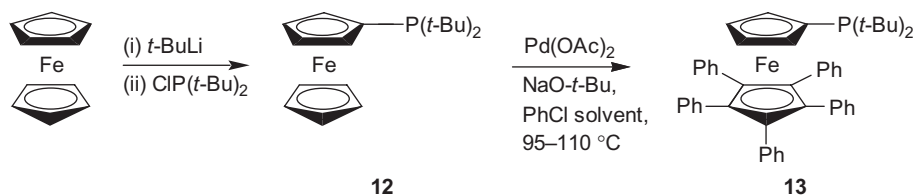


**Scheme 1.15** A ferrocenyl–rhenium complex (**11**)

Although the coordination chemistry of tertiary phosphine ligands is well-known, that of primary and secondary ferrocenylphosphines has been largely neglected as most of these phosphines are highly air-sensitive and therefore difficult to handle. Nevertheless, Hey-Hawkins and co-workers have successfully bound species such as  $\text{FcPH}_2$  to molybdenum(II) and tungsten(II) complexes and used them as single-component catalysts for the metathesis polymerisation of norbornene and norbornadiene.<sup>98, 99</sup>

For several years, Hartwig has been interested in the development of ligand structures for palladium-catalysed cross-coupling reactions, whereby the ligands can activate aryl chlorides under mild conditions, and effect high conversions with very low catalyst loadings.<sup>100–105</sup> Electron rich, sterically hindered monodentate ligands have been investigated, with di(*t*-butyl)phosphinoferrrocene (**12**) and its 1',2',3',4',5'-pentaphenyl analogue **13** a particular focus.<sup>106</sup> The ligands can be synthesised in relatively facile fashion and in reasonable yields (Scheme 1.16). In the coupling of phenoxides with unactivated aryl halides, complexes of **12** showed excellent activities. However, it was discovered that perarylation occurred in the catalytic process and the true catalyst was based on ligand **13** which indeed exhibited higher activities when isolated in its pure form. This remarkable ligand, known as Q-phos has been shown to be a very general ligand for cross-coupling processes, and examples include Suzuki reactions of aryl and primary alkylboronate esters, aryl halide etherifications at room temperature, aryl halide aminations, arylation of malonates and the Heck arylation of olefins at room temperature.<sup>107</sup>

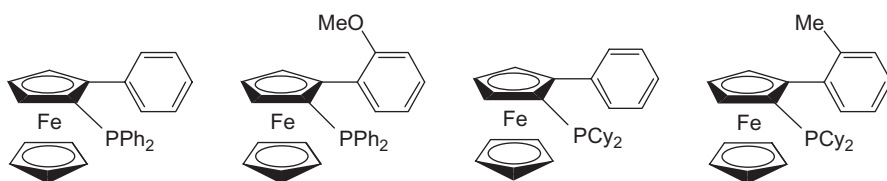
Ligand **13** is indefinitely stable in air as a solid and also in solution. This stability was assumed to be a kinetic phenomenon and probably results from a steric hindrance of the ligand that is increased by a preferential conformation of **13** that



**Scheme 1.16** Formation of di(*t*-butyl)phosphinoferrocene ligands **12** and **13**

pushed the lone pair towards the aryl groups on the ferrocene. Although not trivial due to mixtures of products being formed, the authors have formed a series of arylated di(*t*-butyl)phosphinoferrocenes to investigate the effects of sterics and electronics on catalytic activity.

Dicyclohexylphosphinoferrocene has recently been used in the annulation of aromatic imines via directed C–H bond activation<sup>107</sup> and the general class of ferrocenyl monophosphines can catalyse the Suzuki–Miyaura coupling of aryl chlorides.<sup>107</sup> The efficient activation of the latter remains an important goal due to their inexpensive costs and convenient availability, and electron-rich ferrocenylphosphines have a role to play in this area. Xiao and co-workers<sup>108</sup> have formed a series of *ortho*-arylated ferrocenyl phosphines (Scheme 1.17) based on Buchwald’s biphenyl-based ligands – now ubiquitous in palladium-catalysed cross-coupling reactions.<sup>109</sup> The ligands can be synthesised in three steps from ferrocenyl phosphine oxides. The first step is *ortho*-lithiation of the oxides to give the iodo-substituted product, then the aryl groups are introduced by reaction with arylboronic acids and finally, the free phosphines can be easily obtained from the oxides by reduction with trichlorosilane. This neat method allows for the facile synthesis of (arylferrocenyl)phosphines and these electron-rich species were very effective ligands for the palladium-catalyzed Suzuki–Miyaura process, coupling aryl chlorides with efficiently low catalyst loadings.



**Scheme 1.17** Examples of (monoarylferrocenyl)phosphines<sup>108</sup>

Examples of other phosphorus-containing substituents on monofunctional ferrocenes include phosphinate, phosphonate and thiophosphonate derivatives. Though not widespread, these species present a potential useful alternative to the straightforward phosphine ligands, via the incorporation of harder oxygen or softer sulfur donor atoms. Phosphinates are usually resistant to oxidation and hydrolysis, the phosphinate groups acting as bridging ligands and have found application in hybrid organic–inorganic materials and molecular level devices. The synthesis of the ligands is relatively straightforward

depending on the availability of starting materials. For example, ethyl ferrocenylphenylphosphinate ( $\text{FcP}(\text{O})(\text{Ph})(\text{OEt})$ , **14**) is formed via the reaction of monolithioferrocene with chloroethyl phenylphosphonate, itself obtained by chlorination of ethyl phenylphosphinate, prepared by ethanolysis of  $\text{PhPCl}_2$ .<sup>110</sup> Zinc, cadmium and manganese complexes are known with the structures involving tetracoordinated metals doubly-bridged by the phosphinate groups and exhibiting high thermal stability. Other alkyl derivatives of these ligands have been reported<sup>111</sup> as have some interesting ferrocenyl hydroxymethylphosphines ( $\text{FcP}(\text{CH}_2\text{OH})_2$ ) and their oxide, sulfide and selenide derivatives.<sup>112</sup> These hydroxymethylphosphines are attractive ligands as the hydroxyl groups confer water-solubility and their reactivity with amines and alkenes for example provide access to a wide range of derivatives. Their formation is via reaction of the primary phosphine  $\text{FcPH}_2$  with formaldehyde and purification by dynamic vacuum gives the hydroxymethylphosphine as a brown crystalline solid, soluble in polar organic solvents and indefinitely stable in air. The chalcogenide derivatives,  $\text{FcP}(\text{E})(\text{CH}_2\text{OH})$  (E = oxygen, sulfur, selenium), can be formed by reaction of the parent phosphine with hydrogen peroxide, and powdered sulfur or selenium and ultrasound. All derivatives are crystalline and soluble in polar organic solvents and their coordination chemistry and applications in catalysis is certainly worthy of investigation.

Reaction of the ferrocenyl Lawesson's Reagent  $\text{Fc}(\text{S})\text{PS}_2\text{P}(\text{S})\text{Fc}$  with  $\text{NaOR}$  (R = Me, *i*-Pr) gives the nonsymmetric phosphonodithiolato anions  $[\text{Fc}(\text{RO})\text{PS}_2]^-$ , which can be complexed to a range of metals.<sup>113</sup> The versatile coordination behaviour and stability may find application as phosphodithiolates in general have been used in many commercial applications.

The search for redox-active ligands has seen the formation of a ferrocenyl-functionalised phosphaneiminato ligand<sup>114</sup> and a phosphido ligand which can be generated by ring-opening of the P–C bond of a phosphorus-bridged [1]ferrocenophane, and subsequent insertion of a  $\text{Cp}(\text{CO})\text{Fe}$  fragment (see Chapter 5).<sup>115</sup>

## 1.6 Chalcogen-Substituted Ferrocenes

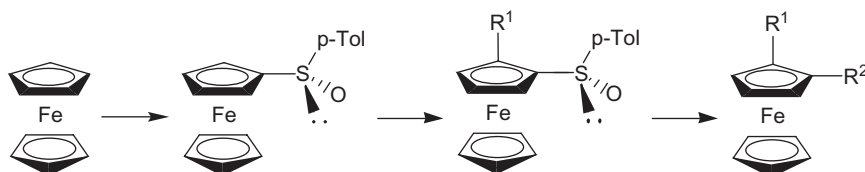
There are two main routes into sulfur-substituted ferrocenes: (i) the electrophilic sulfonation of ferrocene to form  $\text{FcSO}_3\text{H}$  and (ii) the insertion of sulfur into the carbon–lithium bond of lithioferrocene. With the improvements in mono-lithiation techniques (see earlier in this Chapter) the latter method is perhaps most useful, especially in the preparation of mercaptoferrocene ( $\text{FcSH}$ ) and the related thioethers,  $\text{FcSR}$ .

The original method of forming  $\text{FcSH}$  featured the hydrogenation of the sulfonyl chloride derivative  $\text{FcSO}_2\text{Cl}$ ,<sup>116</sup> and this can be improved upon by forming an intermediate and easily purified ammonium salt  $\text{FcSO}_3\text{NH}_4$ , which is then treated with  $\text{PCl}_3$  to give  $\text{FcSO}_2\text{Cl}$ . Following reduction with lithium aluminium hydride,  $\text{FcSH}$  can be isolated as an orange–brown solid. The dimeric  $\text{FcS}–\text{SFc}$  can also be treated with  $\text{LiAlH}_4$  to give the desired  $\text{FcSH}$ , and although this route requires extra steps the dimer can be purified and handled easily thus ensuring more efficient conversion to the thiol.<sup>117</sup>

Insertion of sulfur into the  $\text{Fc}–\text{Li}$  bond, leads to  $\text{FcSLi}(\text{THF})$  when the reaction is carried out in THF.<sup>118</sup> This is a light yellow, very air-sensitive solid that can be easily hydrolysed to give  $\text{FcSH}$ , though mixtures of products are often obtained.

FcSH is a very reactive compound, easily combining with activated olefins<sup>118</sup> and acyl chlorides,<sup>119</sup> where once again the crucial step in the synthesis involves insertion of sulfur into the Li–C bond followed by treatment with acyl chloride (RC(O)Cl). Ferrocenylthioethers can be conveniently prepared via the lithiation route and quenching with a suitable electrophile, such as alkyl disulfides or phenyl disulfide, where the weak S–S bond is broken.<sup>120</sup> Another route involves reaction of iodoferrocene with a copper bronze and an organic thiol.<sup>121</sup> Though not versatile the route does give FcSR ligands in reasonable yields. In 2002, Bonini *et al.* produced a series of enantiomerically pure hydroxyalkyl- and aminoalkyl- ferrocenyl sulfides from the reaction of FcSLi and substituted epoxides.<sup>122</sup> Meanwhile, Brown and co-workers have reported that ferrocenyl sulfides afford *meta*-lithiation products with up to 94 % regioselectivity on reaction with *s*-BuLi.<sup>123</sup> The FcSR species were prepared by either reaction of ferrocenyllithium and the corresponding disulfide<sup>124</sup> or via the corresponding sulfoxide.<sup>125</sup> This route thus enabled the formation of a range of 1,3-disubstituted ferrocenes – an unusual but desirable substitution pattern.

In recent years, chiral ferrocenyl sulfoxides have proven to be of great interest due to their involvement in the preparation of enantiopure 1,2-disubstituted ferrocenes with a predictable absolute configuration.<sup>126–128</sup> The three step process is shown in Scheme 1.18 and involves a highly diastereoselective *ortho*-functionalisation step. The routes should lead to a diverse range of 1,2-disubstituted ferrocenes for use in asymmetric catalytic reactions. Other S=O substituted ferrocene systems include substituents featuring (i) chiral sulfinyl groups<sup>129</sup> – a useful chiral controller in asymmetric aziridination and allylation of hydrazones – and (ii) chiral sulfoximido groups.<sup>130</sup>



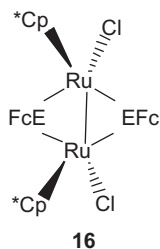
**Scheme 1.18** Formation of chiral ferrocenyl sulphoxide and subsequently enantiopure 1,2-disubstituted ferrocenes

As could be expected, the coordination chemistry of FcSH and FcSR is well-established (though not nearly as widespread as with the ferrocenediyl analogues), especially when softer donating atoms are called for; some representative examples of transition metal complexes are now detailed. In similar studies regarding redox-active hemilabile ligand, as mentioned in Section 1.4, Mirkin *et al.* have formed a square planar rhodium(I) complex featuring bis-bidentate coordination of RHL ligand FcSCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (**15**).<sup>131</sup>

The complex undergoes small molecule-induced intramolecular electron ‘*pinch and catch*’, as the authors remark, i.e. the uptake and release of small molecules can be engineered. The complex reacts with the  $\pi$ -acid CO but is inert towards the  $\sigma$ -donor ligand CH<sub>3</sub>CN. However, oxidation of the complex, via the ferrocene groups effects an uptake of CH<sub>3</sub>CN and in fact the paramagnetic, square planar doubly oxidised

rhodium(I) complex becomes a diamagnetic, octahedral rhodium(III) species with two additional  $\text{CH}_3\text{CN}$  ligands. Thus, this is an initial example of the way ligands can be designed to allow for the controlled uptake and release of small molecules at transition metal centres.

Transition metal complexes with chalcogen ligands have been seen as synthetic models for active sites of metalloenzymes and heterogeneous sulfide catalysts. In this area, several novel ferrocenylchalcogenolate-bridged diruthenium complexes **16** have been formed via the oxidative addition of diferrocenyl dichalcogenides (Scheme 1.19).<sup>132</sup> Ferrocenylchalcogenato bridges have also featured in binuclear cyclopentadienyl vanadium and tantalum complexes, where the chalcogen can be sulfur, selenium or tellurium.<sup>133</sup> Finally, ferrocenylthioethers have been used as supporting ligands for multi-metallic clusters, adding redox-active behaviour and imparting stability via the unique characteristics of the fc unit, e.g. ruthenium carbonyl clusters,<sup>134</sup> iron carbonyl clusters<sup>135</sup> and molybdenum–iron–sulfur clusters.<sup>136</sup>

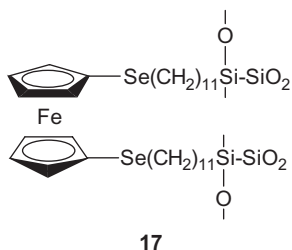


**Scheme 1.19** An example of ferrocenylchalcogenolate-bridged diruthenium complexes (**16**) (E = sulfur, selenium)

The insertion of sulfur into the carbon–lithium bond of lithioferrocenes to give  $\text{FcSLi}$  is a synthetic method that is conveniently extended to the heavier chalcogens selenium<sup>137</sup> and tellurium.<sup>138, 139</sup> The lithium chalcogenates  $\text{FcELi}$  (E = sulfur, selenium, tellurium) can then be used *in situ* for reactions with halogen-containing compounds. In fact, a method has been reported for gaining pure  $\text{FcLi}$  from  $\text{FcTeBu}$ ,<sup>140</sup> and for the synthesis of a range of selenium and tellurium substituted ferrocenes.<sup>140, 141</sup>

Similar methods for the formation of ferrocenyl thioether ligands have been employed for the seleno analogues,<sup>120, 142</sup> i.e. reaction of lithioferrocene with  $\text{RSe–SeR}$ . The ligands and their palladium(II) complexes have been used as catalysts for selective hydrogenation and Grignard cross-coupling reactions. Examples include the selective hydrogenation under both homogeneous and heterogeneous conditions for the reduction of dienes to monoenes, and the Grignard cross-coupling for haloalkanes and allylmagnesium halides.

Ferrocenyl selenoether ligands have also been used in the synthesis of a  $\text{Cd}_4\text{Se}_6$  adamantoid cluster complex, functionalising the surface with redox active centres<sup>143</sup> and as part of polysiloxane-supported metal complexes<sup>144</sup> **17** (Scheme 1.20). The ligand was immobilised on fumed silica and then reacted with potassium chloroplatinate. The platinum complexes were efficient catalysts for hydrosilylation of olefins with triethoxysilane.



**Scheme 1.20** Polysiloxane-supported ferrocenyl selenoether ligands (**17**)

The first examples of ferrocenyltellurium compounds were reported in 1987.<sup>139</sup> Insertion of tellurium into FcLi gives diferrocenylditelluride ( $\text{Te}_2\text{Fc}_2$ ) in 50% yield. The reaction of  $\text{Te}_2\text{Fc}_2$  with organolithium compounds (RLi) was then used to prepare ferrocenyltellurides FcTeR (R = Fc, *n*-Bu). Other ferrocene-containing telluroether ligands (formed via FcLi and FcTe–TeFc respectively) and complexes have been reported by Singh *et al.*<sup>145</sup> and Nishibayashi *et al.*,<sup>146</sup> though overall this is a very underdeveloped area.

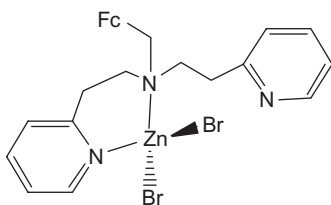
## 1.7 Monosubstituted Ferrocene Donor Ligands Featuring a Carbon Spacer

There is extensive literature on the class of compounds where the donor atom is not directly substituted onto one of the ferrocene cyclopentadienyl rings but attached via a carbon spacer unit. This is largely due to more facile synthetic routes due to the ready availability of stable and inexpensive starting materials (e.g. acetylferrocene, ferrocenylmethanol) and that the final compounds are generally more stable. Compounds with the various donor atoms detailed previously, e.g. nitrogen, oxygen, phosphorus and chalcogen will be reviewed, but it is the nitrogen-containing derivatives that dominate the field.

### 1.7.1 Nitrogen-Donor Compounds

Ferrocene was first aminomethylated in 1955 by Lindsay and Hauser via the reaction of ferrocene with paraformaldehyde and dimethylamine in glacial acetic acid.<sup>147–149</sup> The product (*N,N*-dimethylaminomethyl)ferrocene ( $\text{FcCH}_2\text{NMe}_2$ , **18**) represented a significant breakthrough as it provided a new route to hitherto unavailable ferrocene derivatives, such as alcohols, oximes, imines and aldehydes.

The ligand can be derivatised by reaction with 6-amino-2-picoline to introduce a pyridyl unit alongside the amino-nitrogen donor atom, and then coordinated to metal centres such as gold, silver and copper.<sup>150, 151</sup> Via lithiation, the ligand **18** itself can be bound to silver and platinum.<sup>152</sup> An unusual ligand featuring two ethylpyridine linkages bound to the amino nitrogen centre has been formed by Halcrow and co-workers.<sup>153</sup> A bidentate binding mode is observed when coordinated to zinc (Scheme 1.21), but the compound soon decomposes via C–N bond cleavage. However, the expected tridentate



**Scheme 1.21** The zinc complex of a ferrocenyl bis[2-(pyrid-2-yl)ethyl]amine derivative

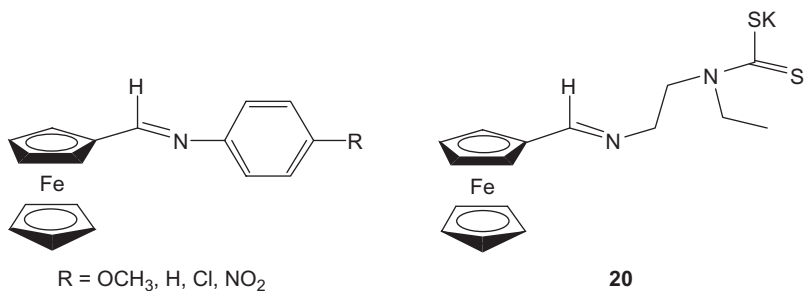
coordination mode is prevalent on coordination to cobalt, nickel and copper and no decomposition is seen.

The aminomethyl ferrocene fragment has also been used as an integral part of redox-responsive systems. As (*N*-propylaminomethyl)ferrocene, the fragment operates as a proton-sensitive redox-responsive unit, illustrated by dramatic changes in the ferrocene/ferrocenium redox potential.<sup>154</sup> The fragment has been bound to naphthalimide, itself an electroluminescent fluorophore used in molecular switches and bioprobes, to investigate whether oxidation state dependence may be a factor in switching on or off the fluorescence. It was found that the *N*-ferrocenyl substituents do not perturb the energy levels of the fluorophore although emission is quenched.<sup>155</sup> An interesting application of the derivatised aminomethyl ferrocene fragment has been in pseudorotaxane formation.<sup>156</sup> The potential to form molecular shuttles and machines continues to excite and so it was of note when the redox active unit was reported to form a pseudorotaxane with a crown ether via an electrochemical stimulus and in the presence of a suitable hydrogen source.

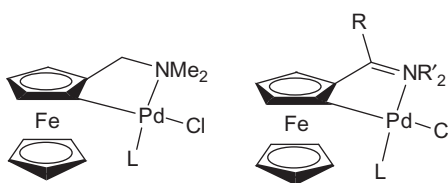
Ugi has shown that ferrocenyl derivatives such as a C-chiral amine  $\text{FcCH}(\text{Me})\text{NMe}_2$  can be lithiated with high diastereoselectivity, and the resulting organolithium may be trapped with various electrophiles ( $\text{E}^+$ ) to provide 1,2-disubstituted ferrocenes [ $\text{Fe}\{\eta^5\text{-C}_5\text{H}_3(\text{E})(\text{CH}(\text{Me})\text{NMe}_2)\text{-1,2}\}(\eta^5\text{-C}_5\text{H}_5)$ ] (**19**; see Chapter 6).<sup>157</sup>

Rather than a methylene spacer unit, a C=N linkage has also commonly been used in the formation of functional ligands. For example, some new ferrocenyl Schiff bases and their aluminium and zinc compounds have been used in catalysis<sup>158</sup> and in second-order nonlinear optics.<sup>159</sup> A series of substituted ferrocenyl compounds have been formed (Scheme 1.22) and analysed for their second-order optical nonlinearity. All show a reasonable response compared to the urea standard and there is correlation with the electron withdrawing nature of the substituted benzene ring.

The C=N linkage from the ferrocenyl unit has also been used in the formation of nickel dithiocarbamate complexes bearing ferrocenyl units (Scheme 1.22).<sup>160</sup> The authors were attempting to form molecular systems capable of exchanging electrons with an electrode, via the coupling of multiple, identical metal-centered fragments. Thus, a new ferrocene ligand **20** (Scheme 1.22) was prepared from ferrocenecarboxaldehyde and then Schiff-base chemistry undertaken. Nickel(II) dithiocarbamate bearing two ferrocenyl groups and its oxidised product nickel(IV) dithiocarbamate featuring three ferrocenyl groups were synthesised. Electrochemical investigations revealed that, in spite of the chemical equivalence of the ferrocene groups, a mixed-valence state persists in solution, presumably due to electrostatic effects.



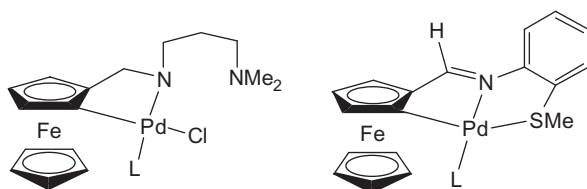
**Scheme 1.22** Some NLO-active Schiff-base linked ferrocenyl compounds



**Scheme 1.23** Cyclopalladated (aminomethyl)ferrocene derivatives

The most widely-studied class of compounds of these C–N substituted ferrocene derivatives has been the cyclometallated compounds of dimethylaminomethylferrocene and its imine analogue, and in particular the cyclopalladated species (Scheme 1.23). The reasons for their ubiquitous nature stem from their use in asymmetric catalysis via their planar chirality (palladium complexes) and their anti-tumour activity (platinum complexes). Shaw and Gaunt produced the first cyclopalladated derivative in 1975<sup>161</sup> reacting **18** with sodium chloropalladate(II) in the presence of sodium acetate.

For many years Lopez and co-workers have been one of the leaders in this field, investigating the effects of the alkyl or other donor substituents,<sup>162</sup> the nature of the nitrogen donor atom ( $sp^2$  versus  $sp^3$ ),<sup>163</sup> formation of diastereomerically pure metallacycles<sup>164</sup> and the inclusion of additional donor atoms to effect tridentate coordination as opposed to bidentate (Scheme 1.24).<sup>165–168</sup> In 1994, they found that in cyclopalladated compounds containing the imine as the chelate ligand, the Pd–N bond

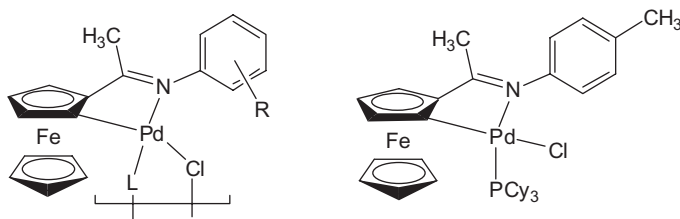


**Scheme 1.24** Cyclopalladated (aminomethyl)ferrocenes with possible bi- or tri-dentate coordination

is clearly less reactive than those containing the amine. In addition, the palladium(II) acts as an electron-withdrawing group in the cyclometallated derivatives and that most of the electron density is withdrawn from the CH=N unit.

An interesting point is that in the cycloplatinated compounds there are two possible centres for antitumour activity – the ferrocene and the platinum. In a series of papers in 1994,<sup>169–171</sup> Robinson and Simpson and co-workers synthesised and characterised a range of cyclometallated ferrocenylamine complexes of platinum(II) with a view to examining their cytotoxic activity. Due to the similarities with *cis*-platin it was thought that the compounds had the potential to produce a spectrum of toxicity and tumour activity. Toxicity, histological and antitumour studies in mice showed that the cyclometallated ferrocenylamines cause kidney rather than liver dysfunction, that they have reasonable toxicity and are mildly cytotoxic against standard tumours. Although only poorly soluble in water or saline solution, they were active against *cis*-platin resistant cell lines.<sup>172</sup> The same group has also produced switchable cycloplatinated ferrocenylamine derivatives of acridone, naphthalimide and anthraquinone.<sup>173</sup>

Catalytic studies with cyclopalladated ferrocenylamines have centered on asymmetric catalysis and the advantages of such catalysts include their ease of synthesis, facile modification and convenience of handling (insensitivity to air and moisture). One of the early examples came from Overman and co-workers<sup>174</sup> who used a series of enantiopure cyclopalladated ferrocenyl amines and imines as catalysts for the [3,3]-rearrangement of allylic benzimidates to allylic benzamides. Reasonable enantioselection was observed and this was also found to be highly dependent upon the nature of the counterion. Mak and co-workers<sup>175</sup> have formed a series of enantiopure bis( $\mu$ -acetato)-bridged planar chiral cyclopalladated species, and air and moisture stable tricyclohexylphosphine adducts of cyclopalladated ferrocenylamines (Scheme 1.25) have been easily synthesised and used in the palladium-catalysed Suzuki cross-coupling of aryl chlorides.<sup>176</sup> The catalysts gave the coupled products in excellent yields in the reaction of nonactivated and deactivated aryl chlorides with phenylboronic acid. The catalyst loadings could also be lowered to 0.01 % mol % without loss of activity. Other palladium-catalysed cross-coupling reactions, such as Heck, Sonogashira<sup>177</sup> and Mizoroki–Heck<sup>178</sup> have also been catalysed by these classes of compounds.



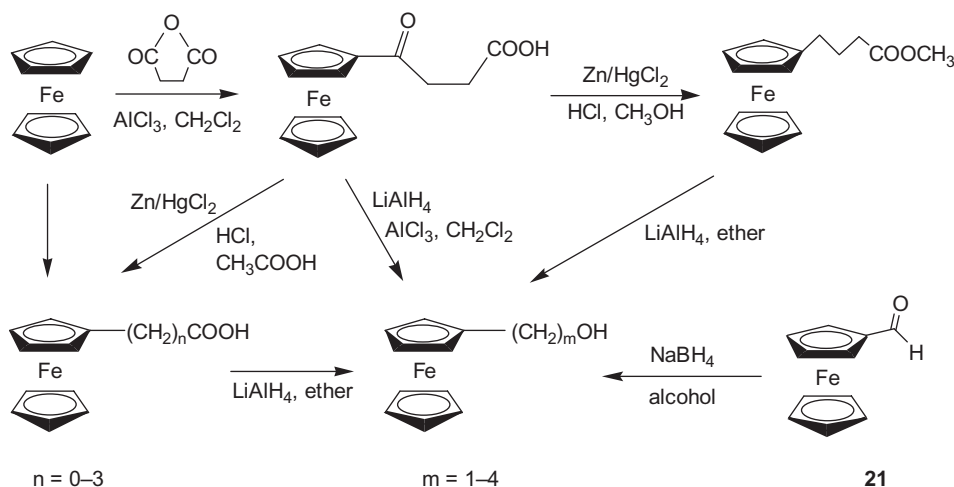
**Scheme 1.25** Cyclopalladated ferrocene Schiff bases and tricyclohexylphosphine adducts

Finally the ligand class has also stabilised main group and transition metal centres via cyclometallation and formed for example, some unusual heterotrimetallic metalloplumbylene compounds ( $(\text{FcN})_2\text{PbM}(\text{CO})_5$  (M = chromium, molybdenum, tungsten)).<sup>179–181</sup>

### 1.7.2 Oxygen-Donor Compounds

Ferrocenecarboxaldehyde (FcCHO, **21**) was first prepared in the late 1950s by two different methods, though both used (*N,N*-dimethylaminomethyl)ferrocene methiodide ([FcCH<sub>2</sub>NMe<sub>3</sub>]I) as the starting material. Hauser and Lindsay<sup>182</sup> showed that **21** would undergo typical addition and condensation reactions to form a range of other ferrocene derivatives. Pauson and co-workers<sup>183</sup> produced **21** via the Sommelet reaction and also illustrated its versatility as a starting material, forming the analogous oxime, nitrile, alcohol and carboxylic acid derivatives. Ferrocenylmethanol is probably the most studied and reacted species in this class of compounds, largely due to its ready availability. Displacement of the hydroxyl group by amines is relatively easy when carried out in dilute acid<sup>184</sup> and FcCH<sub>2</sub>OH reacts smoothly with mercaptosuccinic acid to give ferrocenylmethylthiosuccinic acids.<sup>185</sup> The alcohol can also be deprotonated with NaN(SiMe<sub>3</sub>)<sub>2</sub> to form an unsolvated sodium alkoxide which is a useful intermediate in the preparation of early transition metal and lanthanide derivatives containing the ferrocenylmethoxide ligand.<sup>186</sup>

Swarts and co-workers<sup>187</sup> have formed a series of primary ferrocenylalcohols Fc(CH<sub>2</sub>)<sub>m</sub>OH (*m* = 1–4) via the reduction of the appropriate ferrocenecarboxylic acids (Scheme 1.26). In-depth electrochemical measurements were carried out and the ferrocene group showed reversible electrochemistry with the reduction potential of the ferrocene group being inversely proportional to the side chain length. The influence of the side chain length on reduction potential was more pronounced for the acids because the electron-withdrawing properties of the carbonyl group are stronger than that of the alcohol group. Ion pairing was also found to play a major role in the electrochemical behaviour of ferrocenylmethanol. Finally, gematranes bearing a ferrocenylalkoxyl moiety have been obtained by the reaction of HOGe(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N with various ferrocenyl alcohols<sup>188</sup> and used for antitumour and antibacterial activity.



**Scheme 1.26** Synthesis of some ferrocene-containing alcohols<sup>187</sup>

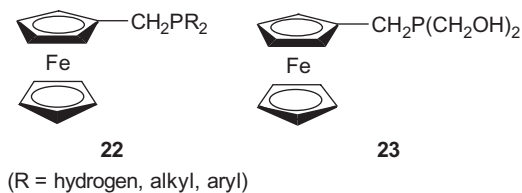
### 1.7.3 Phosphorus-Donor Compounds

In contrast to the large number of ferrocene-derived phosphines, ligands where there is a carbon spacer between the two functionalities are rare.<sup>189, 190</sup> However in recent years the chemistry of ferrocene alkylphosphines (**22**) and ferrocene hydroxymethylphosphines (**23**) has developed (Scheme 1.27). Henderson and co-workers have been very active in this area and have investigated the properties and coordination abilities of various primary phosphines and an arsine bearing ferrocene substituents.<sup>191–194</sup> Although these ligand types are usually very air-sensitive, they found that primary phosphines with an alkyl linkage between the cyclopentadienyl ligand of ferrocene and the phosphorus or arsenic atom were unexpectedly stable in air over two years. In comparison, ferrocenylphosphine oxidises in air after a few days.

The same group has also described the synthesis of the first example of a ferrocene-derived hydroxymethylphosphine ligand, together with some derivatives.<sup>195, 196</sup> Reaction of  $[\text{FcCH}_2\text{NMe}_3]\text{I}$  with an excess of  $\text{P}(\text{CH}_2\text{OH})_3$  gives the air-stable ferrocenylphosphine  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$ . Further reaction of the  $\text{CH}_2\text{OH}$  groups on phosphorus is facile and a range of derivatives are now known, such as the phosphine oxide, phosphine sulfide and various cyano- and amino-derivatives. Removal of formaldehyde from  $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$  with one mole equivalent of  $\text{Na}_2\text{S}_2\text{O}_5$  gives the crystalline and completely air-stable primary phosphine  $\text{FcCH}_2\text{PH}_2$  and exhibits all the typical coordinative properties of a primary phosphine.<sup>193, 194</sup> Electrochemical studies of **22** and **23** and other derivatives show that the free ligands exhibit complex voltammetric responses due to participation of the P lone pair in the redox reactions. Uncomplicated ferrocene-based redox chemistry is observed for phosphorus(V) derivatives and when the ligands are coordinated to metal centres.<sup>192</sup>

In 2001, Henderson and co-workers reported the synthesis of ferrocenyl-phosphonic and -arsonic acids<sup>197</sup> and showed that platinum(II) complexes of these ligands show moderate activity against P388 leukaemia cells, whereas the parent ligands are inactive.<sup>198</sup> More recently, **23** has been reacted with a range of amino acids to form novel phosphino amino acids, being notably water soluble.<sup>199</sup> The same group has bound the related primary phosphine ligands **22** (where  $\text{R} = \text{H}$ ) to molybdenum and tungsten centres and examined the dynamic behaviour of the complexes in solution,<sup>200, 201</sup> whilst Laguna *et al.* have formed gold and silver complexes with the same ligand.<sup>202</sup>

Tertiary ferrocenylmethylphosphines are known and have been used as ligands for Suzuki–Miyaura palladium catalysts.<sup>203</sup> These phosphines possess an aryl substituent on the methyl bridge in order to maximise steric bulk. Catalytic activity of the

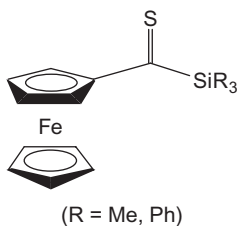


**Scheme 1.27** Ferrocene alkylphosphines (**22**) and ferrocene hydroxymethylphosphines (**23**)

complexes is high but the *t*-butyl substituted ligand is not stable in air. In contrast, di(*t*-butyl)(ferrocenylmethyl)phosphine, which lacks the phenyl group on the methylene bridge, is reasonably air-stable as a solid and possesses an electron donating ability similar to that of tri-*i*-propylphosphine.<sup>204</sup> Palladium complexes of this ligand can catalyse room temperature Suzuki–Miyaura coupling reactions with aryl bromides, and exhibit modest yields in Heck couplings. The modest activity seems to stem from the fact that whilst oxidative addition occurs efficiently, other steps in the catalytic cycle, such as transmetallation or migratory insertion, are inefficient. Butler and co-workers have shown that ferrocenylmethylphosphine ligands can have an effect in the palladium-catalysed reaction of carbon monoxide, methanol and ethane to obtain methyl propionate, a key intermediate in the preparation of methyl methacrylate.

#### 1.7.4 Chalcogen-Donor Compounds

There are only a very few reports in the literature on this type of compound. In 1999, Laguna and co-workers formed the ferrocene derivative  $\text{FcCH}_2\text{N}(\text{CH}_2)_2\text{SH}$  from the condensation reaction of **21** with  $\beta$ -mercaptoethylamine. It can be easily oxidised to its disulfide and the parent ligand reacts smoothly with gold (I) phosphine cations.<sup>205</sup> Some ferrocene-containing penicillins and cephalosporins (featuring thioglycolic acids) are known<sup>206</sup> and Bonini *et al.* have synthesised a range of new thioferrocenylsilanes (Scheme 1.28). The derivatives can lead to planar enantiomerically pure chiral thioferrocenylsilanes, and have been investigated for applications within asymmetric catalysis.<sup>207</sup>



**Scheme 1.28** Structure of thioferrocenylsilanes

## 1.8 Conclusions

As stated previously, the field of monofunctional ferrocene ligands has been overshadowed by that of its nearest neighbour, the disubstituted ferrocenes. Difficulties in preparing the monofunctional species cleanly (free from the difunctional analogues) and in high yields has held back research in this area. However, with more facile and reproducible synthetic routes now available, the monosubstituted species are once again being focused on and the field has become topical. For instance, Hartwig's work on the donor-substituted pentamethylferrocenyl species has brought catalysis by this type of ligand class into a wider arena. Although many of the ligands and substitution patterns are now well-established, there does seem enormous scope for further growth. Admittedly, having the donor heteroatom directly attached to the Cp ring often

leads to stability problems and careful handling is required. Nevertheless, with more sophisticated glassware and laboratory equipment, this is not such a handicap anymore. Indeed, derivatives of ferrocenylamine are now widespread and even those of ferrocenol are increasing. As with the difunctional analogues, the P-substituted species dominate, especially in catalysis where the ligand properties (i.e. electronics, sterics and chirality) can easily be harnessed and tuned. Importantly, a carbon spacer can be used to aid stability with little loss in donating behaviour or power and air- and water-stable and water-soluble ligands such as ferrocene alkylphosphines and ferrocene hydroxymethylphosphines respectively will surely be further exploited.

## References

1. A. Togni, R.L. Halterman (Eds), *Metallocenes*, Wiley-VCH Verlag GmbH, Weinheim, Germany, 1998.
2. N.J. Long, *Metallocenes: An Introduction to Sandwich Complexes*, Blackwell Science, Oxford, UK, 1998.
3. A. Togni, T. Hayashi (Eds), *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*, VCH, Weinheim, 1995.
4. For some excellent reviews on ferrocene ligands see: (a) R.C.J. Atkinson, V.C. Gibson, N.J. Long, *Chem. Soc. Rev.*, 2004, **33**, 313–328; (b) P. Barbaro, C. Bianchini, G. Gianbastini, S.L. Parisel, *Coord. Chem. Rev.*, 2004, **248**, 2131–2150; (c) U. Siemeling, T.-C. Auch, *Chem. Soc. Rev.*, 2005, **34**, 584–594; (d) T.J. Colacot, *Platinum Met. Rev.*, 2001, **45**, 22–30.
5. M. Herberhold, *Ferrocene Compounds Containing Heteroelements*, in *Ferrocenes: Homogeneous Catalysis–Organic Synthesis–Materials Science*, VCH, Weinheim (1995), pp. 219–278.
6. (a) T. Renk, W. Ruf, W. Siebert, *J. Organomet. Chem.*, 1974, **64**, C45–C47; (b) W. Ruf, T. Renk, W. Siebert, *Z. Naturforsch.*, 1977, **31b**, 1028–1034.
7. J.J. Bishop, A. Davison, M.L. Katcher *et al.* *J. Organomet. Chem.*, 1971, **27**, 241–249.
8. B. McCulloch, D.L. Ward, J.D. Woollins, C.H. Brubaker, Jr., *Organometallics*, 1985, **4**, 1425–1532.
9. F. Rebiere, O. Samuel, H.B. Kagan, *Tetrahedron Lett.*, 1990, **31**, 3121–3124.
10. D. Guillaneux, H.B. Kagan, *J. Org. Chem.*, 1995, **60**, 2502–2505.
11. R.W. Fish, M. Rosenblum, *J. Org. Chem.*, 1965, **30**, 1253–1254.
12. M.D. Rausch, L.P. Klemann, A. Siegel *et al.* *Synth. React. Inorg. Metal-Org. Chem.*, 1973, **3**, 193–199.
13. M. Sato, I. Motoyama, K. Hata, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 812–815.
14. M.D. Rausch, *J. Org. Chem.*, 1961, **26**, 1802–1805.
15. M. Sato, I. Motoyama, K. Hata, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1860–1863.
16. M. Sato, T. Ito, I. Motoyama *et al.* *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1976–1981.
17. A.N. Nesmeyanov, E.G. Perevalova, R.V. Golovnya, L.S. Shilovtseva, *Dokl. Akad. Nauk SSSR*, 1955, **102**, 535–538.
18. A.N. Nesmeyanov, V.A. Sazonova, V.I. Romanenko, *Chem. Ber.*, 1960, **9**, 2717–2729.
19. A.N. Nesmeyanov, V.A. Sazonova, V.I. Romanenko, *Dokl. Akad. Nauk SSSR*, 1964, **157**, 922–925.
20. A.N. Nesmeyanov, V.N. Drozd, V.A. Sazonova, *Dokl. Akad. Nauk SSSR*, 1963, **150**, 321–324.
21. F.S. Arimoto, A.C. Haven, Jr., *J. Am. Chem. Soc.*, 1955, **77**, 6295–6297.

22. E.M. Acton, R.M. Silverstein, *J. Org. Chem.*, 1959, **24**, 1487–1490.
23. M. Herberhold, M. Ellinger, W. Kremnitz, *J. Organomet. Chem.*, 1983, **241**, 227–240.
24. B. Bildstein, M. Malaun, H. Kopacka *et al.* *Organometallics*, 1999, **18**, 4325–4336.
25. D.C. Butler, C.J. Richards, *Organometallics*, 2002, **21**, 5433–5436.
26. D. van Leusen, B. Hessen, *Organometallics*, 2001, **20**, 224–226.
27. A. Hassner, P. Munger, B.A. Belika, *Tetrahedron Lett.*, 1982, **23**, 699–702.
28. G. Smolinsky, *J. Org. Chem.*, 1962, **27**, 3557–3559.
29. W.E. Britton, R. Kashyap, M. El-Hashash *et al.* *Organometallics*, 1986, **5**, 1029–1031.
30. B. Wrackmeyer, H.E. Maisel, M. Herberhold, *J. Organomet. Chem.*, 2001, **637–639**, 727–732.
31. F. Carre, C. Guerin, B.J.L. Henner, C. Uerpmann, *J. Organomet. Chem.*, 2002, **654**, 210–215.
32. I. Sapountzis, P. Knochel, *Angew. Chem., Int. Ed.*, 2004, **43**, 897–900.
33. A. Mendiratta, S. Barlow, M.W. Day, S.R. Marder, *Organometallics*, 1999, **18**, 454–456.
34. M. Malaun, R. Kowallick, A.M. McDonagh *et al.* *Dalton Trans.*, 2001, 3025–3038.
35. S-M. Lee, R. Kowallick, M. Marcaccio *et al.* *Dalton Trans.*, 1998, 3443–3450.
36. G.R. Knox, P.L. Pauson, D. Willison *et al.* *Organometallics*, 1990, **9**, 301–306.
37. B. Wrackmaeyer, H.E. Maisel, O.L. Tok *et al.* *Z. Anorg. Allg. Chem.*, 2004, **630**, 2106–2109.
38. P.J. Shapiro, R. Zehnder, D.M. Foo *et al.* *Organometallics*, 2006, **25**, 719–732.
39. T.C. Holovics, S.F. Deplazes, M. Toriyama *et al.* *Organometallics*, 2004, **23**, 2927–2938.
40. I.A. Alekseeva, G.N. Yashchenko, T.A. Sinitsyna, L.A. Petrov, *Zh. Obshch. Khim.*, 1977, **47**, 1874–1878.
41. M. Bracci, C. Ercolani, B. Floris *et al.* *Guastini Dalton Trans.*, 1990, 1357–1363.
42. V.C. Gibson, C.K.A. Gregson, C.M. Halliwell *et al.* *J. Organomet. Chem.*, 2005, **690**, 6271–6283.
43. V.C. Gibson, C.M. Halliwell, N.J. Long *et al.* *Dalton Trans.*, 2003, 918–926.
44. C.K.A. Gregson, V.C. Gibson, N.J. Long *et al.* *J. Am. Chem. Soc.*, 2006, **128**, 7410–7411.
45. R.C.J. Atkinson, V.C. Gibson, N.J. Long *et al.* *Organometallics*, 2007, **26**, 316–320.
46. R.K.J. Bott, M. Schormann, D.L. Hughes *et al.* *Polyhedron*, 2006, **25**, 387–396.
47. B. Bildstein, M. Malaun, H. Kopacka *et al.* *J. Organomet. Chem.*, 1999, **572**, 177–187.
48. R. Jackstell, A. Frisch, M. Beller *et al.* *J. Mol. Cat. A: Chem.*, 2002, **185**, 105–112.
49. G.R. Knox, P.L. Pauson, D. Willison, *J. Organomet. Chem.*, 1993, **450**, 177–184.
50. W. Imhof, *J. Organomet. Chem.*, 1997, **541**, 109–116.
51. T.G. Sprigings, C.D. Hall, *Organometallics*, 2001, **20**, 2560–2564.
52. A.N. Nesmeyanov, V.A. Sazonova, V.N. Drozd, L.A.M.V. Nikonova, *Dokl. Akad. Nauk SSSR*, 1960, **133**, 126–129.
53. A.N. Nesmeyanov, V.A. Sazonova, V.N. Drozd, *Tetrahedron Lett.*, 1959, **1**, 13–17.
54. A.N. Nesmeyanov, W.A. Ssazonowa, V.N. Drozd, *Chem. Ber.*, 1960, **93**, 2717–2729.
55. R. Epton, G. Marr, G.K. Rogers, *J. Organomet. Chem.*, 1978, **150**, 93–100.
56. S. Akabori, M. Sato, S. Ebine, *Synthesis*, 1981, **4**, 278–279.
57. K. Shibata, Y. Saito, M. Matsui, Y. Takase, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 3349–3350.
58. M.R. Van der Heiden, G.D. Frey, H. Plenio, *Organometallics*, 2004, **23**, 3548–3551.
59. M. Herberhold, H-D. Brendel, A. Hofmann *et al.* *J. Organomet. Chem.*, 1998, **556**, 173–187.
60. (a) R.C.J. Atkinson, V.C. Gibson, N.J. Long, *et al.* *Organometallics*, 2004, **23**, 2744–2751; (b) R.C.J. Atkinson, V.C. Gibson, N.J. Long, *et al.* *Dalton Trans.*, 2004, 1823–1826.
61. S. Akabori, Y. Habata, M. Sato, S. Ebine, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 537–541 and 1459–1461.
62. M. Herberhold, A. Hofmann, W. Milius, *J. Organomet. Chem.*, 1998, **555**, 187–200.
63. M. Herberhold, A. Hofmann, W. Milius, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1599–1608.

64. A.N. Nesmeyanov, N.N. Sedova, S.K. Moiseev, V.A. Sazonova, *Dokl. Akad. Nauk SSSR*, 1981, **256**, 98–101.
65. A.N. Nesmeyanov, E.G. Perevalova, K.I. Grandberg, *et al. J. Organomet. Chem.*, 1974, **65**, 131–144.
66. L.L. Troitskaya, S.T. Ovseenko, Y.L. Slovokhotov *et al. J. Organomet. Chem.*, 2002, **642**, 191–194.
67. E.T. Singewald, C.A. Mirkin, C.L. Stern, *Angew. Chem., Int. Ed.*, 1995, **34**, 1624–1627.
68. G.P. Sollott, H.E. Mertwoy, S. Portnoy, J.L. Snead, *J. Org. Chem.*, 1963, **28**, 1090–1092.
69. G.R. Knox, P.L. Pauson, D. Willison, *Organometallics*, 1992, **11**, 2930–2933.
70. R. Pietschnig, E. Niecke, *Bull. Soc. Chim. Fr.*, 1997, **134**, 605–608.
71. S.I. Pereira, J. Adrio, A.M.S. Silva, J.C. Carretero, *J. Org. Chem.*, 2005, **70**, 10175–10177.
72. T.J. Colacot, *Chem. Rev.*, 2003, **103**, 3101–3118.
73. C.J. Richards, A.J. Locke, *Tetrahedron: Asymmetry*, 1998, **9**, 2377–2407.
74. J.M. Brown, J.C.P. Laing, *J. Organomet. Chem.*, 1997, **529**, 435–444.
75. (a) S. Jugé, J-P. Genet, *Tetrahedron Lett.*, 1989, **30**, 2783–2786; (b) S. Jugé, M. Stephan, R. Merdes *et al. J. Chem. Soc., Chem. Commun.*, 1993, 531–532.
76. E.A. Colby, T.F. Jamison, *J. Org. Chem.*, 2003, **68**, 156–166.
77. R.M. Moslin, T.F. Jamison, *Org. Lett.*, 2006, **8**, 455–458.
78. K.M. Miller, T.F. Jamison, *Org. Lett.*, 2005, **7**, 3077–3080.
79. S.J. Patel, T.F. Jamison, *Angew. Chem., Int. Ed.*, 2005, **97**, 3941–3944.
80. A. Alexakis, J. Burton, J. Vastra *et al. Eur. J. Org. Chem.*, 2000, **24**, 4011–4027.
81. W. Chen, W. Mbafor, S.M. Roberts, J. Whittall, *J. Am. Chem. Soc.*, 2006, **128**, 3922–3923.
82. N.J. Long, A.J.P. White, D.J. Williams, M. Younus, *J. Organomet. Chem.*, 2002, **649**, 94–99.
83. S. Otto, A. Roodt, J. Smith, *Inorg. Chim. Acta*, 2000, **303**, 295–299.
84. S. Otto, A. Roodt, *Inorg. Chim. Acta*, 2004, **357**, 1–10.
85. F. Estevan, J. Latorre, E. Peris, *Polyhedron*, 1993, **12**, 2153–2156.
86. L-C. Song, G-A. Yu, H-T. Wang *et al. Eur. J. Inorg. Chem.*, 2004, **4**, 866–871.
87. T.C. Zheng, W.R. Cullen, S.J. Rettig, *Organometallics*, 1994, **13**, 3594–3604.
88. W.R. Cullen, S.J. Rettig, T.C. Zheng, *J. Organomet. Chem.*, 1993, **452**, 97–103.
89. W.R. Cullen, S.J. Rettig, T.C. Zheng, *Organometallics*, 1992, **11**, 853–858.
90. W.R. Cullen, S.T. Chacon, M.I. Bruce *et al. Organometallics*, 1988, **7**, 2273–2278.
91. W.R. Cullen, S.J. Rettig, T.C. Zheng, *Organometallics*, 1992, **11**, 277–283.
92. J.C. Kotz, C.L. Nivert, J.M. Lieber, R.C. Reed, *J. Organomet. Chem.*, 1975, **91**, 87–95.
93. F. Estevan, P. Lahuerta, J. Latorre *et al. Dalton Trans.*, 1993, 1681–1688.
94. B. Therrien, L. Vielle-Petit, J. Leanneret-Gris *et al. J. Organomet. Chem.*, 2004, **689**, 2456–2463.
95. P. Štěpnička, R. Gyepes, O. Lavastre, P.H. Dixneuf, *Organometallics*, 1997, **16**, 5089–5095.
96. S. Perruchas, N. Avarvari, D. Rondeau *et al. Inorg. Chem.*, 2005, **44**, 3459–3465.
97. T.M. Miller, K.J. Ahmed, M.S. Wrighton, *Inorg. Chem.*, 1989, **28**, 2347–2355.
98. R. Sommer, P. Loennecke, J. Reinhold *et al. Organometallics*, 2005, **24**, 5256–5266.
99. S.I.M. Paris, F.R. Lernke, R. Sommer *et al. J. Organomet. Chem.*, 2005, **690**, 363–370.
100. Q. Shelby, N. Kataoka, G. Mann, J.F. Hartwig, *J. Am. Chem. Soc.*, 2000, **122**, 10718–10719.
101. G. Mann, C. Incarvito, A.L. Rheingold, J.F. Hartwig, *J. Am. Chem. Soc.*, 1999, **121**, 3224–3225.
102. J.P. Stambuli, S.R. Stauffer, K.H. Shaughnessy, J.F. Hartwig, *J. Am. Chem. Soc.*, 2001, **123**, 2677–2678.
103. J.P. Wolkowski, J.F. Hartwig, *Angew. Chem., Int. Ed.*, 2002, **41**, 4289–4291.
104. S.R. Stauffer, J.F. Hartwig, *J. Am. Chem. Soc.*, 2003, **125**, 6977–6985.

105. F. Barrios-Landeros, J.F. Hartwig, *J. Am. Chem. Soc.*, 2005, **127**, 6944–6945.
106. N. Kataoka, Q. Shelby, J.P. Stambuli, J.F. Hartwig, *J. Org. Chem.*, 2002, **67**, 5553–5566.
107. R.K. Thalji, K.A. Ahrendt, R.G. Bergman, J.A. Ellman, *J. Org. Chem.*, 2005, **70**, 6775–6781.
108. C. Baille, L. Zhang, J. Xiao, *J. Org. Chem.*, 2004, **69**, 7779–7782.
109. J. Yin, M.P. Rainka, X.X. Zhang, S.L. Buchwald, *J. Am. Chem. Soc.*, 2002, **124**, 1162–1163.
110. O. Orms, J. Le Bideau, A. Vioux, D. Leclercq, *J. Organomet. Chem.*, 2005, **690**, 363–370.
111. O. Orms, F. Maurel, F. Carre *et al.* *J. Organomet. Chem.*, 2005, **689**, 2654–2661.
112. W. Henderson, S.R. Alley, *J. Organomet. Chem.*, 2002, **658**, 181–190.
113. I.P. Gray, H.L. Milton, A.M.Z. Slawin, J.D. Woollins, *Dalton Trans.*, 2003, 3540–3457–.
114. U. Siemeling, A. Stammler, H-G. Stammler, O. Kuhnert, *Z. Anorg. Allg. Chem.*, 1999, **625**, 845–847.
115. T. Mizuta, M. Onishi, T. Nakazono *et al.* *Organometallics*, 2002, **21**, 717–726.
116. G.R. Knox, P.L. Pauson, *J. Chem. Soc.*, 1958, 692–696.
117. M. Herberhold, O. Nuyken, T. Pohlmann, *J. Organomet. Chem.*, 1991, **405**, 217–227.
118. M. Herberhold, O. Nuyken, T. Poehlmann, *J. Organomet. Chem.*, 1995, **501**, 13–22.
119. M. Herberhold, P. Leitner, C. Doernhoefer, J. Ott-Lastic, *J. Organomet. Chem.*, 1989, **377**, 281–289.
120. R.V. Honeychuck, M.O. Okoroafor, L.H. Shen, C.H. Brubaker, Jr, *Organometallics*, 1986, **85**, 482–490.
121. M.D. Rausch, *J. Org. Chem.*, 1961, **26**, 3579–3580.
122. L. Bernardi, B.F. Bonini, M. Comes-Franchini *et al.* *Eur. J. Org. Chem.*, 2002, **16**, 2776–2784.
123. C. Pichon, B. Odell, J.M. Brown, *Chem. Commun.*, 2004, **5**, 598–599.
124. P. Diter, S. Taudien, O. Samuel, H.B. Kagan, *J. Org. Chem.*, 1994, **59**, 370–373.
125. K. Nagasawa, A. Yoneta, T. Umezawa, K. Ito, *Heterocycles*, 1987, **26**, 2607–2609.
126. O. Riant, G. Argouarch, D. Guillaneux *et al.* *J. Org. Chem.*, 1998, **63**, 3511–3514.
127. D.H. Hua, N.M. Nadege, Y. Chen *et al.* *J. Org. Chem.*, 1996, **61**, 4508–4509.
128. F. Rebiere, O. Riant, L. Ricard, H.B. Kagan, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 568–570.
129. I. Fernandez, V. Valdivia, B. Gori *et al.* *Org. Lett.*, 2005, **7**, 1307–1310.
130. C. Bolm, K. Muniz, N. Aguilar, M. Kesselgruber, G. Raabe, *Synthesis*, 1999, **7**, 1251–1260.
131. I.V. Kourkine, C.S. Slone, C.A. Mirkin *et al.* *Inorg. Chem.*, 1999, **38**, 2758–2759.
132. D. Marquarding, H. Klusacek, G. Gokel *et al.* *J. Am. Chem. Soc.*, 1980, **92**, 5389–5393.
133. M. Herberhold, J. Peukert, M. Kruger *et al.* *Z. Anorg. Allg. Chem.*, 2000, **626**, 1289–1295.
134. W.R. Cullen, S.J. Rettig, T.C. Zheng, *Polyhedron*, 1995, **14**, 2653–2661.
135. J. Adeleke, M. Adebajo, Y.W. Chen, L.K. Liu, *Organometallics*, 1992, **11**, 2543–2550.
136. K. Tanaka, M. Nakamoto, Y. Tashiro, T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 316–321.
137. R. Broussier, A. Abdulla, B. Gautheron, *J. Organomet. Chem.*, 1987, **332**, 165–173.
138. M. Herberhold, P. Leitner, C. Dornhofer, J. Ott-Lastic, *J. Organomet. Chem.*, 1989, **377**, 281–289.
139. M. Herberhold, P. Leitner, *J. Organomet. Chem.*, 1987, **336**, 153–161.
140. A. Chieffi, J.V. Cornassetto, V. Snieckus, *Synlett*, 2000, **2**, 269–271.
141. M.R. Burgess, C.P. Morley, M. Di Vaira, *J. Organomet. Chem.*, 2005, **690**, 3099–3104.
142. A.A. Naiini, C-K. Lai, D.L. Ward, C.H. Brubaker, Jr., *J. Organomet. Chem.*, 1990, **390**, 73–90.
143. T.P. Lebold, D.L.B. Stringle, M.S. Workentin, J. Corrigan, *Chem. Commun.*, 2003, **12**, 1398–1399.
144. J-Z. Yao, Y-Y. Chen, B-S. Tian, *J. Organomet. Chem.*, 1997, **534**, 51–56.

145. H.B. Singh, A.V. Regini, J.P. Jasinski *et al.* *J. Organomet. Chem.*, 1994, **464**, 87–94.
146. Y. Nishibayashi, T. Chiba, J.D. Singh *et al.* *J. Organomet. Chem.*, 1994, **473**, 205–213.
147. C.R. Hauser, J.K. Lindsay, D. Lednicer, C.E. Cain, *J. Org. Chem.*, 1957, **22**, 717–718.
148. J.K. Lindsay, C.R. Duke, *J. Org. Chem.*, 1957, **22**, 355–358.
149. C.R. Hauser, J.K. Lindsay, *J. Org. Chem.*, 1956, **21**, 382–383.
150. E.M. Barranco, O. Crespo, M.C. Gimeno *et al.* *Eur. J. Inorg. Chem.*, 2004, **24**, 4820–4827.
151. E.M. Barranco, M.C. Gimeno, A. Laguna, M.D. Villacampa, *Inorg. Chim. Acta*, 2005, **358**, 4177–4182.
152. K. Jacob, F. Voigt, K. Merzweiler, C. Pietzsch, *J. Organomet. Chem.*, 1997, **545–546**, 421–433.
153. Q.F. Mokuolu, C.A. Kilner, S.A. Barrett *et al.* *Inorg. Chem.*, 2005, **44**, 4136–4138.
154. G. De Santis, L. Fabbrizzi, L. Manotti *et al.* *Inorg. Chim. Acta*, 1998, **267**, 177–182.
155. J.C. McAdam, B.H. Robinson, J. Simpson, *Organometallics*, 2000, **19**, 3644–3653.
156. M. Horie, Y. Suzaki, K. Osakada, *J. Am. Chem. Soc.*, 2004, **126**, 3684–3685.
157. D. Marquarding, H. Klusacek, G. Gokel *et al.* *J. Am. Chem. Soc.*, 1980, **92**, 5389–5393.
158. E. Hecht, *Z. Anorg. Allg. Chem.*, 2001, **627**, 2351–2358.
159. S.K. Pal, A. Krishnan, P.K. Das, A.G. Samuelson, *J. Organomet. Chem.*, 2000, **604**, 248–259.
160. K. Oyaizu, K. Yamamoto, Y. Ishii, E. Tsuchida, *Chem. Eur. J.*, 1999, **5**, 3193–3201.
161. J.C. Gaunt, B.L. Shaw, *J. Organomet. Chem.*, 1975, **102**, 511–516.
162. C. Lopez, R. Bosque, X. Solans, M. Font-Bardia, *J. Organomet. Chem.*, 1997, **539**, 99–107.
163. C. Lopez, R. Bosque, X. Solans *et al.* *Dalton Trans.*, 1994, 3039–3046.
164. C. Lopez, A. Caubet, S. Perez *et al.* *Chem. Commun.*, 2004, **5**, 540–541.
165. C. Lopez, S. Perez, X. Solans, M. Font-Bardia, *J. Organomet. Chem.*, 2005, **690**, 228–243.
166. S. Perez, C. Lopez, A. Caubet *et al.* *Organometallics*, 2006, **25**, 596–601.
167. C. Lopez, A. Caubet, S. Perez *et al.* *J. Organomet. Chem.*, 2002, **651**, 105–113.
168. S. Perez, C. Lopez, A. Caubet *et al.* *New. J. Chem.*, 2003, **27**, 975–982.
169. N.W. Duffy, J.C. McAdam, B.H. Robinson, J. Simpson, *Inorg. Chem.*, 1994, **33**, 5343–5350.
170. P. Ranatunge-Bandarage, R. Ramani, J. Simpson *et al.* *Organometallics*, 1994, **13**, 511–521.
171. P. Ranatunge-Bandarage, R. Ramani, J. Simpson, B.H. Robinson, *Organometallics*, 1994, **13**, 500–510.
172. K. McGrouther, D.K. Weston, D. Fenby *et al.* *Dalton Trans.*, 1999, 1957–1966.
173. E.M. McGale, E.R. Murray, J.C. McAdam *et al.* *Inorg. Chim. Acta*, 2003, **352**, 129–135.
174. F. Cohen, L.E. Overman, *Tetrahedron: Asymmetry*, 1998, **9**, 3213–3222.
175. G. Zhao, Q-C. Yang, T.C.W. Mak, *Organometallics*, 1999, **18**, 3623–3636.
176. J. Gong, G. Liu, C. Du *et al.* *J. Organomet. Chem.*, 2005, **690**, 3963–3969.
177. Z. Tibor, A. Csampai, A. Kotschy, *Tetrahedron*, 2005, **61**, 9767–9774.
178. X.M. Zhao, X.Q. Hao, B. Liu *et al.* *J. Organomet. Chem.*, 2006, **691**, 255–260.
179. N. Seidel, K. Jacob, A.K. Fischer, *Organometallics*, 2001, **20**, 578–581.
180. N. Seidel, K. Jacob, A.K. Fischer *et al.* *Eur. J. Inorg. Chem.*, 2001, **1**, 145–151.
181. K. Jacob, F. Voigt, K. Merzweiler, *et al.* *J. Organomet. Chem.*, 1998, **552**, 265–276.
182. C.R. Hauser, J.K. Lindsay, *J. Org. Chem.*, 1957, **22**, 906–908.
183. G.D. Broadhead, J.M. Osgerby, P.L. Pauson, *J. Chem. Soc.*, 1958, 650–656.
184. A.L.J. Beckwith, G.G. Vickery, *Perkin Trans. 1*, 1975, **18**, 1818–1821.
185. R. DAbard, B. Misteriewicz, H. Platin, J. Wasielewski, *J. Organomet. Chem.*, 1987, **328**, 185–192.
186. H. Gornitzka, F.T. Edelman, K. Jacob, *J. Organomet. Chem.*, 1992, **436**, 325–332.
187. W.L. Davis, R.F. Shago, E.H.G. Langner, J.C. Swarts, *Polyhedron*, 2005, **24**, 1611–1616.
188. L. Chen, J-X. Chen, L. Sun, Q. Xie, *Appl. Organomet. Chem.*, 2005, **19**, 1038–1042.

189. S. Hoppe, H. Welchmann, K. Jurkschat *et al.* *J. Organomet. Chem.*, 1995, **505**, 63–72.
190. Y. Yamamoto, T. Tanase, I. Mori, Y. Nakamura, *Dalton Trans.*, 1994, 3191–3192.
191. A.J. Downard, N.J. Goodwin, W. Henderson, *J. Organomet. Chem.*, 2003, **676**, 62–72.
192. W. Henderson, S.R. Alley, *J. Organomet. Chem.*, 2002, **656**, 120–128.
193. N.J. Goodwin, B.K. Nicholson, *Inorg. Chim. Acta*, 1999, **295**, 18–24.
194. N.J. Goodwin, W. Henderson, B.K. Nicholson *et al.* *Dalton Trans.*, 1999, 1785–1794.
195. N.J. Goodwin, W. Henderson, J.K. Sarfo, *Chem. Commun.*, 1996, **13**, 1551–1552.
196. N.J. Goodwin, W. Henderson, B.K. Nicholson *et al.* *Dalton Trans.*, 1997, 4377–4384.
197. S.R. Alley, W. Henderson, *J. Organomet. Chem.*, 2001, **637–639**, 216–229.
198. W. Henderson, S.R. Alley, *Inorg. Chim. Acta*, 2001, **322**, 106–112.
199. A.A. Karasik, R.N. Naumov, R. Sommer *et al.* *Polyhedron*, 2002, **21**, 2251–2256.
200. R. Sommer, P. Loennecke, J. Reinhold *et al.* *Organometallics*, 2005, **24**, 5256–5266.
201. R. Sommer, P. Loennecke, P.K. Baker, E. Hey-Hawkins, *Inorg. Chem. Commun.*, 2002, **5**, 115–118.
202. E.M. Barranco, O. Crespo, M.C. Gimeno *et al.* *Inorg. Chem.*, 2000, **39**, 680–687.
203. Z-Y. Tang, Y. Lu, Q-S. Hu, *Org. Lett.*, 2003, **5**, 297–300.
204. M.D. Sliger, G.A. Broker, S.T. Griffin *et al.* *J. Organomet. Chem.*, 2005, **690**, 1478–1486.
205. E.M. Barranco, M.C. Gimeno, P.G. Jones *et al.* *Inorg. Chem.*, 1999, **38**, 702–706.
206. D. Scutaru, L. Tatani, I. Mazilu *et al.* *J. Organomet. Chem.*, 1991, **401**, 81–85.
207. B.F. Bonini, M. Comes-Franchini, M. Fochi *et al.* *J. Organomet. Chem.*, 2001, **637–639**, 407–417.