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Invited Review

Studies on the cyclometallation of ferrocenylimines

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Abstract

This review describes the cyclometallation reaction, including cyclomercuration, cyclopalladation and cycloplatination of Schiff base type of ferrocenylimines as well as the transmetallation reaction of cyclometallated ferrocenylimines and the stereochemistry associated with these reactions. The applications of cyclopalladated ferrocenylimines in several fields are also demonstrated in this review. The molecular and crystal structures of the products as well as the absolute configurations of optically active products were established by X-ray diffraction, NMR techniques, IR, UV–vis, etc. The general features of these reactions, especially the regioselectivity and the reaction mechanisms, are discussed. In addition, the structure–property relationships are discussed throughout this investigation. The transmetallation of optically pure cyclometallated ferrocenylimines with other metals such as mercury, tin and tellurium was found to proceed with complete retention of stereochemistry. This discovery led to a convenient method for the synthesis of optically pure cyclometallated organic compounds that are difficult to prepare by using conventional methods. Accordingly, a number of cyclometallated ferrocenylimines have been prepared in optically pure forms, which display surprisingly high angles of rotation.

Keywords: Ferrocenylimine; Cyclometallation; Transmetallation; Intramolecular coordination; Structure–property relationships; Stereochemistry; Applications

1. Introduction

The synthesis and isolation of ferrocene was first reported independently by two research groups, Kealy and Pauson from Duquesene University [1], and Miller et al. from British Oxygen Company [2], in late 1951 and early 1952, respectively. Shortly after that, the structural determination of ferrocene revealed an iron metal sandwiched by two cyclopentadienyl (Cp) ligands, which lie in parallel planes. The Cp ligands were bonded covalently to the iron center; however, they rotated freely with respect to each other, and this 'new type of organo-iron compound' was found to be aromatic, highly stable and soluble in most common organic solvents [3–8]. These discoveries marked major milestones and turning points in the evolution of modern organometallic chemistry, and not only renewed and expanded the concept of chemical bonds which inspired many new fields of chemistry, but also laid the foundation for the widespread development of the chemistry of ferrocene and other metallocenes. A half century later, ferrocene chemistry has developed into one of the most fruitful fields in organometallic chemistry [9], and still attracts a great deal of chemical interest. One of the most exciting developments in this area over the last two decades is the cyclometallation of ferrocene derivatives. The cyclometallation reaction is a chemical process involving chelation-controlled regioselective C–H bond activation of a ligand with metallating reagents to form new C–M bonds as well as metallocycles [10]. The cyclometallation of ferrocene and other metallocene derivatives results in the formation of planar chiral cyclometallated metallocenes as

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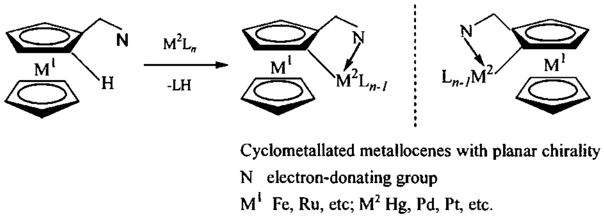
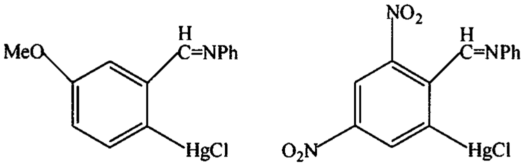
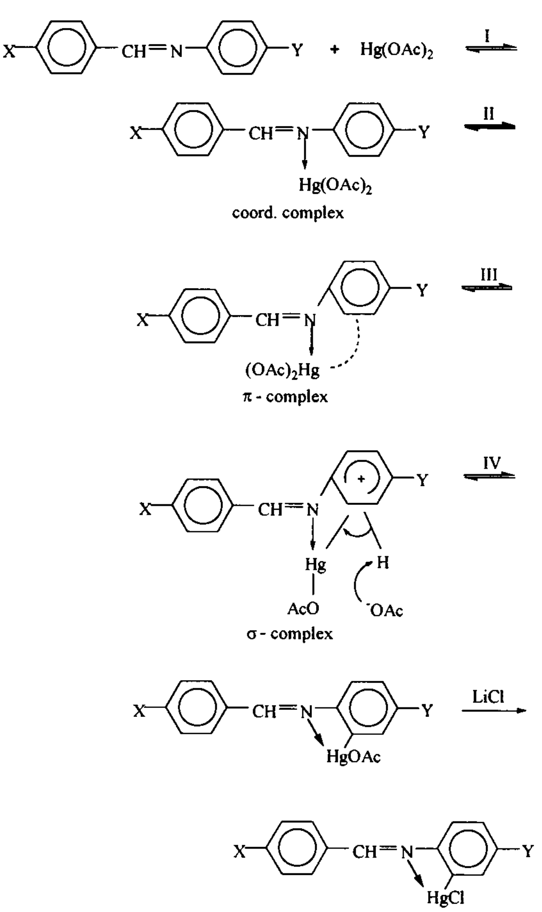
shown in Scheme 1 and this product distinguishes the reaction from the cyclometallation of any other types of ligands, and shows great potential in asymmetric synthesis. In this review, we focus on recent work involving the cyclometallation of ferrocenylimines with both the main group and the transition metal complexes. We attempt to address several important issues in this development, such as structure–property relationships, intramolecular coordination chemistry, transmetallation, stereochemistry, selectivity, and applications of cyclopalladated ferrocenylimines in several fields of chemistry.



Scheme 1.



Scheme 2.

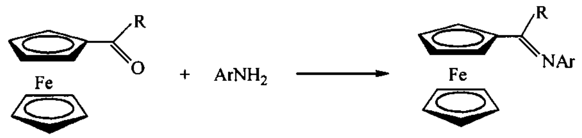


Scheme 3.

2. Cyclomercuration of ferrocenylimines

We initiated studies on the cyclomercuration of Schiff bases of substituted benzylideneanilines about ten years ago [11] because of our interest in C–H activation of aromatic compounds by nontransition metals as well as the effect of intramolecular coordination between the *ortho*-substituted electron donating group and Hg atom on the reactivity and spectral properties of cyclomercurated aromatic compounds [12]. At that time, direct *ortho*-mercuration was primarily restricted to reactions of substituted azobenzenes [13] and phenylhydrazones [14]. Two interesting mercurated molecules (Scheme 2) derived from substituted benzylideneanilines [15] prompted us to investigate the relationship between their structures and physical organic chemical properties.

However, when we repeated the reaction reported by Singh et al., we did not get the reported five-membered cyclomercurated products. Instead, a systematic study on the mercuration of various substituted benzylideneanilines, $XC_6H_4CH{=}NC_6H_4Y$, demonstrated that the Hg atom was directed into the phenyl ring adjacent to the nitrogen atom (*N*-phenyl) as opposed to the ring adjacent to carbon (*C*-phenyl) (Scheme 3). ^{1}H-NMR, ^{13}C-NMR, ^{199}Hg-NMR and X-ray crystal structural analysis of mercurated Schiff bases supported the existence of an N–Hg intramolecular coordination bond within a four-membered ring [16]. MNDO calculation on the electron population in the substrates and kinetic measurements of the reaction confirmed that N–Hg coordination was crucial for the regioselectivity of the reaction and that the cyclomercuration proceeded via a four-membered ring transition state (Scheme 3) [17]. This conclusion serves to amend the rule summarized by Bruce with regard to the formation of a five-membered chelating ring [18]. By means of transmetallation of Schiff base arylmercurials with metallic tin [19] or 4-ethoxyphenyl-tellurium(IV)-trichloride [20], the above-mentioned conclusion has been further verified and proved the existences of four-membered chelating rings with N–Sn and N–Te intramolecular coordination in the products. Moreover, such an intramolecular coordination has a stabilizing effect on the molecules of the products [19]. The effect of N–Hg intramolecular coordination on regioselectivity of the reaction is particularly evident in the cyclomercuration of ferrocenylimines.



R=H(**1**), CH$_3$(**2**), Ph(**3**) R=H(**4**), CH$_3$(**5**), Ph(**6**)
Ar=p-OCH$_3$C$_6$H$_4$(**a**), p-CH$_3$C$_6$H$_4$(**b**), C$_6$H$_5$(**c**), p-ClC$_6$H$_4$(**d**), p-BrC$_6$H$_4$(**e**), p-IC$_6$H$_4$(**f**), p-NO$_2$C$_6$H$_4$(**g**), m-CH$_3$C$_6$H$_4$(**h**), m-ClC$_6$H$_4$(**i**), m-BrC$_6$H$_4$(**j**), m-NO$_2$C$_6$H$_4$(**k**), o-ClC$_6$H$_4$(**l**), 1-naphthyl(**m**), 2-naphthyl(**n**)

Scheme 4.

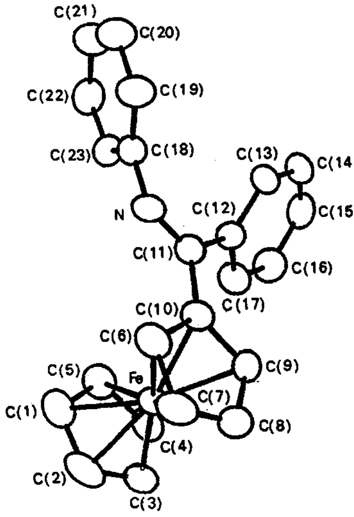
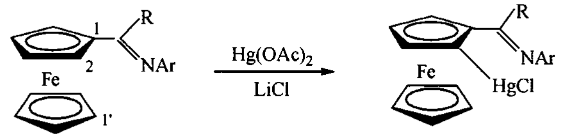


Fig. 1. Molecular structure of **6c**.



R=H(**4**), CH$_3$(**5**), Ph(**6**) R=H(**7**), CH$_3$(**8**), Ph(**9**)

Scheme 5.

2.1. Cyclomercuration of monoferrocenylimines

2.1.1. Preparation of monoferrocenylimines

Ferrocenylaldimines or ferrocenylketimines can be generally prepared by the direct condensation of acylferrocenes with amines. By using formylferrocene (**1**), acetylferrocene (**2**) and benzoylferrocene (**3**) and arylamines as starting materials, the corresponding ferrocenylaldimines (**4**), ferrocenylketimines (**5**) and (**6**) were synthesized, respectively, under different conditions [21–23] (Scheme 4).

It was found that the formed ferrocenylketimines **6** existed as two isomers in solution (2D NOESY determination), in which 90% was the *trans* isomer. The X-ray crystal structure of compound **6c** disclosed a *trans* conformation that is the ferrocenyl moiety and the *N*-phenyl ring lie in the different sides of the C=N bond [24] (Fig. 1). The interesting feature of this molecule is the specific arrangement of two phenyl rings and substituted Cp ring around the C=N plane. The substituted Cp ring is approximately coplanar with the plane by a twist angle of only 8.16° whereas the *C*-phenyl ring forms a much larger angle of 50.68° with the plane, and the dihedral angle between the *N*-phenyl ring and the plane is 61.38°, indicating a considerable extent of nonplanarity of this aromatically substituted imine.

Other procedures have been also reported for the synthesis of similar ferrocenylimines [25–27], involving tedious multiple Dean–Stark condensation operations and/or the use of molecular sieves as promoters in some cases.

2.1.2. Cyclomercuration of monoferrocenylimines

Mercuration of aromatic compounds including ferrocene derivatives has been extensively investigated in organic or organometallic synthesis as well as mechanistically. On one hand, organomercury compounds are valuable intermediates for organic synthesis, permitting a variety of further transformations, such as halogenation, transmetallation, and C–C bond formations [28]; on the other hand, mercuration is a generally mild reaction and the resultant organomercury compounds are very stable and easy to handle, which, therefore, provides excellent opportunities to investigate the reaction mechanism, stereochemistry, and selectivity. Chelation-controlled cyclomercuration (also termed '*ortho*-mercuration') of the aromatic ligands with N or O donors has been one of the major topics in this area.

Although direct mercuration of substituted azobenzenes, phenylhydrozones and benzylideneanilines has been reported [11,13,14], the development of cyclomercuration of ferrocenylimines appeared only recently [23,29,30]. The cyclomercuration of **4**–**6**, in a total of 37 ferrocenylimines, had been carried out. The reaction of ferrocenylimines with mercuric acetate followed by subsequent treatment with lithium chloride proceeded smoothly to produce predominantly 2-chloromercurated ferrocenylimines (Scheme 5).

Obviously, N → Hg intramolecular coordination played an important role in this reaction. The effect of an aryliminomethyl group (ArN=CH–) on ferrocene can be twofold: steric and electronic. Electronically, this group will deactivate the substituted Cp ring towards electrophilic substitution, and sterically, this substituent can inhibit the attack at the 2-position of the substituted Cp ring, so the mercuration of aryliminomethylferrocene should have occurred predominantly on the 1′-position due to the higher reactivity of the unsubstituted Cp ring. But in fact, mercuration occurs predominantly on the 2-position. The regiospecificity of this reaction suggests that mercury is directed into the *ortho*-position by coordination of mercury to imino nitrogen with subsequent electrophilic substitution. The chromatographic and spectral properties of the 2-mercurated products show the presence of an intramolecular N → Hg coordination *via* a five-membered ring in these molecules, and this was further confirmed by X-ray single-crystal structure analysis, which will be discussed in the following section.

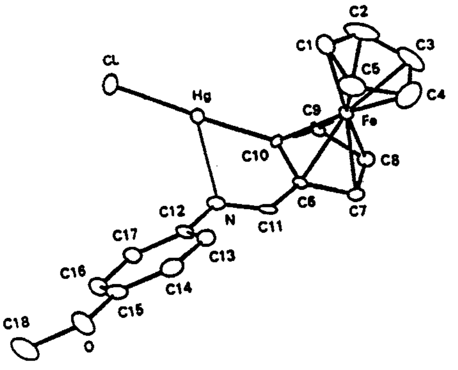


Fig. 2. Molecular structure of **7a**. N–Hg, 2.897(2) Å; C(10)–C(6)–C–(11), 123.4°; C(6)–C(10)–Hg, 120.7°; C(10)–Hg–Cl, 176.84°; angles (°) between planes: A and B, 52.0; A and C, 41.78.

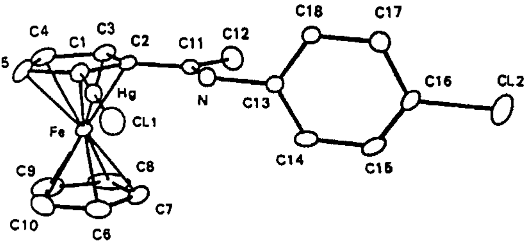


Fig. 3. Molecular structure of **8d**. N–Hg, 2.766 Å; Hg–C(1)–C(2), 121.3°; C(1)–C(2)–C(11), 124.0°; C(1)–Hg–Cl(1), 179.1°; angles (°) between planes: A and B, 91.68; A and C, 88.0.

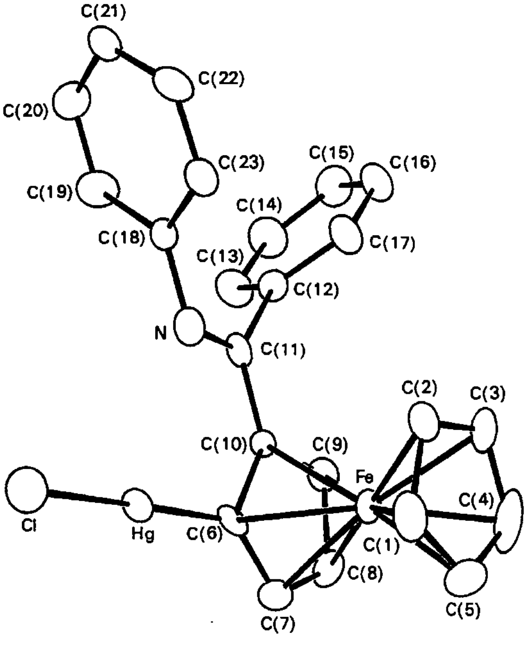


Fig. 4. Molecular structure of **9c**. N–Hg, 2.870 Å; Hg–C(6)–C(10), 120.6°; C(6)–C(10)–C(11), 125°; C(6)–Hg–Cl, 177.3°; angles (°) between planes: A and B, 78.55; A and C, 72.26.

2.1.3. Structural, spectral and chromatographic characteristics of cyclomercurated monoferrocenylimines

X-ray crystal structure analysis has been the most powerful tool used in the elucidation of structures of organometallic compounds. The structures of three cyclomercurated ferrocenylimines **7a**, **8d** and **9c** were determined to confirm the intramolecular N → Hg coordination present in these molecules. The structures are shown in Figs. 2–4, in which A, B and C represent the N-aryl ring, substituted Cp ring and plane of C=N, respectively. The distances between nitrogen and mercury in **7a**, **8d** and **9c** are 2.897 [29], 2.766 [30] and 2.870 Å [24], respectively. They are shorter than the sum of van der Waals radii of Hg, 1.5–1.6 Å [31–34], and N, 1.55 Å [35], indicating the presence of an intramolecular coordination in the molecules.

A number of spectroscopic techniques, such as IR, ^{1}H-NMR, ^{13}C-NMR, 2D-NMR, ^{199}Hg-NMR, and UV–vis, have been utilized to characterize cyclomercurated ferrocenylimines. In their IR spectra, the C=N absorptions are uniformly shifted down to lower energy by the range of 4–25 cm^{-1}, when compared with the corresponding starting ferrocenylimines, indicating an intramolecular N → Hg coordination. The ^{13}C-NMR spectra of three series of cyclomercurated ferrocenylimines **7**–**9** have been recorded. Good to excellent linear relationships between the chemical shifts and Hammett substituent constants σ were discovered. The differing sensitivities of the chemical shifts to the substituent effect for the three types of cyclomercurated compounds reflected their differing twist angles between the *N*-phenyl ring and the C=N plane [36].

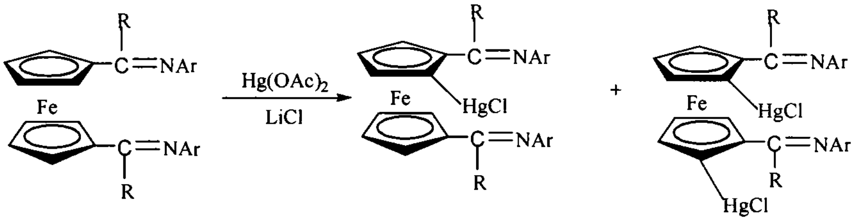
The ^{199}Hg chemical shifts of the compounds **7**–**9** are regularly disturbed by the substituents in the *N*-phenyl rings, and excellent linear correlations between ^{199}Hg shifts (δ) and Hammett constants σ_m or σ_p were obtained for all three series (Eqs. (1)–(3) for compounds **7**–**9**, respectively) [37].

$$\delta_7 = 733.8 - 15.7\sigma \quad N = 10 \; r = -0.993 \tag{1}$$

$$\delta_8 = 755.6 - 19.3\sigma \quad N = 10 \; r = -0.995 \tag{2}$$

$$\delta_9 = 761.3 - 19.9\sigma \quad N = 10 \; r = -0.986 \tag{3}$$

The directions of the substituent effect on δ are the same in three series of compounds (i.e. electron-donating substituents cause shifts to lower field), which is in agreement with the paramagnetic shielding theory for organomercury compounds derived by Jamson and Gutowsky [38] and the works reported by Xu et al. [39] and us [40,41]. The sensitivities of the ^{199}Hg shifts toward the substituent effect are different, ascending in the order of **7**–**9**. In general, there are two pathways for



10 **11** **12**

R=CH$_3$, Ar=*p*-OCH$_3$C$_6$H$_4$(**a**), *p*-CH$_3$C$_6$H$_4$(**b**), C$_6$H$_5$(**c**), *p*-ClC$_6$H$_4$(**d**), *p*-BrC$_6$H$_4$(**e**), *p*-NO$_2$C$_6$H$_4$(**f**), *m*-CH$_3$C$_6$H$_4$(**g**), *m*-ClC$_6$H$_4$(**h**), *m*-BrC$_6$H$_4$(**i**), *m*-NO$_2$C$_6$H$_4$(**j**), 1-naphthyl(**k**)
R=Ph, Ar= *m*-CH$_3$C$_6$H$_4$(**a**), *m*-BrC$_6$H$_4$(**b**)

Scheme 6.

the substituents in the *N*-phenyl ring to affect mercury: one is the transmission of electronic effects through the C=N bond and Cp ring, and the other involves the N → Hg intramolecular coordination. The structure determinations have shown that the most striking features for compounds **7**–**9** are the nonplanar nature of the *N*-phenyl ring with respect to the Cp rings or the plane, C–C=N–C, and that the twist angles θ of the *N*-phenyl ring out of the plane in compounds **8** and **9** are much larger than those in compounds **7** (88.0 and 72.26° for **8d** and **9c**, respectively, and 41.78° for **7a**). It becomes apparent that the substituent effects cannot be transmitted efficiently through the C=N bond and Cp ring *via* resonance effects especially in the case of **8** and **9**. It can be considered that the substituents affect mercury essentially by way of N → Hg interaction rather than through resonance effects. The larger twist angle θ is more favorable to n–π conjugation; as a result, the substituent in the *N*-phenyl ring for compounds **8** and **9** can disturb the n-electrons of nitrogen in a more efficient way and further influence the N–Hg coordination. The ^{199}Hg-NMR features support the intramolecular secondary interaction between n-electrons of the imino nitrogen atom and unoccupied 6p orbital of the mercury atom as well as the n–π conjugation between the imino nitrogen and the *N*-phenyl ring.

The comparative studies on the chromatographic affinity of ferrocenylimines and that of their derivatives of mercury have shown that the cyclomercurated compounds exhibit higher R_f values than the corresponding starting ferrocenylimines. The substituent effects on the R_f values show that the higher the electron density in the imino nitrogen atom, the lower the R_f value. This observation indicates the existence of an intramolecular N → Hg coordination in the molecules of cyclomercurated ferrocenylimines. The examination of UV–vis spectra of these compounds also supports the existence of the intramolecular N → Hg coordination. The effect of the substituent situated at the carbon atom of the imino group and in the *N*-phenyl ring on the UV–vis spectra was investigated. Compared with the λ_{max} of the ferrocenylimine in which there is no substituent on the *N*-phenyl ring, a good linear relationship was found between the $\Delta\lambda_{max}$ of the π–π^* CT band and the Hammett–Brown constants σ^+ [42].

2.2. Double cyclomercuration of bisferrocenylimines

The reaction of bisferrocenylimines with mercuric acetate and subsequent treatment with LiCl led to the formation of mono and double cyclomercurated derivatives [43,44] (Scheme 6).

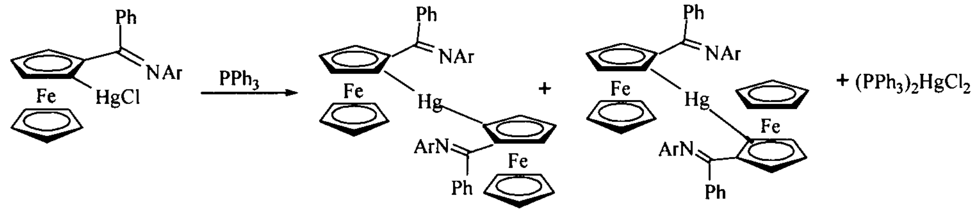
2.3. Symmetrization reaction of mercurated ferrocenylimines

The symmetrization reaction of mercurated anils of benzoylferrocene (**9**) was achieved by refluxing **9** and PPh$_3$ in CHCl$_3$ which afforded the symmetrized products [Hg{(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$–CPh=NAr)}$_2$] (Ar = a variety of substituted phenyls and 2-naphthyl) (**13**) (Scheme 7) [45].

During the reaction the organometallic complex salts [RHgPPh$_3$]Cl were formed, which could disproportionate to give the symmetrized products. The molecular structure of [Hg{(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$CPh=NC$_6$H$_4$-*m*-Br)}$_2$] (**13i**) (*meso*) has been determined by single-crystal X-ray analysis (Fig. 5). The distance between N(2) and Hg is 2.981(6) Å, shorter than the sum of van der Waals radii of N and Hg (3.05–3.15 Å), indicating an intramolecular coordination of N(2) and Hg. The ^{1}H-NMR spectra of [Hg{(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$CPh=NAr)}$_2$] (Ar = C$_6$H$_4$-*o*-Cl and 2-naphthyl) show that both compounds exist as rotamers in solution.

2.4. Regioselectivity in Hg(II) cyclomercurated complexes

The regioselectivity in the cyclomercuration of 1′-benzoyl-[1-(arylimino)phenylmethyl]ferrocenes (**14**) was



9 **13** *dl* **13** *meso*

Ar= p-OCH$_3$C$_6$H$_4$(**a**), p-CH$_3$C$_6$H$_4$(**b**), C$_6$H$_5$(**c**), p-ClC$_6$H$_4$(**d**), p-BrC$_6$H$_4$(**e**), p-IC$_6$H$_4$(**f**), m-CH$_3$C$_6$H$_4$(**g**), m-ClC$_6$H$_4$(**h**), m-BrC$_6$H$_4$(**i**), o-ClC$_6$H$_4$(**j**), 2-naphthyl(**k**)

Scheme 7.

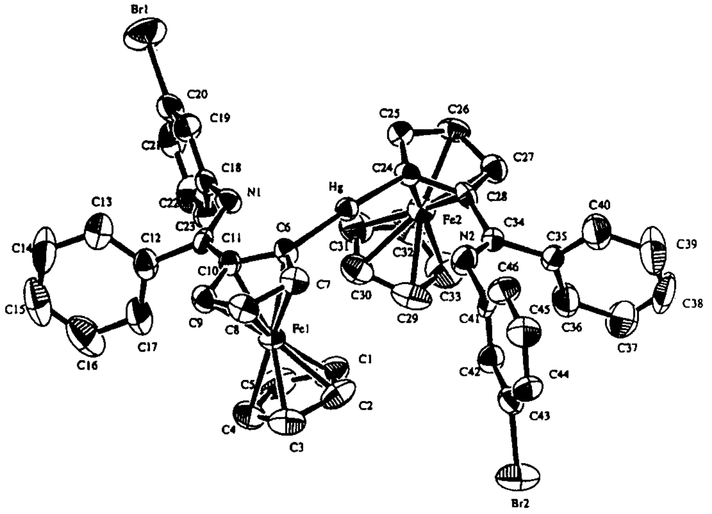
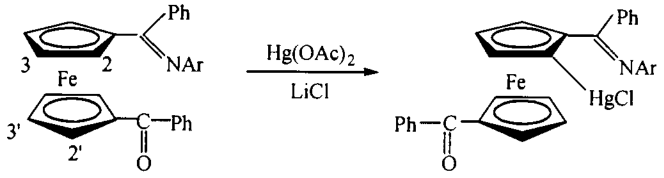


Fig. 5. Molecular structure of **13i**(*meso*).

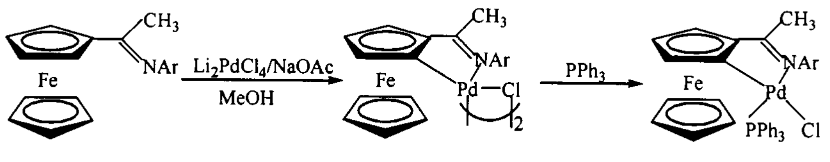


14 **15**

Ar= p-OCH$_3$C$_6$H$_4$(**a**), p-CH$_3$C$_6$H$_4$(**b**), C$_6$H$_5$(**c**), p-ClC$_6$H$_4$(**d**), p-BrC$_6$H$_4$(**e**), m-ClC$_6$H$_4$(**f**), m-BrC$_6$H$_4$(**g**), o-ClC$_6$H$_4$(**h**), o-BrC$_6$H$_4$(**i**)

Scheme 8.

studied (Scheme 8) [46]. In all cases, the mercuration occurred at the 2-position of the ferrocene ring, which indicated that the coordination ability of nitrogen was much stronger than that of oxygen. The results obtained indicated that yields were clearly influenced by the position of the substituent in the N-phenyl ring, and decreased in sequence *para* > *meta* > *ortho*. In view of this fact, it seems that the steric hindrance hindered the double cyclomercuration.



5 **16** **17**

Ar= p-$OCH_3C_6H_4$(**a**), p-$CH_3C_6H_4$(**b**), C_6H_5(**c**), p-ClC_6H_4(**d**), p-BrC_6H_4(**e**), p-IC_6H_4(**f**), p-$NO_2C_6H_4$(**g**), m-$CH_3C_6H_4$(**h**), m-ClC_6H_4(**i**), m-BrC_6H_4(**j**), m-$NO_2C_6H_4$(**k**), o-ClC_6H_4(**l**), 1-naphthyl(**m**), 2-naphthyl(**n**)

Scheme 9.

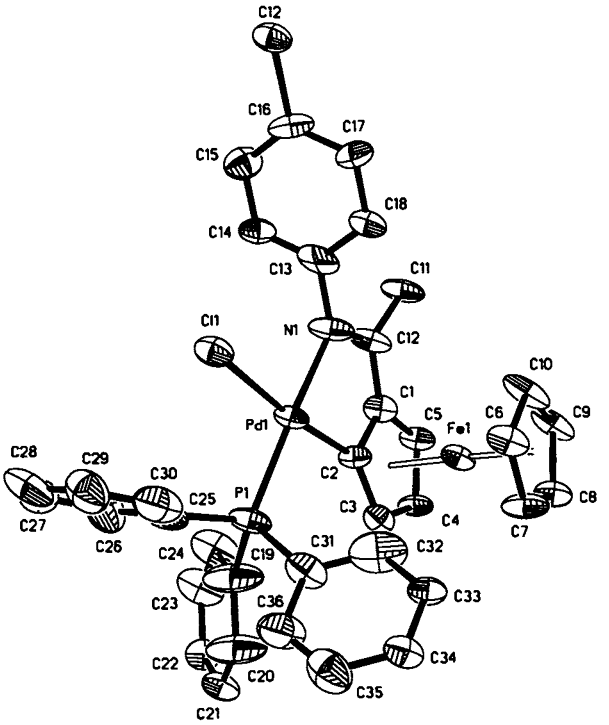


Fig. 6. Molecular structure of **17d**.

3. Cyclopalladation of ferrocenylimines

3.1. Cyclopalladation of monoferrocenylimines

The study of cyclopalladated ferrocene derivatives has increased considerably during the last two decades due to a wide variety of interesting and novel applications in different fields [26,27,47–57]. The initial favorable results obtained with cyclomercuration of ferrocenylimines [23,29,30] and our long-term interest in intramolecular coordination chemistry prompted us to carry out the cyclometallation reaction via use of transition metal complexes, such as Pd and Pt, as metallating reagents. Duff and Shaw and their co-workers have previously shown that an acetate ion promotes internal metallation reactions [58] and Sokolov et al. further demonstrated that the acetate ion not only serves as an acid binding agent consuming the hydrogen chloride liberated in the cyclopalladation, but participates in the formation of the reaction transition state as well [59,60]. As expected, we found that Schiff base type ferrocenylketimines **5** underwent cyclopalladation readily when treated with molar equivalents of Li_2PdCl_4 and NaOAc to produce a red crystalline solid, assigned to be a chlorine bridged binuclear complex of palladium **16** [61]. Compound **16** was converted into the monomeric derivative **17** quantitatively by treatment with triphenylphosphine as shown in Scheme 9.

In contrast, the reaction of **5** with Li_2PdCl_4 in the absence of NaOAc yielded a small amount of **16**, together with a considerable amount of the $Cl_2Pd(PPh_3)_2$(II) [61].

The X-ray crystal structure of cyclopalladated ferrocenylimine **17d** was determined. The structure, as shown in Fig. 6, indicated that the substituted Cp ring was palladated in an *ortho*-position, which formed a five-membered metallocycle as expected. The *N*-phenyl ring formed a dihedral angle of 76.0° with the C=N plane whereas the palladated Cp ring formed an angle of only 8.4°.

A series of cyclopalladated ferrocenylketimines $[Pd\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CPh{=}NAr)\}\text{-}Cl(PPh_3)]$ (**18**) can also be synthesized by the reaction of corresponding ferrocenylketimines **6** with Li_2PdCl_4 or Na_2PdCl_4/NaOAc followed by treatment with PPh_3 [62,63].

3.2. Double cyclopalladation of 1,1′-bis[1-(arylimino)ethyl]ferrocenes

Double cyclopalladation of a series of 1,1′-bis[1-(arylimino)ethyl]ferrocenes (**10**) ($R = CH_3$) with Li_2PdCl_4 followed by treatment with PPh_3 afforded *meso* and *dl* stereoisomers of bis(palladium)complexes **20** (Scheme 10). A mechanism for the formation of stereoisomers in the cyclopalladation reaction was suggested [64].

4. Cycloplatination of ferrocenylimines

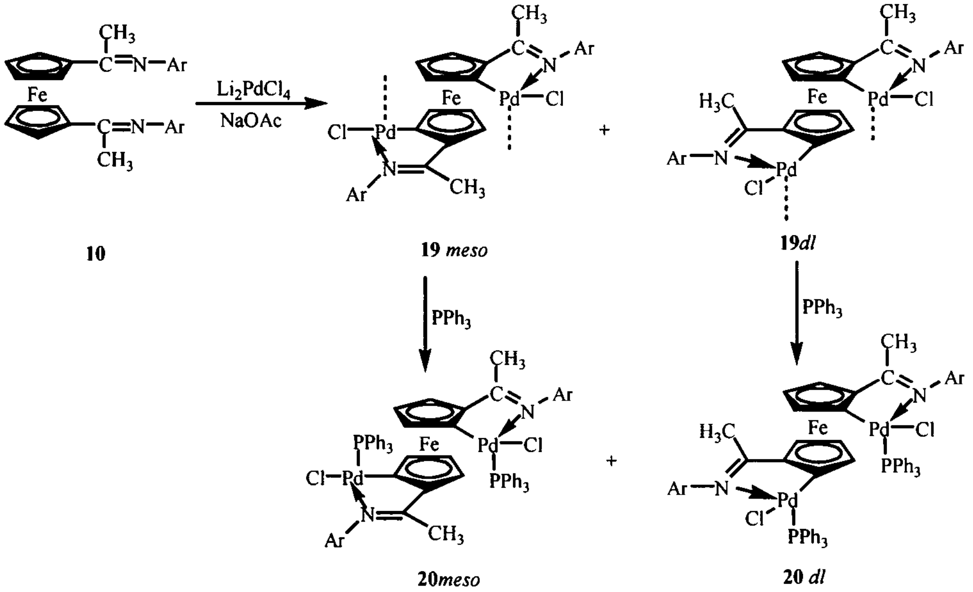
4.1. Cycloplatination of monoferrocenylimines

In contrast to the intensive studies on intramolecular cyclomercuration and cyclopalladation, there are only a few examples concerning the cycloplatination of nitrogen-containing ferrocene derivatives [65–77]. The first cycloplatinated ferrocene derivative was synthesized by Sokolov and his co-worker [65], via transmetallation reaction. The direct cycloplatination of ferrocene derivatives was achieved by using the *cis*-Pt(DMSO)$_2$Cl$_2$ as the precursor [66–73]. The bis(hexafluoroacetylacetonato)platinum was also found to be a useful platination reagent for 2-ferrocenylbenzothiazoline to afford a novel trinuclear Pt(II) complex, which has a six-membered Pt$_3$S$_3$ ring with thiolate bridging [74]. However, the *cis*-Pt(DMSO)$_2$Cl$_2$ is still most commonly used in direct cycloplatination.

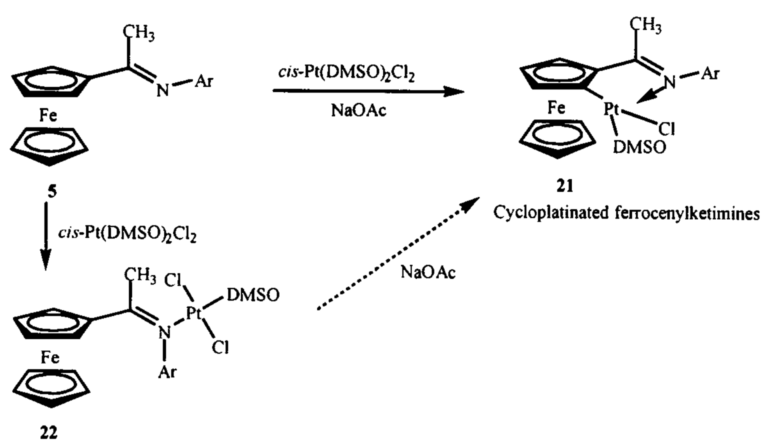
The reaction of ferrocenylimines **5** with *cis*-Pt(DMSO)$_2$Cl$_2$ in the presence of NaOAc led to the cycloplatinated compounds **21** (Scheme 11) [69].

In the absence of NaOAc, however, the coordinated complexes **22** were obtained. Several experimental examples have shown that **22** are stable intermediates before ring closure. The mechanism of cycloplatination of ferrocenylimines has been proposed (Scheme 12).

The X-ray crystal structures show that the C=N bond adopts a *trans* configuration in complex **22c**, as opposed to a *cis* configuration in compound **21c** (Figs. 7 and 8). Therefore, a transition state **23** might be in-

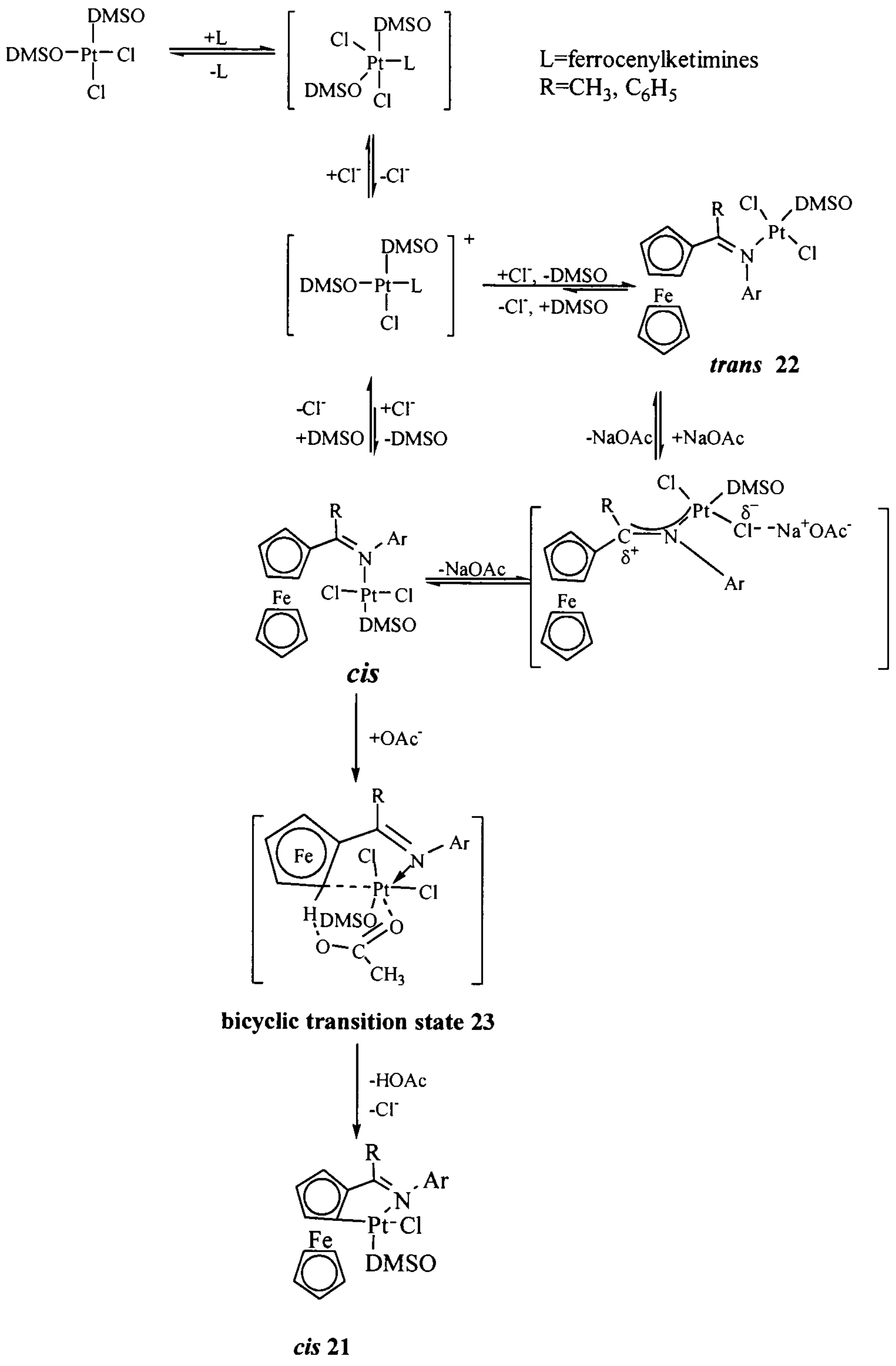


Scheme 10.



Ar = *p*-CH$_3$OC$_6$H$_4$(**a**), *p*-CH$_3$C$_6$H$_4$(**b**), C$_6$H$_5$(**c**), *p*-ClC$_6$H$_4$(**d**), *p*-BrC$_6$H$_4$(**e**), *p*-IC$_6$H$_4$(**f**), *p*-NO$_2$C$_6$H$_4$(**g**), *m*-CH$_3$C$_6$H$_4$(**h**), *m*-ClC$_6$H$_4$(**i**), *m*-NO$_2$C$_6$H$_4$(**j**), *o*-CH$_3$OC$_6$H$_4$(**k**), *o*-ClC$_6$H$_4$(**l**).

Scheme 11.



Scheme 12.

volved in the conversion of **22** into **21**. Excellent linear correlations existed between ^{195}Pt chemical shifts and Hammett constants of the substituents on the *N*-phenyl rings in both **21** and **22** [70], suggesting the existence of N → Pt intramolecular coordination as well as n–π conjugation between the nitrogen and the *N*-phenyl ring.

$$\delta\ (^{195}\mathrm{Pt})_2 = -3800.2 - 23.3\sigma \quad N=9 \quad r=-0.975 \qquad (4)$$

$$\delta\ (^{195}\mathrm{Pt})_3 = -2970.5 - 21.7\sigma \quad N=9 \quad r=-0.991 \qquad (5)$$

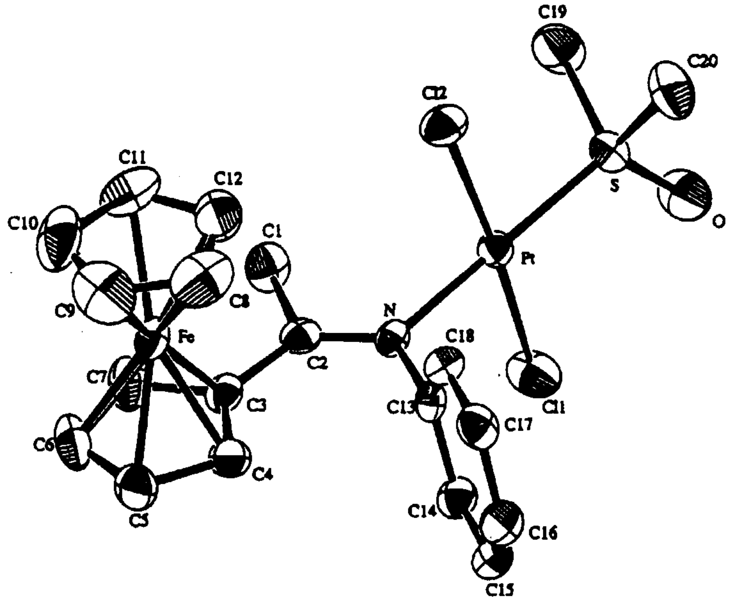


Fig. 7. Molecular structure of **22c**.

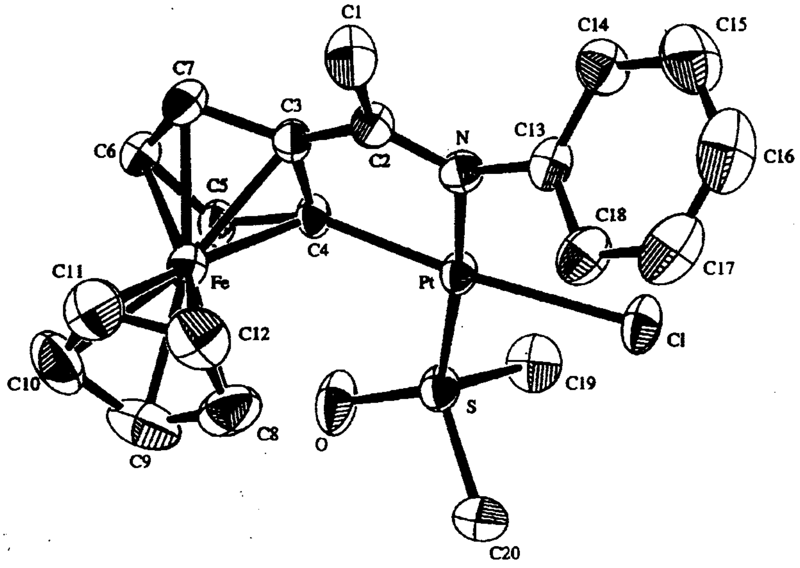


Fig. 8. Molecular structure of **21c**.

4.2. Double cycloplatination of bisferrocenylimines

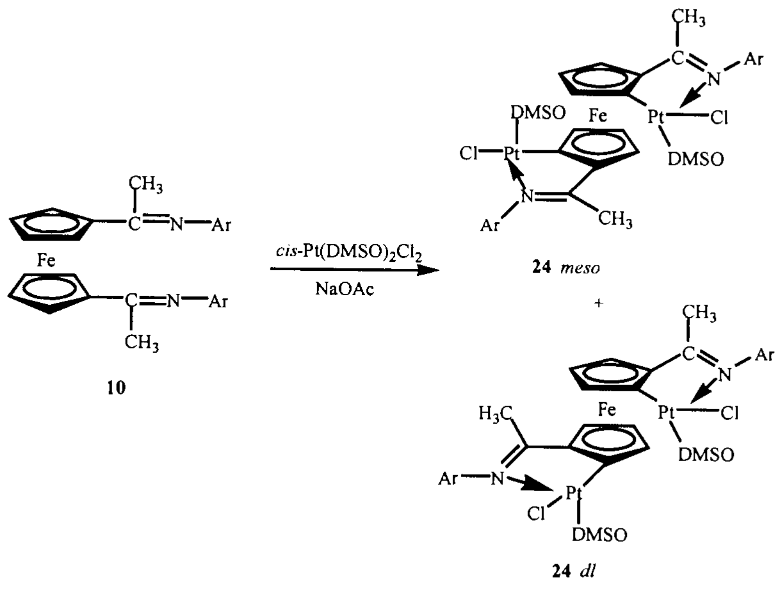
When 1,1′-bis(ferrocenylketimines) **10** (R = CH_3) were employed in cycloplatination, both *meso* and *dl* stereoisomers **24** were generated (Scheme 13) [71]. Similarly to double cyclopalladation, isomerism could be attributed to the sequential cycloplatination of the two cyclopentadienyl rings.

A study of the antitumor activity revealed that only the cycloplatinated compounds **21** had antiproliferative properties [78].

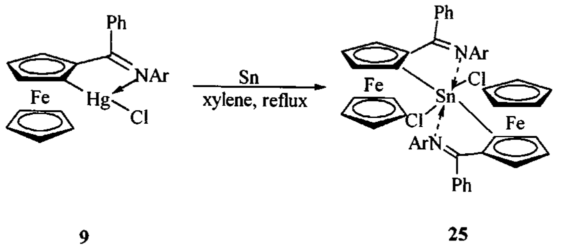
5. Transmetallation of cyclometallated ferrocenylimines

5.1. Transmetallation reaction of cyclomercurated anils of benzoylferrocene with metallic tin

The transmetallation reaction is one of the most powerful methods to synthesize the organometallic compounds which are not obtainable by direct cyclometallation. Cyclostannated ferrocenylimines could so far only be synthesized via transmetallation of corresponding cyclomercurated or cyclopalladated com-

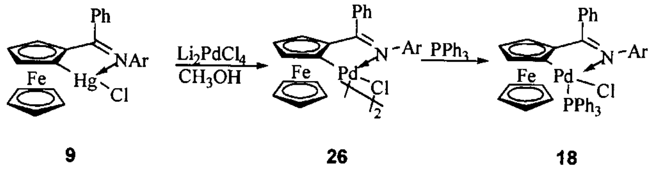


Scheme 13.



Ar= p-OCH$_3$C$_6$H$_4$(**a**), p-CH$_3$C$_6$H$_4$(**b**), C$_6$H$_5$(**c**), p-ClC$_6$H$_4$(**d**), p-BrC$_6$H$_4$(**e**), m-CH$_3$C$_6$H$_4$(**f**), m-ClC$_6$H$_4$(**g**), m-BrC$_6$H$_4$(**h**)

Scheme 14.



Scheme 15.

pounds with metallic tin [79,80]. When cyclomercurated ferrocenylketimines **9** were employed as the starting material, the cyclostannated compounds **25** were formed in moderate to good yields [79] (Scheme 14).

The molecular structure of **25b** showed the coordination sphere of the tin atom to be a highly distorted octahedron with two *trans*-positioned ferrocenyl groups in the axial sites (Fig. 9). The coordination between the

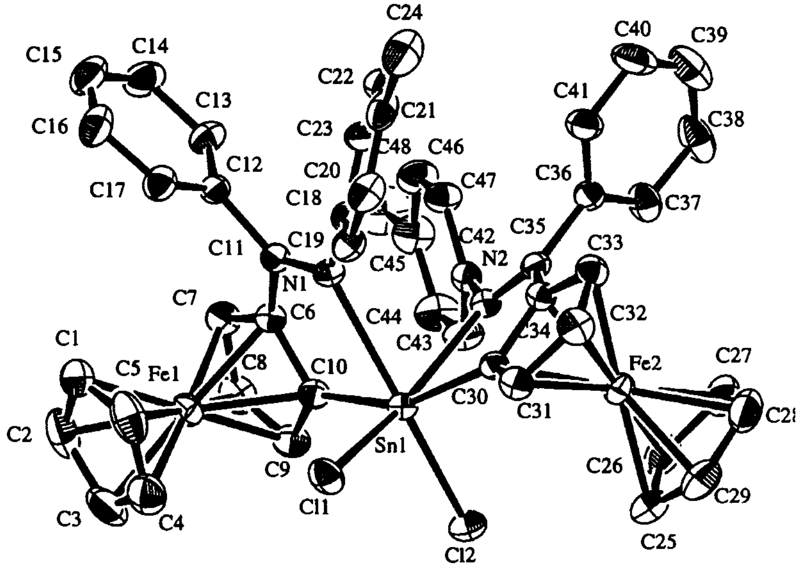
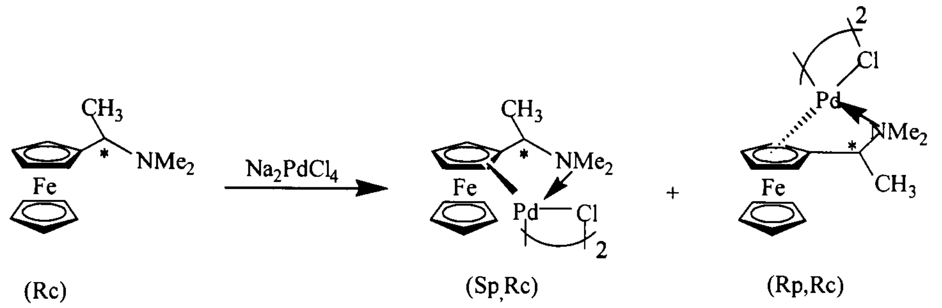
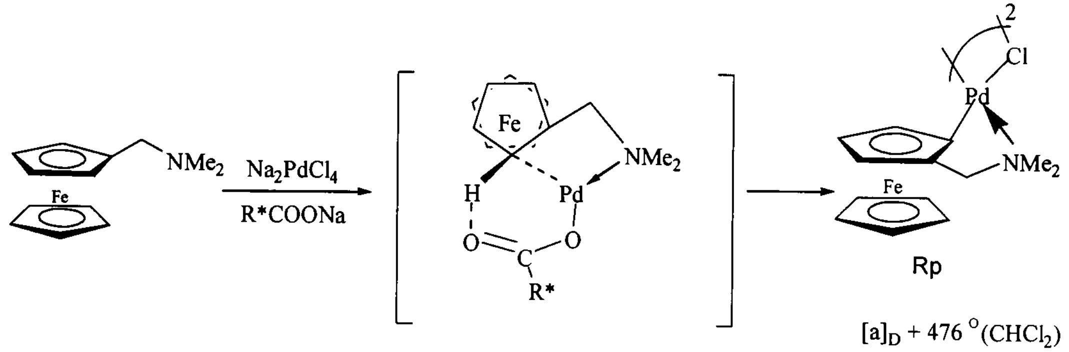


Fig. 9. Molecular structure of **25b**.



Scheme 16.



Scheme 17.

nitrogen atom and tin atom as well as the *n*–π conjugation allowed the substituents of the *N*-phenyl ring to affect the chemical shifts of ^{119}Sn. Thus a satisfactory linear correlation was found between ^{119}Sn shifts with Hammett substituent constants σ

$$\delta\ (^{119}\mathrm{Sn}) = 395.45 + 32.27\sigma \quad N = 8 \quad r = 0.977 \qquad (6)$$

5.2. Synthesis of cyclopalladated anils of benzoylferrocene

Synthesis of cyclopalladated anils of benzoylferrocene via transmetallation reaction of mercurated ferrocenylketimines with Li_2PdCl_4 followed by the treatment of the resulting products with triphenylphosphine in moderate to good yields [62] (Scheme 15).

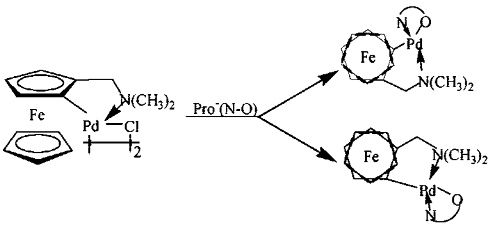
6. Stereochemistry of cyclometallation and transmetallation

It is well known that ferrocene is an ideal framework on which planar chirality can be introduced. The optically active 1,2-disubstituted ferrocenes have proved to be of particular interest for their application in material science, asymmetric synthesis, catalysis, photochemistry and bioinorganic chemistry [9c,81–88]. Some of the cyclometallated planar chiral ferrocene derivatives have been used in industrial process [89,90]. Therefore, it is highly demanding to develop new and efficient methods for the synthesis of planar chiral ferrocenes.

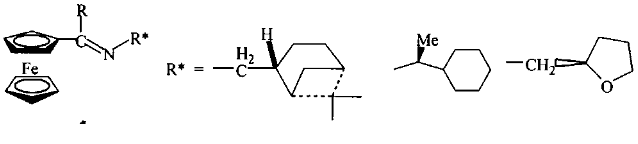
Generally, the planar chirality in the ferrocene moiety can be induced by the use of a chiral substrate, as reported by Sokolov et al. in the following reaction (Scheme 16) [91].

When the chiral *N*,*N*-dimethylaminoethylferrocene was reacted with sodium tetrachloropalladate, planar chirality was induced, with 85/15 diastereoselectivity.

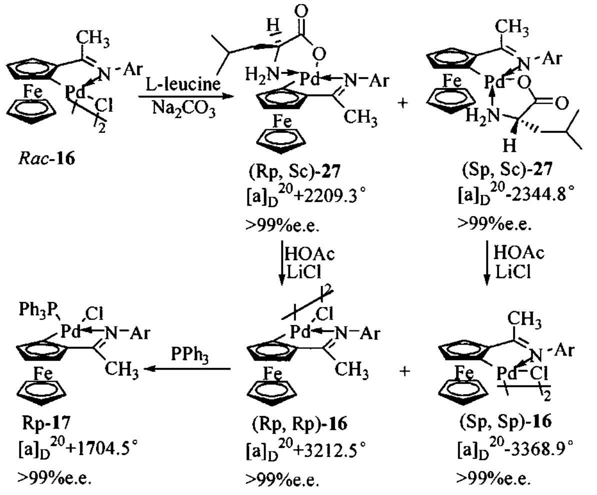
Sokolov et al. also reported the asymmetric cyclopalladation of achiral dimethylaminomethylferrocene with the salts of optically active carboxylic acids as nucleophilic catalysts. They suggested that the reaction proceeded *via* a bicyclic transition state (Scheme 17) [59,92].



Scheme 18.



Scheme 19.

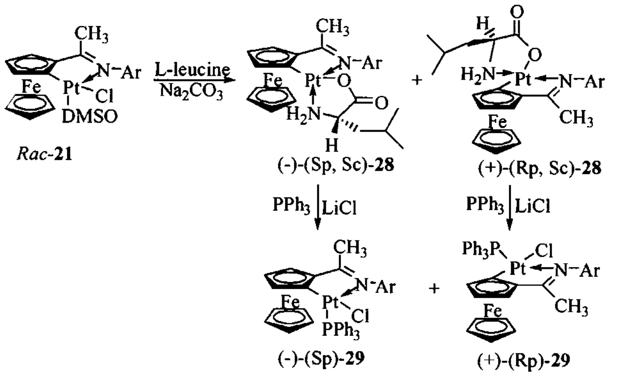


Ar=p-OCH$_3$C$_6$H$_4$(a), p-CH$_3$C$_6$H$_4$(b), p-ClC$_6$H$_4$(c), m-CH$_3$C$_6$H$_4$(d), m-BrC$_6$H$_4$(e), o-OCH$_3$C$_6$H$_4$(f), o-CH$_3$C$_6$H$_4$(g)

Scheme 20.

The optical resolution of cyclometallated ferrocene derivatives by using an amino acid as a chiral auxiliary was firstly reported by Nonoyama et al. [93]. Cyclopalladated dimethylaminomethylferrocene was reacted with optically pure (S)-proline to produce two diastereomers, which were separated by recrystallization to give optically pure cyclopalladated ferrocenes (Scheme 18).

Recently, Mak et al. reported the asymmetric cyclopalladation of chiral ferrocenylimines (Scheme 19) [27,94]. The diastereoselectivity was very high, and no trace of other isomers was found. Planar chiral cyclopalladated ferrocenylhydrozones [95] have also been conveniently synthesized with a high level of diastereoselectivity. It was found that the use of Pd(OAc)$_2$ instead of commonly used Na$_2$PdCl$_4$ resulted in a superior yield and significantly higher diastereoselectivity.



Ar= p-OCH$_3$C$_6$H$_4$(a), p-CH$_3$C$_6$H$_4$(b), C$_6$H$_5$(c), p-ClC$_6$H$_4$(d), p-BrC$_6$H$_4$(e)

Scheme 21.

6.1. Optical resolution of cyclopalladated ferrocenylimines

The reaction of racemic ± **16** and (S)-leucine in the presence of Na$_2$CO$_3$ gave the (S)-leucinato complex of cyclopalladated ferrocenylketimines **27** as solids in high yields. ^{1}H-NMR spectra of the crude products showed

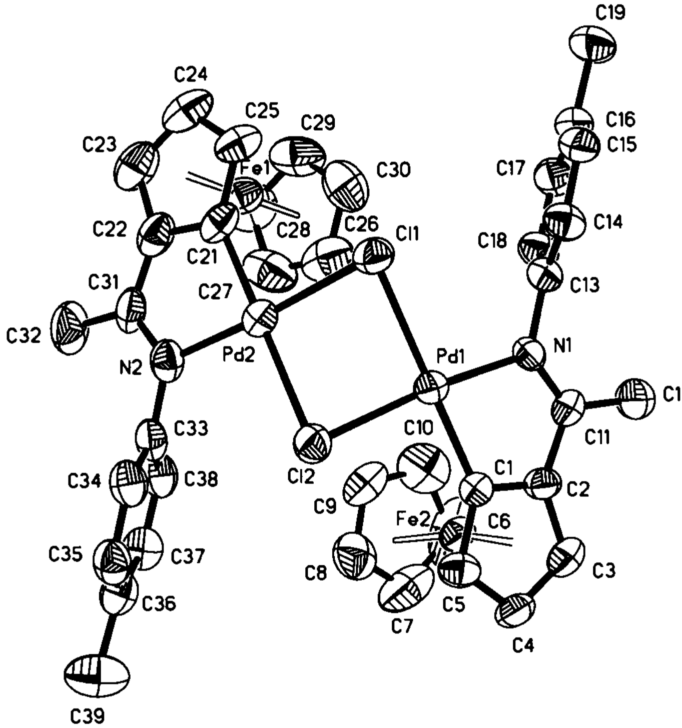


Fig. 10. Molecular structure of (Rp,Rp)-**16b**.

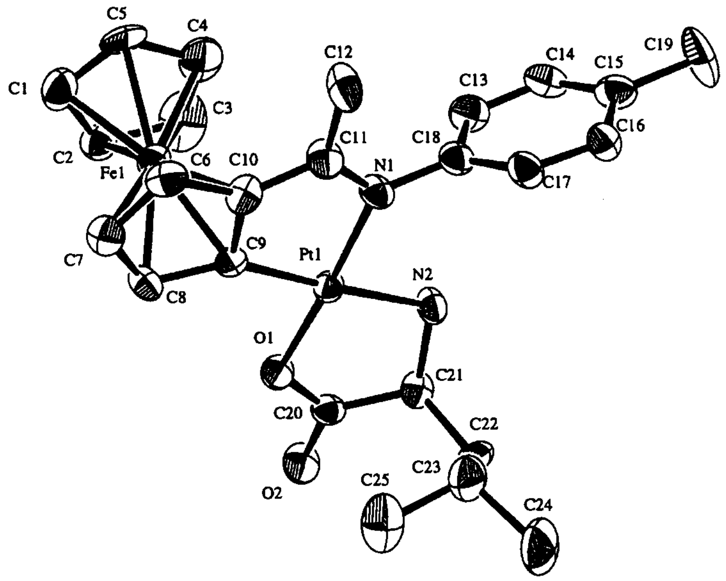


Fig. 11. Molecular structure of (−)-(Sp,Sc)-**28b**.

that d.e.% values varied depending upon the substituents in the *N*-phenyl ring: the ratio of its diastereomers was nearly 1:1 when the substituents were in the *para* or *meta*-position of the *N*-phenyl ring, and the ratio was about 36:64 when the substituents were in the *ortho*-position of the *N*-phenyl ring. The diastereomers **27** could be separated by either chromatography or fractional crystallization techniques. The optically pure (*S*)-leucinato complexes **27** were converted into optically pure dimers **16** with the same absolute configurations in the ferrocene moiety by the treatment of the diastereomers with lithium chloride in acetic acid (Scheme 20) [96].

The optically pure dimers (+)-**16** were chosen to determine the absolute configuration by X-ray diffraction. The crystal and molecular structure shows clearly that compound (+)-**16b** has the *R*-configuration (Fig. 10). So the compound (+)-**27** has the same absolute *R*-configuration in the ferrocene moiety, and (−)-**27** has the *S*-configuration in the ferrocene moiety. On the basis of the absolute configuration of *R*(+)-**16b**, the absolute configuration of all the other compounds can be assigned. The absolute configurations have also been checked by CD spectra.

6.2. Optical resolution of cycloplatinated ferrocenylimines

The first optically active cycloplatinated ferrocene derivatives were obtained by the resolution of **21**, using (*S*)-leucine as a chiral auxiliary [72]. The resulting diastereomers **28** were further reacted with PPh_3 and LiCl to give the compounds **29**, containing only planar chirality. The absolute configuration of planar chirality was retained during the removal of the chiral auxiliary (Scheme 21, Figs. 11 and 12).

6.3. Transmetallation of planar chiral cyclopalladated ferrocenylimines with metallic mercury

A series of optically active 2-chloromercurio-1-[1-(arylimino)ethyl]ferrocenes (**8**) were synthesized by

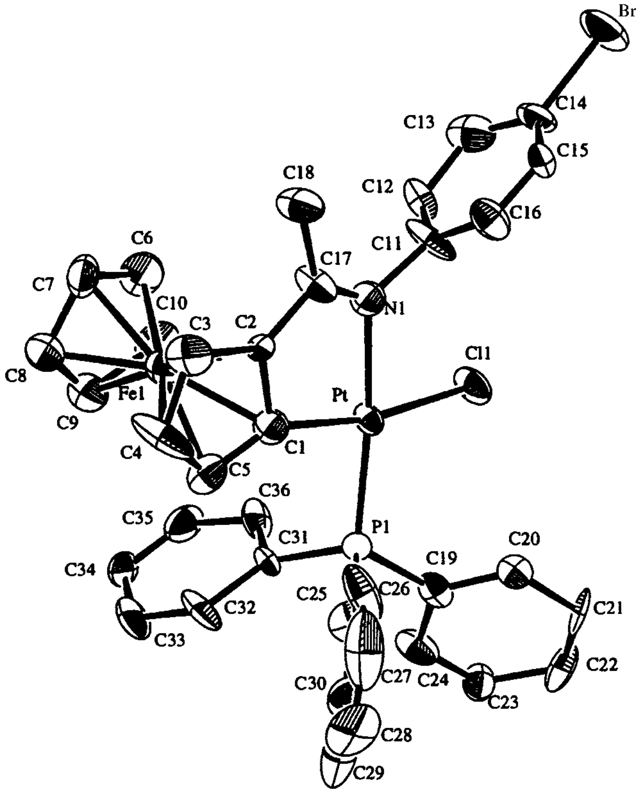
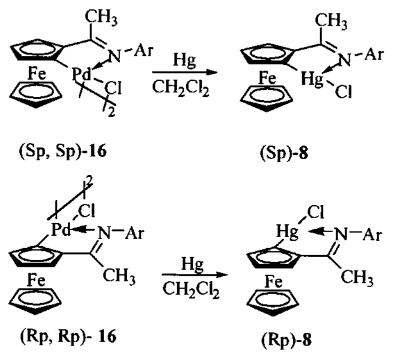


Fig. 12. Molecular structure of (−)-(Sp)-**29e**.



Ar=p-OCH$_3$C$_6$H$_4$(**a**), p-CH$_3$C$_6$H$_4$(**b**), p-ClC$_6$H$_4$(**c**), m-BrC$_6$H$_4$(**d**), o-OCH$_3$C$_6$H$_4$(**e**), o-CH$_3$C$_6$H$_4$(**f**)

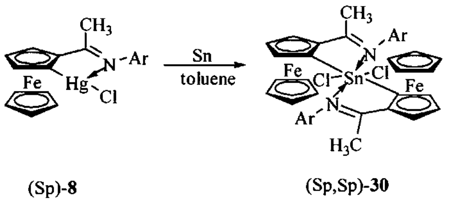
Scheme 22.

transmetallation of optically active cyclopalladated ferrocene derivatives **16** with metallic mercury (Scheme 22).

The structure and absolute configuration of complex Rp-**8b** was determined by X-ray diffraction, and the absolute configuration of other optically active compounds was ascertained by comparison of CD spectra to Rp-**8b** [97] (Fig. 13).

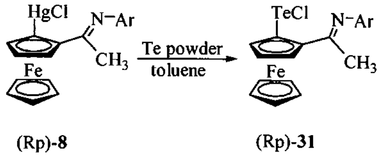
6.4. Transmetallation of planar chiral cyclomercurated and cyclopalladated ferrocenylimines with metallic tin or metallic tellurium

Using compounds Sp-**8** and Rp-**8** as starting materials, the optically active organotin (Sp,Sp)-**30** [80] (Scheme 23) and organotellurium Rp-**31** (Scheme 24) compounds were obtained by transmetallation with



Ar= p-CH$_3$C$_6$H$_4$(**a**), p-OCH$_3$C$_6$H$_4$(**b**), p-ClC$_6$H$_4$(**c**), m-ClC$_6$H$_4$(**e**), m-CH$_3$C$_6$H$_4$(**g**),

Scheme 23.



Scheme 24.

metallic tin and tellurium, respectively. The experimental results including X-ray structure analysis (Fig. 14) and/or CD spectra (Fig. 15) indicated that the planar chiral mercury complexes were converted into tin and tellurium complexes with retention of absolute configuration in the ferrocene moiety.

As in the case of the transmetallation reaction of cyclopalladated ferrocenylimines with metallic mercury, the planar chiral cyclostannated ferrocenylimines (Sp,Sp)-**30** were easily obtained by transmetallation of cyclopalladated ferrocenylimines (Sp,Sp)-**16** with metallic tin with the retention of absolute configuration in the ferrocene moiety [80].

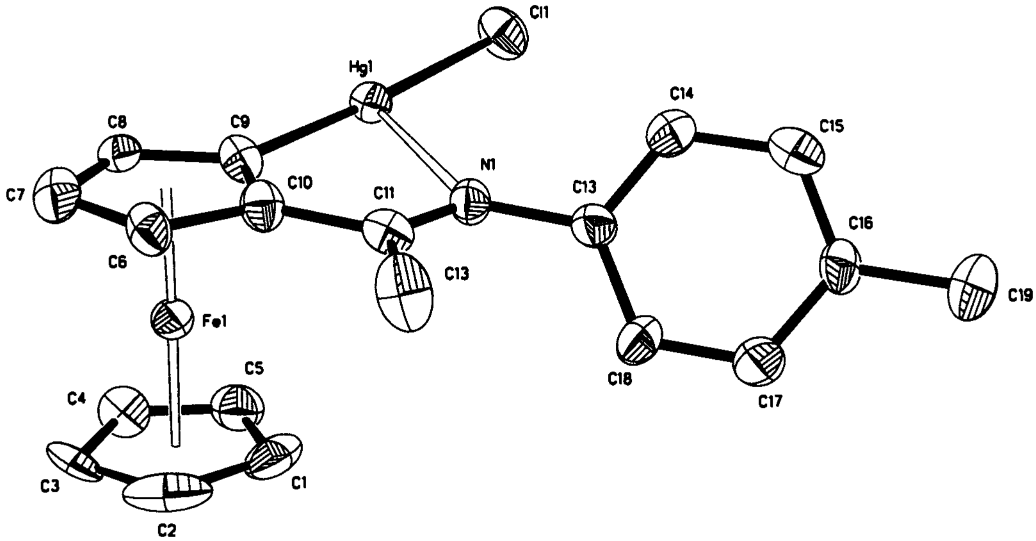


Fig. 13. Molecular structure of (Rp)-**8b**.

6.5. Asymmetric cyclomercuration of chiral ferrocenylimines

Asymmetric cyclomercuration of chiral ferrocenylimines (+)-(*R*)-**32** and (−)-(*S*)-**32** with mercuric acetate and subsequent treatment with lithium chloride gave two different pairs of diastereomeric cyclomercurated ferrocenylimines. The pure enantiomers **33** with both planar and central chirality were separated by thin layer chromatography. The structures and absolute configurations of these complexes were determined by X-ray diffraction [98] (Scheme 25, Fig. 16).

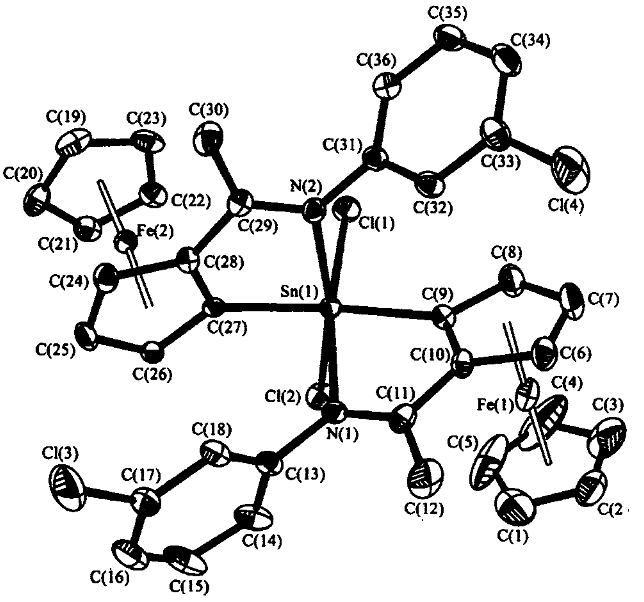


Fig. 14. Molecular structure of (Sp,Sp)-**30e** obtained from (Sp)-**8e**.

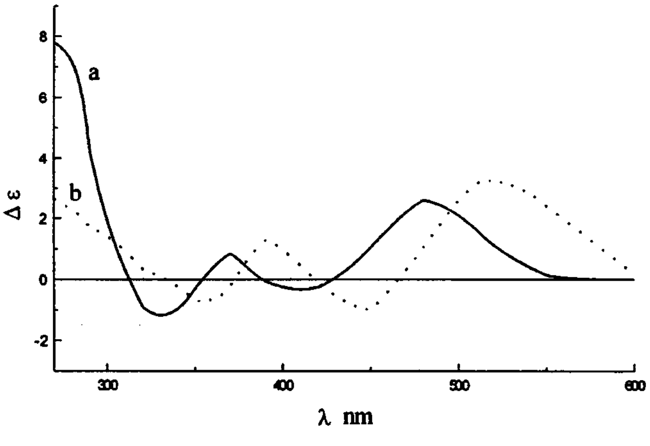


Fig. 15. CD spectra in dichloromethane of compounds (a) (Rp)-**8a** and (b) (Rp)-**31a**.

7. Some applications of cyclopalladated ferrocenylimines

As mentioned above, the optically pure α-amino acid could be used as a chiral auxiliary for the optical resolution of cyclopalladated ferrocenylimines. On the other hand, the optically pure cyclopalladated ferrocenylimines were found to be equally useful in the resolution of racemic α-amino acids. By using the chiral dimer *R*-(+)-$\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CMe{=}NAr)](\mu\text{-}Cl)\}_2$ (Ar = *p*-$CH_3C_6H_4$) (**16b**) as a resolving agent, the optical resolution of racemic α-amino acids was successfully carried out [99] (Scheme 26).

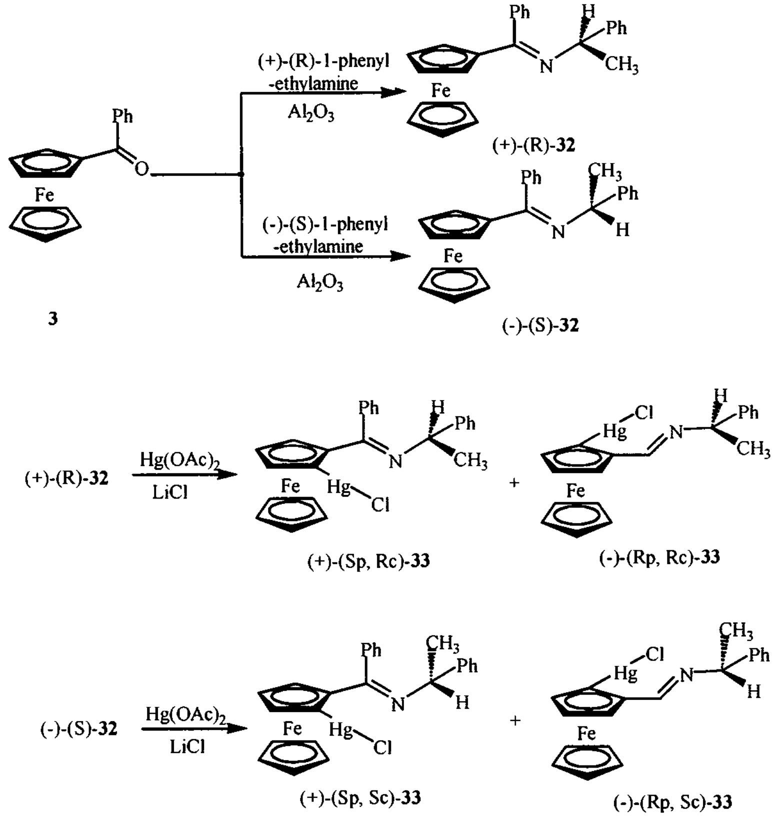
The mixture of diastereomers (Rp,Sc)-**35,** (Rp,Rc)-**35** could be separated by chromatography. The optically active α-amino acids were obtained by the treatment of (Rp,Sc)-**35** and (Rp,Rc)-**35** with glacial acetic acid and lithium chloride, respectively, and the dimer (Rp,Rp)-**16b** was recovered without a loss of the optical activity. In this case we also provided an efficient method for determination of the e.e.% values of three α-amino acids.

The cyclopalladated ferrocenylimines $\{Pd[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3CMe{=}NAr)]Cl(PPh_3)\}$ (Ar = *p*-$CH_3C_6H_4$, *m*-BrC_6H_4) (**17**) were successfully used as carriers to prepare novel kind of anion selective polymeric membrane electrodes (chemical sensors). Electrode I (Ar = *m*-BrC_6H_4) displays the following selectivity sequence: $Pic^- > SCN^- > I^- > ClO_4^- > Sal^- > NO_3^- > Br^- > Cl^- > Ac^-$, which is not in accordance with the Hofmeister series. Electrode II (Ar = *p*-$CH_3C_6H_4$) is similar to those of electrode I. Electrode I was used as a Sal^-, I^- and SCN^- sensitive electrode for the determination of corresponding Sal^- in the aspirin tablets, I^- in the meglumine injection and SCN^- in the urine sample, respectively. The results obtained are in reasonable agreement with those determined by the standard pharmacopeia method for Sal^- and I^- and colorimetric method for SCN^-, respectively. The response mechanism was also investigated [100].

Finally, it is noteworthy that the cyclopalladated ferrocenylimines have been successfully used as highly active catalysts in Heck reactions.

8. Summary

As this review illustrates, the achievements of the studies on the cyclometallation of ferrocenylimines in various fields mark the recent advances in the chemistry of ferrocene. Ferrocene chemistry has a flourishing half-century history, and a long-range developmental research program looms bright ahead. It is believed that this research area will be continually developed both in theoretical and applied aspects, especially in organic synthesis, asymmetric synthesis and material science.



Scheme 25.

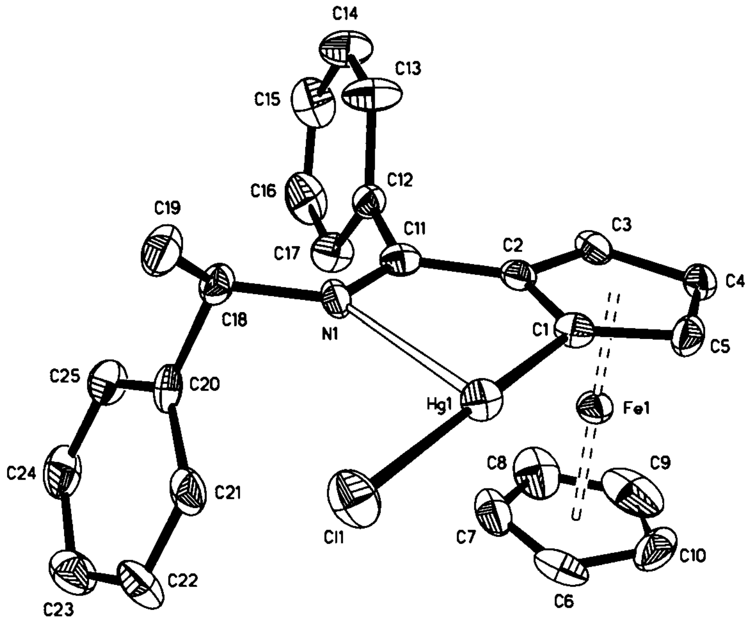
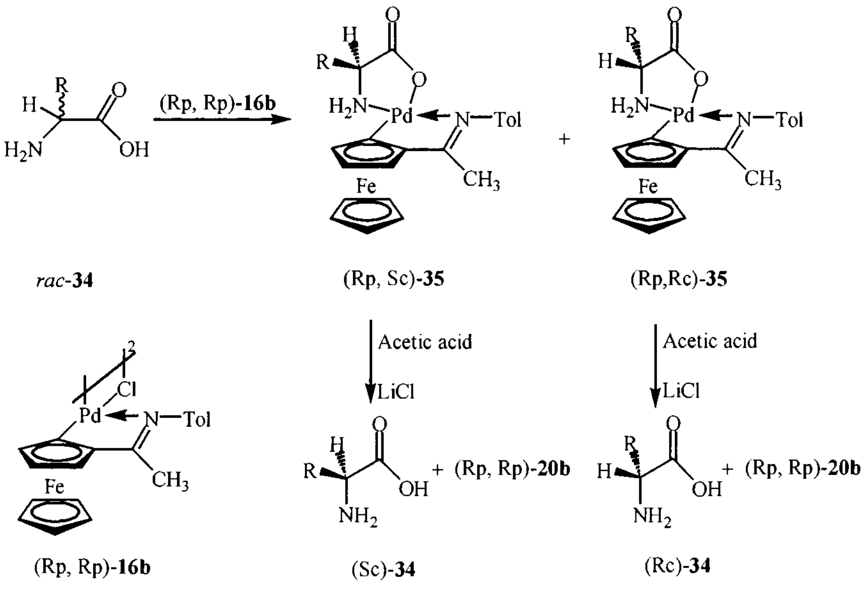


Fig. 16. Molecular structure of (Rp,Rc)-**33**. Selected bond distances (Å) and angles (°) are Hg(1)–N(1), 2.774; Hg(1)–C(1), 2.017(8); C(1)–Hg(1)–Cl(1), 175.9(2); Hg(1)–C(1)–C(2), 119.7(7); C(1)–C(2)–C(11), 124.8(8); C(2)–C(11)–N(1), 117.8(7).



R=$-CH_2(CH_2)_2CH_3$ Norleucine (**a**), $-CH_2CH(CH_3)_2$ Leucine (**b**), $-CH_2C_6H_5$ Phenylalanine (**c**)

Scheme 26.

Acknowledgements

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