1,1′-Di(heteroatom)-functionalised ferrocenes as [N,N], [O,O] and [S,S] chelate ligands in transition metal chemistry

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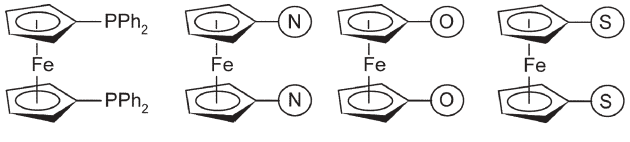
Dppf is one of the most useful and popular ligands in coordination chemistry. Its overwhelming success has overshadowed and arguably even delayed the development and use of closely related ferrocene-based ligands with two ligating N, O or S atoms. Recently, however, dynamic progress concerning such homo-donor ligands can be noted. This *tutorial review* describes the main results obtained over the past decade in order to introduce the reader to an exciting field which currently shows particularly rapid development. The material is organised in sections according to ligand type, followed by a section which summarises the applications reported so far.

1 Introduction

The modification of ferrocenes by phosphanyl groups has led to a large family of chelating ligands that have found widespread application in homogeneous catalysis with a recent emphasis on asymmetric variants.[1] The archetype of such compounds is 1,1′-bis(diphenylphosphanyl)ferrocene (dppf, **1**). It was first reported in 1965, and chiral variants were described in 1974. The development of dppf chemistry took off in the 1980s and continues to flourish, since dppf has proved useful for numerous applications in metal-catalysed organic transformations, including, *inter alia*, Kumada-Hayashi, Suzuki, Heck and Hartwig–Buchwald coupling reactions.[1a,1c]

In view of the great success achieved with dppf and similar ferrocene-based [P,P] chelate ligands, the transition metal coordination chemistry of related [N,N], [O,O] and [S,S] chelate ligands (Fig. 1) seems underdeveloped. This is in contrast to related cyclopentadienyl complexes containing *pendant* N-, O- and S-donors, where the donor heteroatoms are not directly connected to the cyclopentadienyl rings.[2] This review describes the progress in this field which has been achieved during the past decade. It complements a recent treatment of the syntheses and catalytic applications of unsymmetrical ferrocenes, which focuses on unsymmetrical 1,1′-disubstituted ferrocenes of the [P,P], [P,S] and [P,O] type.[3] For earlier work, readers are referred to the comprehensive review of ferrocene chemistry published in 1995.[1a]



1

Fig. 1 Schematic representation of ferrocene-based [N,N], [O,O] and [S,S] ligands closely related to dppf (**1**, left).

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2 [N,N] ligands

2.1 The diamido framework $[Fe\{C_5H_4(NR)\}_2]^{2-}$

Diamido chelate ligands have been exploited extensively in the search for new non-metallocene α-olefin polymerisation catalysts,[4] and this has provided an important stimulus for the great current interest in such species.

First examples of transition metal chelates containing the ferrocene-based diamido ligand framework $[Fe\{(C_5H_4(NR)\}_2]^{2-}$ were published in 2001 by three different research teams (Arnold,[5] R = $SiMe_3$; Bildstein and Siemeling,[6] R = Ph; Gibson and Long,[7] R = CH_2Ph). The repertoire of the parent ferrocenes $[Fe\{(C_5H_4(NHR)\}_2]$ (**2**) has been extended to compounds containing bulky aryl groups[8] instead of simple phenyl and also includes the C_2-symmetric species **2c**[9] (Fig. 2).

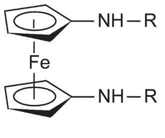
To date, only titanium and zirconium chelates have been reported with this ligand platform, utilising mainly metathesis reactions of the parent 1,1′-diaminoferrocenes **2** with $M(CH_2Ph)_4$ and $M(NMe_2)_4$ (M = Ti, Zr), respectively (Fig. 3).[5–9]

Diamido ligands which contain an additional neutral donor group represent an interesting extension of the simple diamido paradigm.[10] Such donor-functionalised species form a very prominent subclass now, since the presence of the additional donor may give rise to emergent properties. Facial and meridional coordination modes have been realised, depending on the donor topology used. In olefin polymerisation chemistry, the aim of introducing the additional donor is to form more stable, four-coordinate cationic alkyl complexes.[4]

The group of Arnold has addressed the question whether the ferrocene unit can act as such an additional donor.[11] Treatment of $[\{Fe[C_5H_4(NSiMe_3)]_2\}TiMe_2]$ (**3b**) with $B(C_6F_5)_3$ afforded the contact ion pair $[\{Fe[C_5H_4(NSiMe_3)]_2\}TiMe]$-$[MeB(C_6F_5)_3]$ (**4**), whose Fe–Ti distance of 307 pm is 25 pm shorter than that of its dimethyl precursor **3b** and is compatible with a weak Fe–Ti donor bond present in the electron-poor cationic alkyl complex (Fig. 4).

A further dramatic decrease of the Fe–Ti distance was found for the chloro-bridged dimer $[\{Fe[C_5H_4(NSiMe_3)]_2\}Ti(\mu\text{-}Cl)]_2$-$[B(C_6F_5)_4]_2$ (**6**), which was obtained from solutions of $[\{Fe[C_5H_4(NSiMe_3)]_2\}TiMe][B(C_6F_5)_4]$ (**5**) in dichloromethane by reaction with the solvent. In this case, the Fe–Ti distance is only 249 pm, which is equal to the sum of the covalent radii for Fe and Ti and compares well to Fe–Ti single bond lengths reported in the literature. This is a unique result, since the question whether the iron atom may act as an additional electron donor to chelated metal centres has been addressed before exclusively with ferrocene-based [P,P], [O,O] and [S,S] chelates of late transition metals (*vide infra*).[1a] The additional iron-metal donor interaction can give rise to a hemilabile binding profile of such chelate ligands. However, its potential role in catalysis has not been addressed so far.

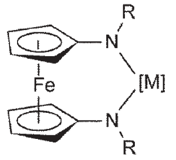
$[\{Fe[C_5H_4(NSiMe_3)]_2\}TiMe][B(C_6F_5)_4]$ (**5**) oligomerises 1-hexene, producing short-chain oligomers of 5–6 monomer units with an activity of 102 g (oligomer) (mmol catalyst)$^{-1}$ h^{-1}. The related zirconium complex



2

a R = $SiMe_3$
b R = CH_2Ph
c R = CHMePh
d R = Ph
e R = 2,6-$C_6H_3Me_2$
f R = 2,4,6-C_6H_2*i*-Pr_3
g R = 2,4,6-$C_6H_2Me_3$
h R = 2,6-$C_6H_3Cl_2$

Fig. 2 Current repertoire of 1,1′-diamidoferrocenes usable for the preparation of transition metal diamido chelates.



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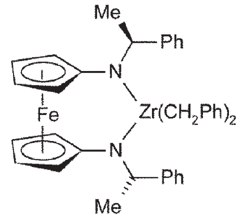


3 f *trans*-diastereomer

	R	[M]
a	$SiMe_3$	$TiCl_2$
b		$TiMe_2$
c		$Ti(CH_2Ph)_2$
d		$Zr(CH_2Ph)_2$
e	CH_2Ph	$Zr(NMe_2)_2$
f	CHMePh	$Zr(CH_2Ph)_2$
g	Ph	$Ti(NMe_2)_2$
h		$Zr(NMe_2)_2(HNMe_2)$
i		$ZrCl_2(HNMe_2)$
j	Mes	$Zr(CH_2Ph)_2$

Fig. 3 Transition metal chelates containing the 1,1′-diamidoferrocene ligand framework. These compounds serve as precursors for cationic derivatives relevant to α-olefin polymerisation.

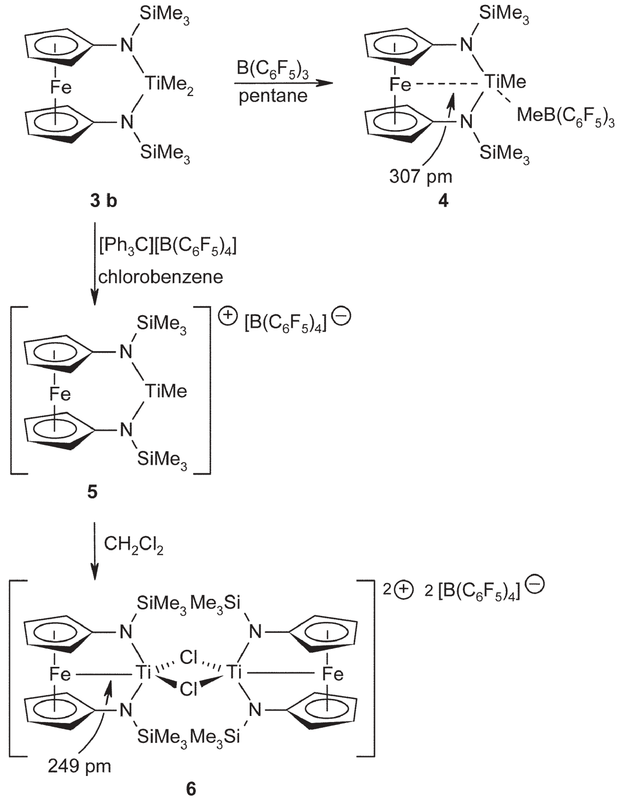


Fig. 4 Synthesis of titanium chelates with Fe → Ti dative bond.

$[\{Fe[C_5H_4(NSiMe_3)]_2\}Zr(CH_2Ph)][B(C_6F_5)_4]$ was found to polymerise ethylene with an activity of 102 g of PE (mmol catalyst)$^{-1}$ h^{-1} bar^{-1}.[12] When $[(PhCH_2)B(C_6F_5)_3]^-$ was used as the counter anion, close ion pairing occurred in the solid state and also in solution, leading to a greatly reduced activity towards ethylene. The reaction was sufficiently slow to detect the formation of the mono-, di- and tri-insertion products by ^{1}H NMR spectroscopy after 20 min. The reaction was even slower, when the $SiMe_3$ substituents were replaced by mesityl groups. $[\{Fe[C_5H_4(NMes)]_2\}Zr(CH_2Ph)][PhCH_2B(C_6F_5)_3]$ (**7**) afforded the mono-insertion product **8** in the presence of an excess of ethylene (4 equiv.) on a time scale of ca. 30 min at room temperature (Fig. 5).[8b] Compound **7** failed to oligomerise 1-hexene.

With the essentially non-coordinating $[B(C_6F_5)_4]^-$ counter anion, however, $[\{Fe[C_5H_4(NMes)]_2\}Zr(CH_2Ph)]^+$ proved to be able to polymerise up to 400 equiv. of 1-hexene, yielding poly-1-hexene with molecular weights up to 20 000 with relatively low polydispersities (PDI = 1.3–1.4). Ethylene polymerisation was also attempted with $[\{Fe[C_5H_4(NPh)]_2\}Zr(NMe_2)_2(HNMe_2)]$ (**3h**) and $[\{Fe[C_5H_4(NPh)]_2\}Ti(NMe_2)_2]$ (**3g**) under industrially relevant conditions (40 bar ethylene, 70 °C, complex/MAO = 1/280), resulting in rather low activities of 6.5 and 11.2 g PE (mmol catalyst)$^{-1}$ h^{-1} bar^{-1}, respectively.[13]

We have started investigations concerning the influence of various aryl groups on the properties of these zirconium chelates (Fig. 6).

In the case of Ar = Ph, the crystal structures of the zirconium chelates $[\{Fe[C_5H_4(NPh)]_2\}Zr(NMe_2)_2(HNMe_2)]$ (**3h**) and $[\{Fe[C_5H_4(NPh)]_2\}ZrCl_2(HNMe_2)]$ (**3i**) show that the zirconium centre is competing with the respective phenyl ring for each nitrogen lone pair of the $[Fe(C_5H_4NPh)_2]$ ligand, the phenyl rings being in the N–Zr–N chelate plane (Fig. 7, left).[6] The zirconium atom is pentacoordinate in these compounds, containing $HNMe_2$ as an additional ligand, which is liberated in the metathesis reaction of $[Fe\{C_5H_4(NHPh)\}_2]$ (**2d**) with $Zr(NMe_2)_4$. In $[Fe\{C_5H_4(NCH_2Ph)\}_2Zr(NMe_2)_2]$ (**3e**), no such coordination of $HNMe_2$ is observed, which is most likely related to the electron-donating properties of the alkylamido units present.[7] Owing to steric reasons, the orientation of the aryl groups is perpendicular to the N–M–N plane in the case of zirconium chelates with Ar = 2,4,6-*i*-$Pr_3C_6H_2$, each aryl π-system being decoupled from the respective nitrogen lone pair. The zirconium centre does not compete with the aryl rings for the nitrogen lone pairs of the chelate ligand (Fig. 7, right), leading to a higher π-loading of the metal centre. Consequently, no coordination of $HNMe_2$ is observed in the structurally characterised chelate $[\{Fe[C_5H_4(NC_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3)]_2\}Zr(NMe_2)_2]$ (**3k**).[14]

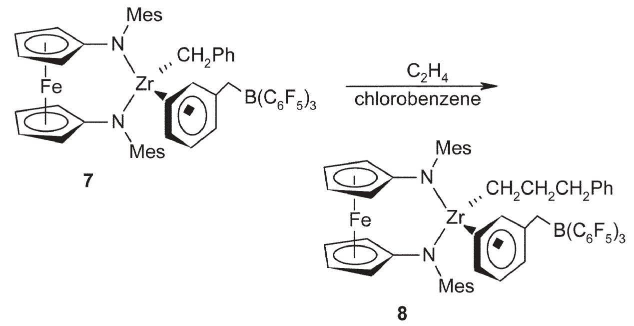


Fig. 5 Reaction of **7** with ethylene, affording the mono-insertion product **8**.

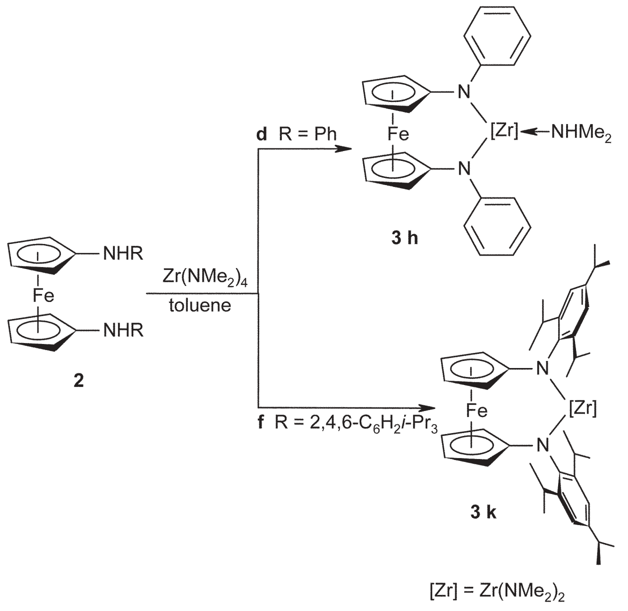


Fig. 6 Metathesis of $Zr(NMe_2)_4$ with **2d** and **2f**.

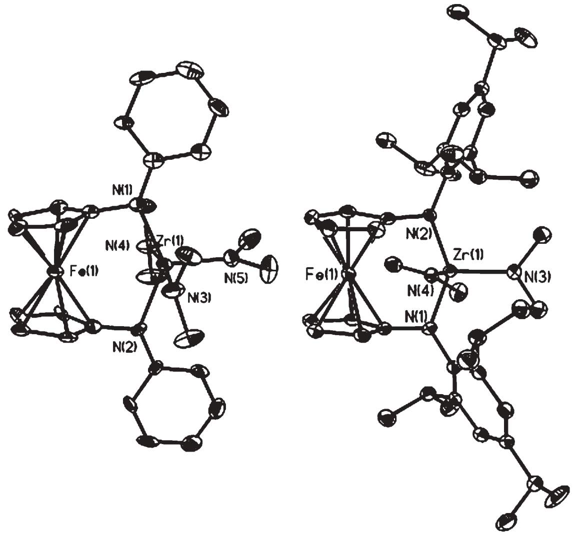


Fig. 7 Molecular structure of $[\{Fe[C_5H_4(NPh)]_2\}Zr(NMe_2)_2(HNMe_2)]$ (**3h**, left) and $[\{Fe[C_5H_4(NC_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3)]_2\}Zr(NMe_2)_2]$ (**3k**, right) in the crystal.

The synthesis of the C_2 symmetric zirconium chelate **3f** was described by the group of Arnold (Fig. 8).[9] Such species are relevant to the stereospecific polymerisation of α-olefins. However, catalytic studies have not been reported to date.

2.2 The diamino framework $[Fe(C_5H_4NR_2)_2]$

Transition metal chelates of this ligand family have been investigated by Plenio and coworkers, who have used

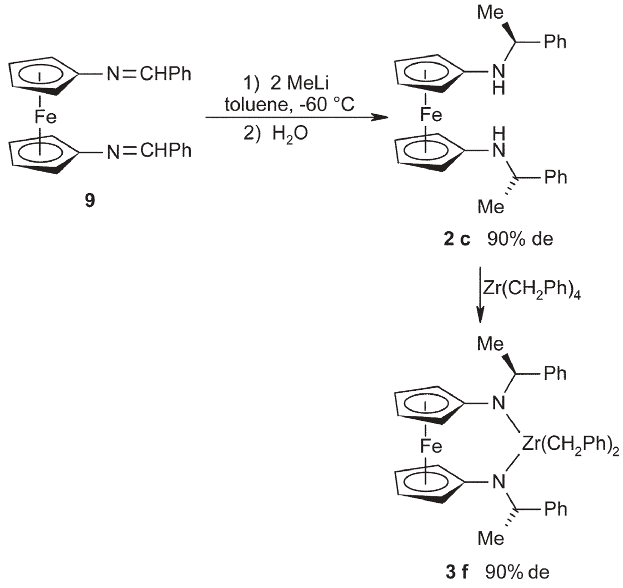
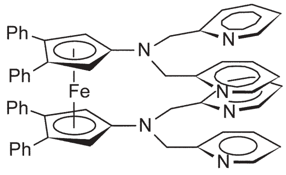


Fig. 8 Synthesis of the C_2-symmetric zirconium chelate **3f**.

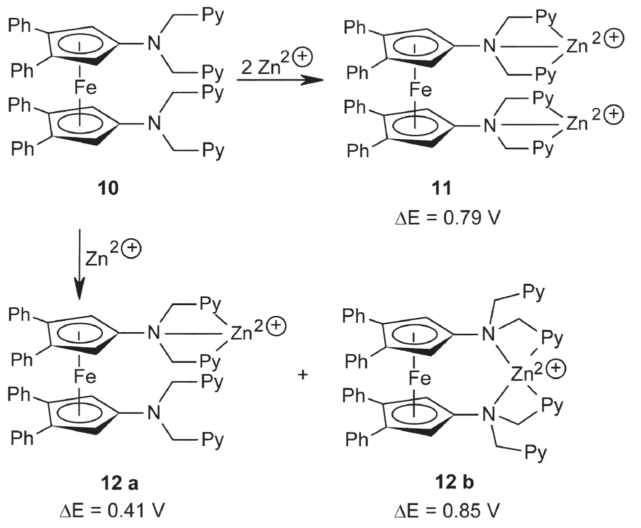


10

Fig. 9 The hexadentate ligand **10**.

compound **10** in their studies (Fig. 9).[15] This species contains six potentially ligating nitrogen atoms.

A detailed electrochemical study of the behaviour of **10** towards zinc triflate in acetonitrile revealed that this system is rather complicated (Fig. 10). **10** can accommodate up to two zinc centres, each one being coordinated by two pyridyl N atoms and the corresponding cyclopentadienyl-connected N atom. The presence of two zinc centres in **11** leads to a pronounced anodic shift of the redox potential of **10** of 0.79 V. The situation is less obvious for a 1:1 stoichiometry of **10** and zinc triflate. Two different isomers, **12a** and **12b**, can be formed, which differ dramatically in their redox potentials. In one of these species, the presence of one zinc centre leads to an anodic shift of the redox potential of **10** of 0.41 V, which is approximately half as large as the effect observed for the 2:1 complex. It is therefore very likely that the single zinc centre is coordinated in the same fashion as each of the two zinc centres in the 2:1 complex. This is compatible with isomer **12a**. The second isomer possible in the case of a 1:1 stoichiometry seems to be chelate **12b**, where the zinc centre is coordinated by both cyclopentadienyl-connected N-atoms (plus two pyridyl N atoms). This leads to a very short distance between the redox-active unit and the coordinated metal centre and hence to an anodic shift of the redox potential of **10** which, owing to particularly large electrostatic interactions, is even higher than that found for a 2:1 stoichiometry. Essentially the same behaviour was observed towards Co^{2+}. In principle, therefore, **10** can be used as a molecular electrochemical sensor for metal ions in solutions.



Py = 2-pyridyl

Fig. 10 Reaction of **10** with one and two equivalents of Zn^{2+}.

2.3 The diimino framework [Fe(C_5H_4N=CR)$_2$]

Hor and coworkers have prepared the palladium chelate [$PdCl_2${Fe(C_5H_4N=CHPh)$_2$}] (**13**) by reaction of [$PdCl_2$(MeCN)$_2$] with [Fe(C_5H_4N=CHPh)$_2$] (**9**) (Fig. 11).[16] This compound proved to be stable towards air and moisture. It effectively catalyses Suzuki cross-coupling reactions of aryl iodides and bromides with aryl boronic acids in aqueous media under non-homogeneous conditions in which the products can be easily isolated and the catalyst retrieved. Reusability of the catalyst proved to be good, with yields decreasing only marginally in five consecutive runs.

Complexes containing more elaborate diimino ligands were investigated by the group of Arnold, who utilised the Salen type derivatives **14a** and **14b** (Fig. 12).[17]

Deprotonation with dibutyl magnesium and subsequent reaction with MCl_4 (M = Ti, Zr) yielded the chelates **15** and **16**, respectively. Metathesis of **14a** and **14b** with $Zr(CH_2Ph)_4$ afforded **17a** and **17b**, respectively. **15–17** exhibit hexacoordinate Group 4 metal centres with a square-planar conformation of the chelate ligand. An analogous product (**19**) was formed with the closely related diimine **18** (Fig. 13).[17]

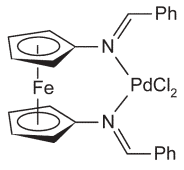


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Fig. 11 The palladium chelate **13**.

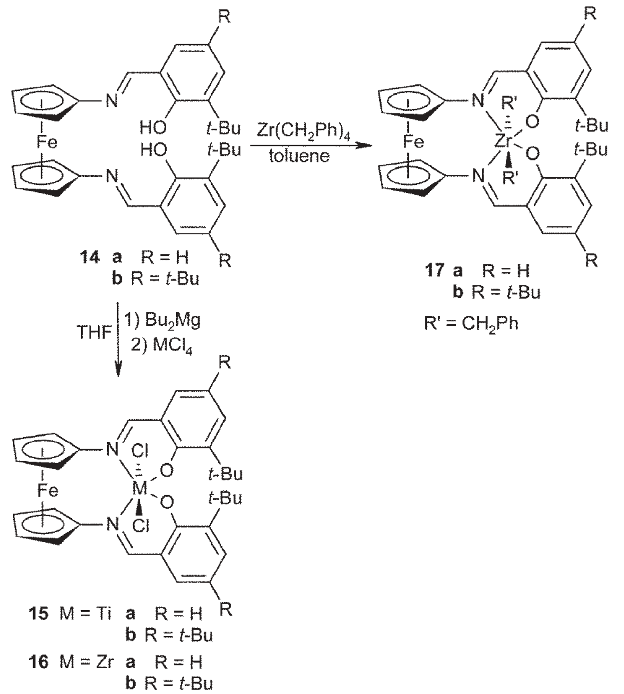


Fig. 12 Synthesis of the Group 4 metal complexes **15–17**, containing a Salen type ligand.

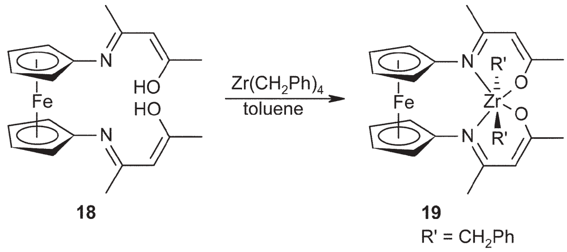


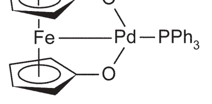
Fig. 13 Synthesis of the zirconium chelate **19**.

3. [O,O] ligands

3.1 The dialkoxo framework $[Fe(C_5H_4O)_2]^{2-}$

Akabori *et al.* have published the palladium chelate $[Fe(C_5H_4O)_2]Pd(PPh_3)$ (**20**) (Fig. 14), which was obtained from the reaction of the sodium salt $Na_2[Fe(C_5H_4O)_2]$ with $[PdCl_2(PPh_3)_2]$.[18]

The ruthenocene analogue $[Ru(C_5H_4O)_2]Pd(PPh_3)$ was structurally characterised by X-ray diffraction and exhibits a Ru–Pd distance of 269.2(1) pm, compatible with a weak dative bond. Probably, therefore, $[Fe(C_5H_4O)_2]Pd(PPh_3)$ (**20**) exhibits an Fe → Pd interaction. No further reports of related chelates have been published. This paucity is rather surprising in view of the great importance of transition metal dialkoxo chelates. For example, Ti dialkoxo complexes are known to be useful not only for α-olefin polymerisation,[4] but also for the addition, both stoichiometric and catalytic, of nucleophiles to carbonyl groups, and enantioselective reactions of this type are easily feasible with chiral dialkoxo ligands.[19]



20

Fig. 14 The only transition metal chelate containing the dialkoxo ligand $[Fe(C_5H_4O)_2]^{2-}$.

3.2 The diether framework $[Fe(C_5H_4OR)_2]$

First examples of transition metal chelates containing this type of ligand were published by Sato *et al.*[20] An interesting modification of this motif was introduced by Mirkin and co-workers, who employed redox-switchable hemilabile phosphane-ether ligands for an investigation of fundamental aspects of hemilability.[21] In a series of Rh^I and Pd^{II} complexes (Fig. 15), electrochemical investigations by cyclic voltammetry revealed a rather dramatic influence of the coordinated metal centre on the redox potential of the respective chelate ligand, which is anodically shifted by *ca.* 0.4 and 0.6 V for Rh^I and Pd^{II}, respectively.

Oxidation of the chelate ligand leads to a decrease of the complex formation constant by factors of more than 10^{10} for Pd^{II} and up to *ca.* 10^7 for Rh^I. The different anodic shifts of the half-wave potential reflect differences in inductive withdrawal of electron density from the ferrocene unit as well as different electrostatic interactions between the oxidised ferrocene unit and the cationic metal centres. The iron–metal distances are *ca.* 4.0 Å for all compounds investigated. A detailed analysis revealed that electrostatic effects contribute substantially to the thermodynamic destabilisation of the chelates upon oxidation. Not surprisingly, the large changes in complex stability coincide with substantial changes in reactivity. Oxidation of the rhodium complex **21b** caused a much larger affinity towards acetonitrile (Fig. 16). The Rh–O bond weakens upon oxidation of the ferrocene unit, which leads to an increase of the complex formation constant of the acetonitrile complex **23** by a factor of more than 10^7.

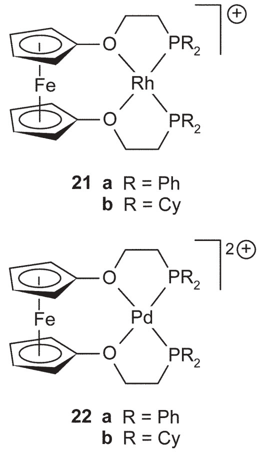
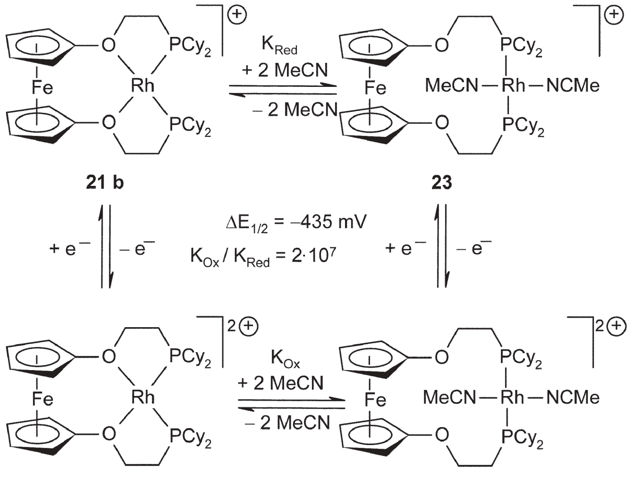


Fig. 15 The cationic chelates **21** and **22**, containing hemilabile phosphane-ether ligands.



21 b **23**

Fig. 16 Square scheme showing the redox-chemical effect on the affinity of **21b** towards acetonitrile.

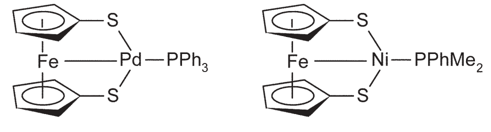
4. [S,S] ligands

4.1 The dithiolato framework $[Fe(C_5H_4S)_2]^{2-}$

A lot of work has been done with this ligand in late transition metal chemistry, addressing, *inter alia*, the question whether the iron atom may act as an electron donor to metal centres chelated by such ligands. The first example, **24**, was prepared by Seyferth *et al.* by reacting $[Pd(PPh_3)_4]$ with 1,2,3-trithia[3]-ferrocenophane (Fig. 17).[22] This compound contains a dative Fe → Pd bond (287.8(1) pm), rendering the palladium centre tetracoordinate.[23]

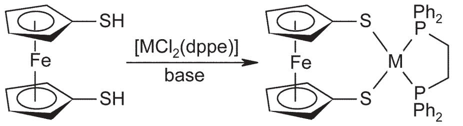
The analogous platinum complex was prepared soon after.[24] It exhibits a Fe–Pt bond length of 293.5(2) pm. The corresponding nickel complex could not be obtained with PPh_3 as a ligand. However, the chelate **25** with a Ni–Fe distance of 288.6(1) pm was obtained from the reaction of $[NiCl_2(PPhMe_2)_2]$ with $[Fe(C_5H_4SH)_2]$ (**26**) in the presence of potassium hydroxide as a base (Fig. 17).[25] Obviously, the comparatively weak Fe → Ni donation is compensated by the more electron-donating nature of the $PPhMe_2$ ligand. Use of the bis(phosphane) ligand dppe enforced formation of chelates without a dative Fe → M bond for M = Ni, Pd, Pt, as evidenced by Fe–M distances well above 400 pm for the structurally characterised chelates of nickel (**27a**) and palladium (**27b**) (Fig. 18).

The group of Herberhold has studied a wide range of late transition metal chelates containing the 1,1′-ferrocenedithiolato ligand utilising 16 valence electron metal ligand fragments of the type Cp*ML (M = Rh, Ir; L = PR_3, CN*t*-Bu).[26] The dithiolato ligand acts a neutral 2 electron donor in these complexes. Treatment of $[\{Fe(C_5H_4S)_2\}Ir(PPh_3)Cp^*]$ (**28**) with elemental sulfur removed the phosphane ligand. This procedure did not lead to the formation of a dative Fe → M bond. Instead, the sulfur-bridged dimeric complex $[Cp^*Ir^{III}\text{-}\{\mu\text{-}Fe(C_5H_4S)_2\}]_2$ (**31**) was formed (Fig. 19, bottom). The same species was obtained from the metathesis reaction of $Li_2[Fe(C_5H_4S)_2]$ with the chloro complex $[Cp^*Ir^{III}(\mu\text{-}Cl)Cl]_2$. In this case, each dithiolato ligand functions as a neutral 4 electron donor.



24 **25**

Fig. 17 The palladium and nickel chelates **24** and **25**, containing the dithiolato ligand $[Fe(C_5H_4S)_2]^{2-}$.

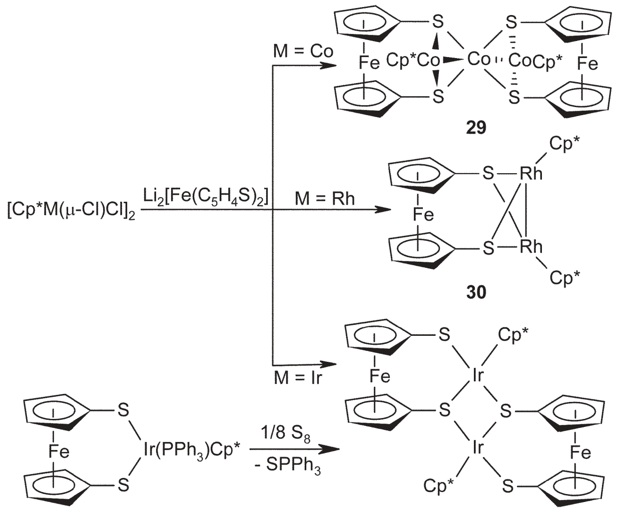


26 **27 a** M = Ni
b M = Pd
c M = Pt

Fig. 18 The Group 10 metal chelates **27** do not exhibit a dative Fe → M bond.

In the analogous reactions with $[Cp^*Rh^{III}(\mu\text{-}Cl)Cl]_2$ and $[Cp^*Co^{III}(\mu\text{-}Cl)Cl]_2$ redox processes occur, which account for the formation of rather different products (Fig. 19). In the case of Rh, the sulfur-bridged $[(Cp^*Rh^{II})_2\{\mu_2\text{-}Fe(C_5H_4S)_2\}]$ (**30**) was obtained. This compound contains a Rh–Rh bond, and the single dithiolato ligand acts a neutral 6 electron donor, bridging two rhodium centres. In the case of Co, the paramagnetic complex $[Co^{II}\{Cp^*Co^{II}[\mu_2\text{-}Fe(C_5H_4S)_2]\}_2]$ (**29**) was formed.[27] It contains a bent Co_3 chain. As in the Rh complex **30**, the $[\mu\text{-}Fe(C_5H_4S)_2]$ unit acts as a neutral 6 electron ligand, bridging in this case two cobalt centres.

The Ru^I chelate $[\{(p\text{-cymene})Ru^I\}_2\{\mu_2\text{-}Fe(C_5H_4S)_2\}]$ (**33**) described by the group of Hidai is a close relative of $[(Cp^*Rh^{II})_2\{\mu_2\text{-}Fe(C_5H_4S)_2\}]$ (**30**).[28] It contains a Ru–Ru



29 **30** **28** **31**

Fig. 19 Reaction of $Li_2[Fe(C_5H_4S)_2]$ with $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Co, Rh, Ir), affording the structurally very different products **29–31**.

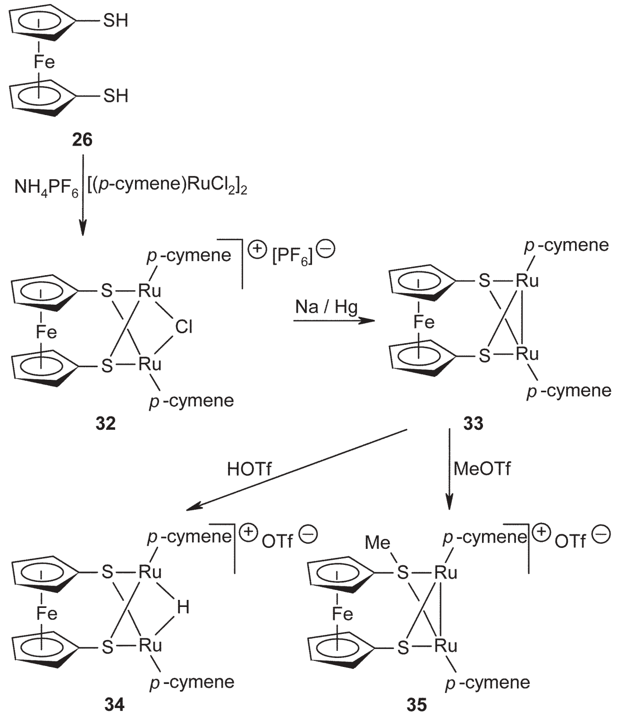


Fig. 20 Synthesis of the ruthenium chelates **32–35**.

bond and its dithiolato ligand acts as a neutral 6 valence electron donor. It was synthesised by chemical reduction of [{(*p*-cymene)Ru^{II}}$_2${μ$_2$-Fe(C_5H_4S)$_2$}(μ-Cl)]PF_6 (**32**) with sodium amalgam (Fig. 20). The Ru^{II} precursor was obtained straightforwardly from [Fe{(C_5H_4(SH)}$_2$] (**26**) and [(*p*-cymene)Ru^{II}Cl$_2$]$_2$. Protonation of [{(*p*-cymene)Ru^{I}}$_2${μ$_2$-Fe(C_5H_4S)$_2$}] (**33**) with triflic acid occurred at the Ru–Ru bond, affording the hydrido-brigded [{(*p*-cymene)Ru^{II}}$_2${μ$_2$-Fe(C_5H_4S)$_2$}(μ-H)]OTf (**34**). Alkylation with methyl triflate occurred at one of the sulfur atoms, yielding [{(*p*-cymene)-Ru^{I}}$_2${μ$_2$-Fe(C_5H_4S)(C_5H_4SMe)}]OTf (**35**), whose cation contains a chelate ligand with a mixed thioether/thiolate donor set. Such species will be dealt with in section 4.3 of this review.

As a last example from late transition metal chemistry, the redox-active iron–sulfur cluster [{Fe(C_5H_4S)$_2$}Fe(μ-S)]$_2$ (**36**) was obtained from the reaction of 1,2,3-trithia[3]ferrocenophane and $FeCl_3$ in the presence of NaS*t*-Bu as reducing agent (Fig. 21).[29] The sulfur-coordinated Fe^{III} centres are antiferromagnetically coupled.

The cluster core of **36** is akin to structural models of [2Fe–2S] redox proteins, the presence of two additional Fe^{II} centres being a new aspect. A reversible one-electron reduction of the Fe^{III}$_2$S$_2$ cluster core was easily achieved. However, in contrast to related Fe_2S_2 type clusters, full reduction to a Fe^{II}$_2$S$_2$ system was not possible down to −2.5 V (*vs.* ferrocenium/ferrocene), probably owing to the presence of the electron-rich ferrocene moieties.

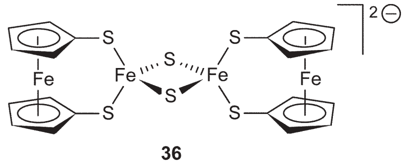


Fig. 21 The iron–sulfur cluster **36**.

Comparatively few early transition metal chelates containing the ferrocene-based dithiolato ligand have been published to date. Steudel *et al.* synthesised [{Fe(C_5H_4S)$_2$}TiCp$_2$] (**37**) from [Fe{C_5H_4(SH)}$_2$] (**26**) and Cp_2TiCl_2 in the presence of triethyl amine as a base (Fig. 22).[30] Gibson *et al.* reported the chelates [{Fe(C_5H_4S)$_2$}M(NMe$_2$)$_2$] (**38**, M = Ti, Zr), which were prepared metathetically from [Fe{C_5H_4(SH)}$_2$] (**26**) and M(NMe$_2$)$_4$ (Fig. 22). In the presence of trimethylaluminium and MAO, both amido complexes polymerised ethylene, albeit with low activities (M = Ti: 3 g mmol^{-1} h^{-1} bar^{-1}, M = Zr: 15 g mmol^{-1} h^{-1} bar^{-1}).[31]

4.2 The dithioether framework [Fe{C_5H_4(SR)}$_2$]

A lot of earlier work in this area has been devoted to the synthesis of thia-crown ether type derivatives for the complexation of soft metal centres. The effect of metal coordination on the redox potential of the ferrocene-based chelate ligand can be very large even for simple non-cyclic ligands. For example, an anodic shift of 0.42 V is observed for [Fe{C_5H_4(S*i*-Pr)}$_2$] upon formation of the silver complex [Ag{Fe[C_5H_4(S*i*-Pr)]$_2$}$_2$]$^+$.[32] Both ferrocene units are oxidised at the same potential and can be considered as identical, non-interacting redox sites. Essentially the same behaviour was observed for the related tetrathia[5.5]ferrocenophane complex [Ag{Fe[C_5H_4(SCH$_2$)]$_2$CH$_2$}$_2$]$^+$ (**39**) (Fig. 23), whereas the corresponding palladium complex [Pd{Fe[C_5H_4(SCH$_2$)]$_2$-CH$_2$}$_2$]$^{2+}$ exhibits two oxidation waves separated by 0.13 V, which indicates a weak interaction between the ferrocene

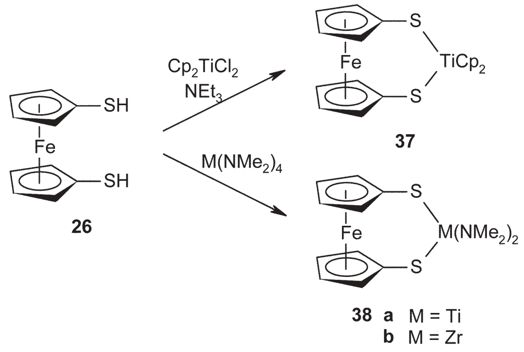


Fig. 22 Early transition metal chelates containing the dithiolato ligand [Fe(C_5H_4S)$_2$]$^{2-}$.

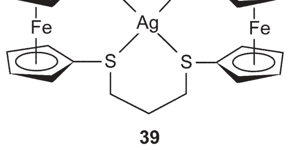


Fig. 23 The thiacrown complex **39**.

units.[33] It appears unlikely, however, that this interaction is based on an electronic contribution by a dative Fe → Pd bond, because the distance between these atoms is *ca.* 4 Å.

Mirkin and coworkers have utilised the potentially tetradentate hemilabile ligand $[Fe\{C_5H_4(SCH_2CH_2PPh_2)\}_2]$ in rhodium chemistry (Fig. 24).[21] Coordination of a Rh^I centre caused an anodic shift of the redox potential of this ligand of 0.64 V. A reversible process could be observed only at high scan rates ($100\ V\ s^{-1}$).

Oxidation of the ferrocene unit of $[Rh\{Fe[C_5H_4(SCH_2CH_2PPh_2)]_2\}]^+$ (**40**) destabilises the complex thermodynamically by a factor of more than 10^{11}. This effect is much larger than that observed for the related ether analogue $[Rh\{Fe[C_5H_4(OCH_2CH_2PPh_2)]_2\}]^+$ (**21a**), where a destabilisation by a factor of *ca.* 10^7 was observed (*vide supra*). The Fe–Rh distance is *ca.* 4.0 Å in both monocationic complexes, so that electrostatic effects are expected to be very similar. Ligand-based oxidation weakens the comparatively strong Rh–S bond more than the less strong Rh–O bond.

Working with the bulky mesityl-substituted $[Fe\{C_5H_4(SMes)\}_2]$ (**41**) Long and coworkers have obtained the chelates $[\{Fe[C_5H_4(SMes)]_2\}MCl_2]$ (**42**, M = Pd, Pt) (Fig. 25).[34] In the case of **42b** (M = Pt), a cyclometalation reaction occurred upon prolonged heating in refluxing toluene solution, afording the hexacoordinate Pt^{IV} complex **43**.

The group of Long has also been addressing more complex thioether-functionalised chelate ligands, *viz.* unsymmetrical and oligodentate systems. In an investigation of the coordination chemistry of the potentially tridentate $[Fe\{C_5H_4(SMe)\}\{C_5H_3(SMe)_2\}]$, which contains a cyclopentadienyl ring functionalised with two neighbouring SMe groups in addition to a monosubstituted cyclopentadienyl ring, it turned out that a $W(CO)_4$ fragment is chelated by the two neighbouring SMe groups of the difunctionalised cyclopentadienyl ring.[35] When the tetrasubstituted analogue $[Fe\{C_5H_3(SMe)\}_2]$ was reacted with $[W(CO)_4(nbd)]$ (nbd = 2,5-norbornadiene), acting as a source of the $W(CO)_4$ fragment, the mononuclear tungsten complex **44** (Fig. 26) was obtained in low yield instead of the expected dinuclear $[\{Fe[C_5H_3(SMe)_2]_2\}\{W(CO)_4\}_2]$.

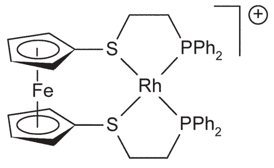


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Fig. 24 The cationic rhodium chelate **40**, containing a phosphane-thioether ligand.

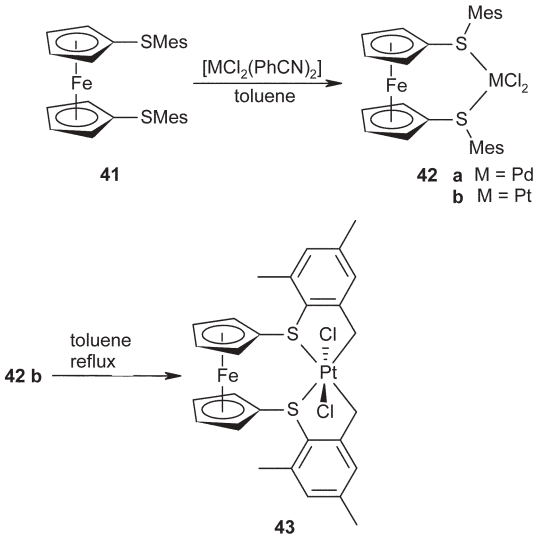

Fig. 25 Synthesis of the Group 10 metal chelates **42** and **43**.

Among the unsymmetrical 1,1′-disubstituted ferrocenes investigated by Long and coworkers, simple examples are $[Fe\{C_5H_4(SR)\}\{C_5H_4(SR')\}]$ (R ≠ R′: Me, *t*-Bu, Ph).[36] Reactions of these ferrocene derivatives with $[MCl_2(PhCN)_2]$ (M = Pd, Pt) afforded the expected chelates $[\{Fe[C_5H_4(SR)][C_5H_4(SR')]\}MCl_2]$. In contrast to the platinum analogues, the palladium chelates tended to decompose upon one-electron oxidation. Formation of the tungsten carbonyl complexes $[\{Fe[C_5H_4(SR)][C_5H_4(SR')]\}W(CO)_4]$ proved unexpectedly difficult by standard methodology, especially with the two SPh substituted ligands. This was ascribed to the comparatively poor donor properties of this substituent. As a further extension of this ligand framework, potentially tetradentate ligands **45–47** which contain two ferrocene moieties connected by a bridging unit were investigated (Fig. 27).[37]

Reaction of **46b** and **47b** with $[Cu(MeCN)_4]PF_6$ afforded the respective dinuclear copper(I) chelate, whose copper centres were connected by two bridging anions. Likewise, dinuclear palladium chelates **48** were obtained upon reaction of **46b** and **47b** with $[PdCl_2(cod)]$ (Fig. 28). Catalytic studies in combination with electrochemical investigations have been announced for these complexes.

In view of the relevance of thioether ligands in the coordination chemistry of gold, it seems surprising that only a single paper has been addressing gold chelates containing $[Fe\{C_5H_4(SR)\}_2]$ type ligands.[38] The reaction of 1,1′-di(phenylthio)ferrocene with $[Au(OTf)PPh_3]$ afforded $[\{Fe[C_5H_4(SPh)]_2\}AuPPh_3]OTf$ (**49**) (Fig. 29). Related silver(I) chelates could be obtained as well.

4.3 The mixed thioether/thiolate framework $[Fe\{C_5H_4(SR)\}(C_5H_4S)]^-$

One of the first examples in this area, $[\{(p\text{-cymene})Ru^I\}_2\{\mu_2\text{-}Fe(C_5H_4S)[C_5H_4(SMe)]\}]OTf$ (**35**),[28] has already been mentioned in section 4.1. Related compounds were described by

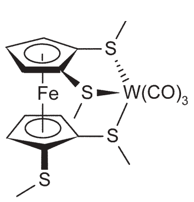

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Fig. 26 The tungsten chelate **44**, with three of the four thioether units coordinating.

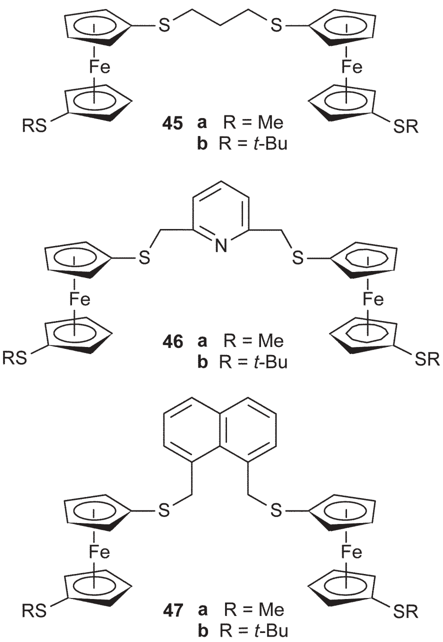

Fig. 27 The oligodentate thioether ligands **45**–**47**.

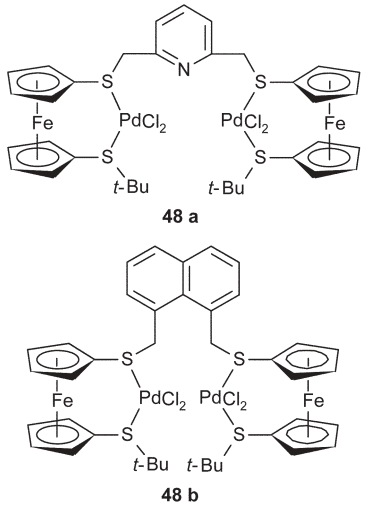

Fig. 28 The palladium chelates **48**.

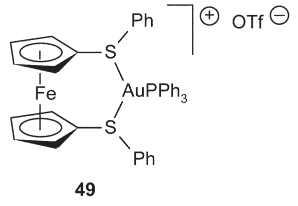

Fig. 29 The cationic gold chelate **49**.

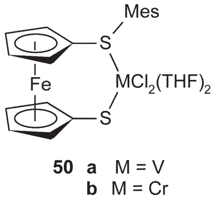

Fig. 30 The early transition metal chelates **50**, containing the thioether/thiolate ligand $[Fe(C_5H_4S)\{C_5H_4(SMes)\}]^-$.

Long and coworkers, who have devised an elegant synthetic route to unsymmetrical 1,1′-disubstitued ferrocenes containing a thiol as well as a thioether substituent, starting from 1,2,3-trithia-[3]ferrocenophane. This opens up the opportunity to develop a rich coordination chemistry of such, potentially hemilabile, ligands. Chelates of the type $[\{Fe(C_5H_4S)[C_5H_4(SMes)]\}MCl_2(THF)_2]$ (**50**, M = V, Cr) were obtained from the metathesis reaction of $[MCl_3(THF)_3]$ with $Li[Fe(C_5H_4S)\{C_5H_4(SMes)\}]$ (Fig. 30).[39] These compounds were used as precatalysts in the polymerisation of ethylene. By far the best result was obtained with the vanadium compound **50a**, which, after activation with dichloromethylaluminium, exhibited an activity of 28 g mmol^{-1} h^{-1} bar^{-1}.

In late transition metal chemistry, the sulfur-bridged dimers $[(MCl)_2\{\mu_2\text{-}Fe(C_5H_4S)[C_5H_4(SMes)]\}_2]$ (**51**, M = Pd, Pt) were synthesised from $[MCl_2(PhCN)_2]$ and $Li[Fe(C_5H_4S)\{C_5H_4(SMes)\}]$ (Fig. 31).[39]

The *t*-Bu analogue $[(PdCl)_2\{\mu_2\text{-}Fe(C_5H_4S)[C_5H_4(S\textit{t}\text{-}Bu)]\}_2]$ (**53**) was formed in an unusual insertion reaction into the S–S bond of $[(\eta^5{:}\eta^5\text{-}C_5H_4SSC_5H_4)\{Fe(C_5H_4(S\textit{t}\text{-}Bu)\}_2]$ (**52**) upon reaction with $[PdCl_2(PhCN)_2]$ (Fig. 32).[36]

5 Applications

A lot of compounds described in the previous chapters show properties which make them potentially useful as molecular electrochemical sensors or as catalysts. Metal ion sensing has explicitly been addressed by the group of Plenio, utilising the diamino framework $[Fe\{C_5H_4(NR_2)\}_2]$ (cf. Chapter 2.2).[15] The close proximity between the metal ion binding site and the redox-active unit leads to very large electrochemical effects, which is highly beneficial for a sensor system. Such advantageous behaviour has also been observed with ferrocene-based phosphane-ether ligands (*cf.* section 3.2) and with several [S,S] type ligands (*cf.* section 4.2).

In the area of homogeneous catalysis, quite a number of early transition metal chelates containing the diamido framework $[Fe\{C_5H_4(NR)\}_2]^{2-}$ have been tested in α-olefin polymerisation (*cf.* section 2.1).[5,6,8*a*,11–13] The best results in ethylene polymerisation have been reported for $[\{Fe[C_5H_4(NSiMe_3)]_2\}Zr(CH_2Ph)][B(C_6F_5)_4]$, which showed an activity

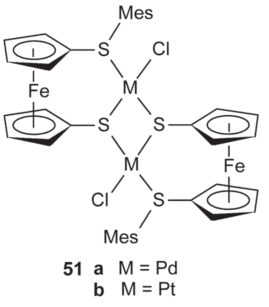

Fig. 31 The Group 10 metal chelates **51**.

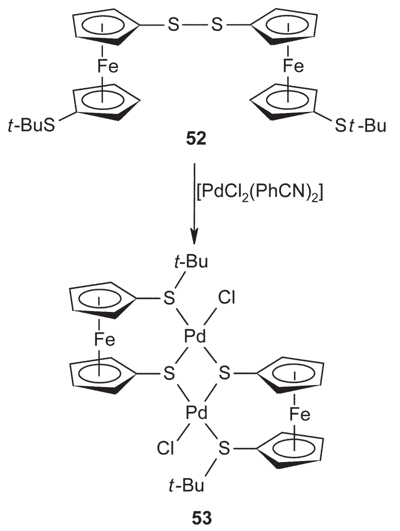

Fig. 32 Syntheses of the palladium chelate **53** by insertion reaction.

of 102 g of PE (mmol catalyst)$^{-1}$ h^{-1} bar^{-1}.[12] In the case of 1-hexene, [{Fe[C_5H_4(NMes)]$_2$}Zr(CH_2Ph)][B(C_6F_5)$_4$] gave the best results reported so far.[8b] The redox-switchable properties of such catalytic systems have been realised and patented.[40] Related Group 4 metal chelates containing the dithiolato framework [Fe(C_5H_4S)$_2$]$^{2-}$ showed rather low activities towards ethylene.[31]

In the chemistry of late transition metal chelates, the use in catalytic reactions has been very limited. We note that [$PdCl_2${Fe(C_5H_4N=CHPh)$_2$}] (**13**) has been used in Suzuki cross-coupling reactions (*cf.* section 2.3).[16]

6 Conclusion and outlook

Much progress has been made in the subject area of this review over the past decade. The focus has clearly been on synthetic methods and structural aspects so far, where, by and large, a state of maturity has now been reached. Considering the number of recent papers, the two most active domains currently are those concerning ferrocene-based diamido ligands and sulfur-containing ligand systems, whereas the chemistry of ferrocene-based [O,O] chelate ligands appears to be in a dormant state. There is a huge lack of knowledge especially in the area of transition metal chelates containing the [Fe(C_5H_4O)$_2$]$^{2-}$ ligand, since just a single example has been reported to date.

Examples for successful applications have been reported with quite a number of compounds already, and it is clear that this is only the beginning, since 'studies on the way' have been announced in several very recent papers, most of them addressing catalytic applications. In view of the rather well-developed synthetic methodology available, this augurs well for new and exciting results, especially in the area of catalysis. The well-behaved redox-chemical properties of ferrocene derivatives will be beneficial for future investigations concerning the redox-tunability of molecular structure and reactivity with these compounds. This fascinating aspect has been addressed in only a few papers so far and is still in its infancy. Another hitherto almost neglected aspect which will most likely attract more attention in the future concerns stereochemistry, since it is easy to introduce chirality into ferrocene derivatives, and the ferrocene-based planar chirality never undergoes racemisation.

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