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Synthesis of new ferrocenyl amine sulfide and selenide complexes of group 10 metals and their catalytic activities toward selective hydrogenation, isomerization, and asymmetric Grignard cross-coupling reactions

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Abstract

Two series of previously unknown ferrocenyl amine sulfide and selenide ligands (*S*,*R*)-[ER]$C_5H_4FeC_5H_3$[CHMeNMe_2] [ER] and [ER]$C_5H_4FeC_5H_3$[CH_2NMe_2]-[ER], where E = S and Se; R = Me, Ph, Bz, 4-tolyl, and 4-ClPh, have been prepared. Lithiation of (*S*)-[1-(dimethylamino)ethyl]ferrocene and [(dimethylamino)methyl] ferrocene first in the presence of ether and then TMEDA followed by treatment with different diselenides and disulfides resulted in the synthesis of these new ligands. Palladium and platinum dichloride adducts of these compounds have been prepared from a benzene solution of $(PhCN)_2MCl_2$ where M = Pd and Pt. The palladium complexes are active catalysts for selective hydrogenation of dienes to monoenes both under homogeneous and heterogeneous conditions. In the case of hydrogenation of 2,3-dimethyl-1,3-butadiene, isomerization has been observed. Nickel complexes of the new sulfide ligands were prepared in situ and used as catalysts for the asymmetric Grignard cross-coupling reactions. The possible structures of Pd and Pt complexes are discussed. The X-ray crystal structure was determined for [SMe]$C_5H_4FeC_5H_3$[CH_2NMe_2][SMe][$PdCl_2$]; it reveals that the Pd atom is coordinated to the S and N atoms of the same cyclopentadienyl ring.

Introduction

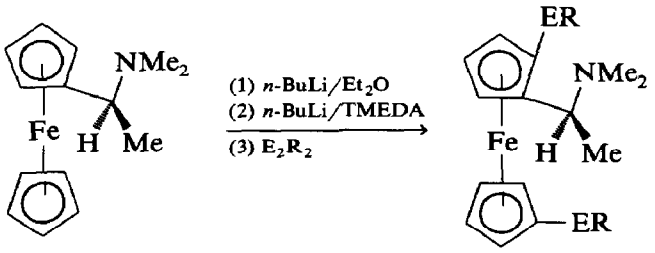
Since the first appearance of dicyclopentadienyliron(II) (ferrocene) [1] its chemistry has attracted much interest, mainly because of stability and unusual reactivity of ferrocene and its derivatives. Ferrocenyl amine phosphines are among the important derivatives of ferrocene [2]. These ligands have been used extensively to prepare Pd, Ni and Rh complexes that are useful catalysts in asymmetric hydrogenation of olefins [3], and ketones [4], asymmetric hydrosilation of ketones [5], and asymmetric Grignard cross-coupling reactions [6].

Recently, preparation, characterization, and catalytic activities of ferrocenyl amine sulfide analogs have been investigated in this laboratory [7–12]. Here, preparation and characterization of two new series of sulfide and selenide ligands and their palladium and platinum complexes are discussed. The new palladium ferrocenylamine sulfide complexes are effective hydrogenation catalysts for selective reduction of dienes. Some nickel-sulfide complexes, prepared in situ, were used as selective catalysts for asymmetric Grignard cross-coupling reactions.

Results and discussion

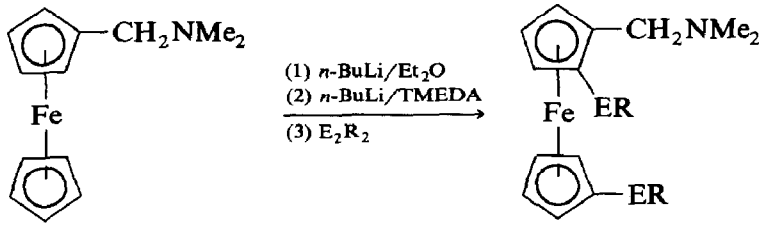
Preparation and characterization of ligands ***2a–2f*** *and* ***4a–4f*** *(Scheme 1)*

Two series of new ferrocenyl amine sulfide and selenide ligands (*S*,*R*)-[ER]$C_5H_4FeC_5H_3$[CHMeNMe_2][ER] and [ER]$C_5H_4FeC_5H_3$[CH_2NMe_2][ER] where E = S and Se; R = Me, Ph, Bz, 4-tolyl, and 4-ClPh were synthesized according to Scheme 1. It was shown that the lithiation product of *S*-[1-(dimethylamino)-ethyl]ferrocene (*S*-**1**) in the presence of ether is (*S*,*S*)-1-[1-(dimethylamino)ethyl]-2-



(**1**) (**2**)

E = S E = Se
a R = Me **f** R = 4-ClPh
b R = Ph
c R = Bz
d R = 4-tolyl
e R′ = 4-ClPh



(**3**) (**4**)

E = S E = Se
a R = Me **e** R = Ph
b R = Ph **f** R = 4-ClPh
c R = 4-tolyl
d R = 4-ClPh

Scheme 1

lithioferrocene in 96% optical yield [13]. Further lithiation in the presence of TMEDA and then reaction with suitable dialkyl or diaryl disulfides or diselenides produced the (*S*,*R*)-amines **2a–2f**. The products were separated by chromatography on a silica gel column. Ligands **4a–4f** (Scheme 1) were also prepared in a similar way, starting from [(dimethylamino)methyl]ferrocene.

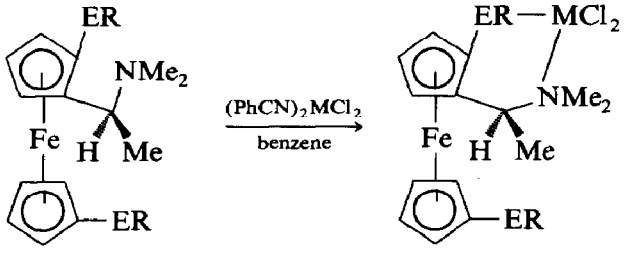
Compounds **2a–2f** are chiral with both central and planar elements of chirality. The (*S*) configuration refers to the asymmetric carbon while the (*R*) configuration refers to the planar chirality. Compound **4a–4f** have planar chirality due to the presence of two different substituents in 1 and 2 positions of one Cp ring (Cp = C_5H_5) [14]. Here the products **4a–4f** were obtained as racemic mixtures. Kumada and coworkers have resolved ferrocenyl phosphine analogs and used them, as well as ligands with both central and planar chirality (analogs to **2a–2f**), for asymmetric Grignard cross-coupling reactions and found that the role of the ferrocene planar chirality is more important than that of the carbon central chirality [6b]. Such resolution has been not carried out here and we intend to investigate the applications of palladium complexes of these new ligands as regioselective hydrogenation catalysts. Compounds **2a–2f** and **4a–4f** were characterized by use of ^1H and ^{13}C NMR, IR, mass spectroscopic, and elemental analysis. Table 1 shows analytical

Table 1

Analytical results, yields, color, and melting points of ligands **2a–2g** and **4a–4g**

Ligand	Color	Yield (%)	M.p. (°C)	Analytical data (Found(calc.) (%))	
				C	H
(*S*,*R*)-[ER]$C_5H_4FeC_5H_3$[CHMeNMe$_2$][ER]					
E = S; R = Me (**2a**)	brown	90	oil	55.04 (55.01)	6.61 (6.64)
E = S, R = Ph (**2b**)	yellow	80	76–78	65.74 (65.96)	5.92 (5.75)
E = S; R = Bz (**2c**)	brown	52	oil	67.31 (67.06)	6.12 (6.27)
E = S; R = 4-tolyl (**2d**)	yellow	75	86–87	67.20 (67.06)	6.20 (6.27)
E = S; R = 4-ClPh (**2e**)	yellow	81	114–116	57.47 (57.59)	4.60 (4.65)
E = Se; R = 4-ClPh (**2f**)	yellow	65	92–93	49.61 (49.09)	3.99 (3.96)
[ER]$C_5H_4FeC_5H_3$[CH$_2$NMe$_2$][ER]					
E = S, R = Me (**4a**)	brown	92	oil	54.14 (53.73)	6.23 (6.31)
E = S; R = Ph (**4b**)	yellow	74	86–87	65.49 (65.35)	5.35 (5.48)
E = S, R = 4-tolyl (**4c**)	yellow	78	71–72	66.43 (66.52)	5.80 (5.60)
E = S, R = 4-ClPh (**4d**)	yellow	81	75	56.62 (56.83)	4.35 (4.39)
E = Se, R = Ph (**4e**)	yellow	78	60–61	54.19 (54.25)	4.74 (4.55)
E = Se, R = 4-ClPh (**4f**)	yellow	67	96–98	48.57 (48.13)	3.89 (3.72)

results, yields, colors, and melting points of the new ligands. ^{1}H NMR spectra of these compounds are given in the supplementary material. Figure 1a shows the ^{1}H NMR spectrum of ligand **4c** (Scheme 1). The two methyl groups of NMe_2 are diastereotopic. They give only one signal, a singlet at 2.05 ppm, because the inversion of the pyramidal N of NMe_2 is faster than the NMR time scale at room temperature. Two methyl groups of 4-tolyl sulfide substituents are chemically



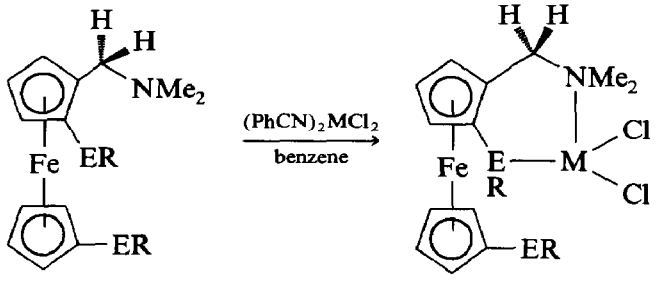
(2) (5)

E = S, M = Pd
a R = Me
b R = Ph
c R = Bz
d R = 4-tolyl
e R = 4-ClPh

E = S, M = Pt
f R = Ph
g R = Bz
h R = 4-tolyl

E = Se, M = Pd
i R = 4-ClPh

E = Se, M = Pt
j R = Ph



(4) (6)

E = S, M = Pd
a R = Me
b R = Et
c R = *n*-Pr
d R = *i*-Pr
e R = Ph
f R = Bz
g R′ = 4-tolyl
h R = 4-ClPh

E = Se, M = Pt
i R = Bz
j R = 4-tolyl

E = Se, M = Pd
k R = Ph

Scheme 2

non-equivalent and they accidentally give a singlet at 2.24 ppm. ^{13}C NMR data are also presented in the supplementary material. Here again, due to the fast inversion of the N of NMe_2 two methyl carbons appear at the same chemical shift.

Table 2

Analytical data, yields, color, and melting points of complexes **5a–5k** and **6a–6n**

Complex	Color	Yield (%)	M.p. (°C)	Analytical Data (Found(calc.) (%))	
				C	H
(*S*,*R*)[ER]$C_5H_4FeC_5H_3$[CHMeNMe$_2$][ER][MCl_2]					
E = S, R = Me, M = Pd (**5a**)	dark purple	90	157–158 (dec)	36.67 (36.49)	4.22 (4.40)
E = S, R = Ph, M = Pd (**5b**)	dark purple	87	142–143 (dec)	48.01 (47.99)	4.51 (4.18)
E = S, R = Bz, M = Pd (**5c**)	dark purple	74	172–174 (dec)	49.91 (49.54)	4.83 (4.60)
E = S, R = 4-tolyl, M = Pd (**5d**)	red	85	163–165 (dec)	49.64 (49.54)	4.76 (4.60)
E = S, R = 4-ClPh, M = Pd (**5e**)	black	90	154–155 (dec)	43.39 (43.50)	3.66 (3.50)
E = S, R = Ph, M = Pt (**5f**)	yellow	61	188–190 (dec)	41.97 (42.23)	3.64 (3.68)
E = S, R = Bz, M = Pt (**5g**)	yellow	49	179–181 (dec)	44.01 (43.82)	4.11 (4.07)
E = S, R = 4-tolyl, M = Pt (**5h**)	yellow	62	190–191 (dec)	43.98 (43.82)	4.21 (4.07)
E = Se, R = 4-ClPh, M = Pd (**5i**)	red	71	161–163 (dec)	38.63 (38.53)	3.10 (3.07)
E = Se, R = Ph, M = Pt (**5j**)	yellow	81	171–173 (dec)	37.50 (37.50)	3.17 (3.27)
[ER]$C_5H_4FeC_5H_3$[CH_2NMe_2][ER][MCl_2]					
E = S, R = Me, M = Pd (**6a**)	deep red	87	153 (dec)	35.59 (35.15)	4.13 (4.13)
E = S, R = Et, M = Pd (**6b**)	black	59	144–146 (dec)	37.65 (37.77)	4.55 (4.66)
E = S, R = n-Pr, M = Pd (**6c**)	purple	63	151–152 (dec)	40.10 (40.13)	5.11 (5.14)
E = S, R = i-Pr, M = Pd (**6d**)	brown	60	131–132 (dec)	40.33 (40.13)	5.31 (5.14)
E = S, R = Ph, M = Pd (**6e**)	brick red	85	133 (dec)	46.99 (47.16)	3.81 (3.98)
E = S, R = Bz, M = Pd (**6f**)	purple	82	161–163 (dec)	48.65 (48.78)	4.43 (4.40)
E = S, R = 4-tolyl, M = Pd (**6g**)	brick red	79	149 (dec)	48.41 (48.78)	4.32 (4.40)
E = S, R = 4-ClPh, M = Pd (**6h**)	brick red	93	151–152 (dec)	43.05 (42.55)	3.31 (3.29)
E = S, R = Bz, M = Pt (**6i**)	yellow	49	176–178 (dec)	43.10 (43.04)	3.78 (3.88)
E = S, R = 4-tolyl, M = Pt (**6j**)	yellow	58	190 (dec)	43.21 (43.04)	3.92 (3.88)
E = Se, R = Ph, M = Pd (**6k**)	dark red	90	128–129 (dec)	41.17 (41.04)	3.50 (3.49)

*Preparation and characterization of complexes **5a–5j** and **6a–6k** (Scheme 2).*

Complexes **5a–5j** and **6a–6k** have been prepared by treatment of appropriate benzene solutions of ferrocenylamine sulfide and selenide ligands with bis(benzonitrile)palladium or platinum chloride $(PhCN)_2MCl_2$ (M = Pt and Pd) according to Scheme 2. The resulting heterobimetallic products are insoluble in benzene. The palladium complexes are soluble in acetone and other polar solvents such as methylene chloride and chloroform, but platinum complexes are not soluble in any common solvents. They are only slightly soluble in acetone. These complexes were characterized by use of ^1H NMR, IR, mass spectroscopic, and elemental analysis. Table 2 presents analytical results, yields, colors, and melting points of complexes **5a–5j** and **6a–6k**. ^1H NMR data are given in the supplementary material. Figure 1b shows the ^1H NMR spectrum of complex **6g** which has been prepared from free ligand **4c**. Comparison of Fig. 1a and 1b is helpful for understanding the structure of these complexes.

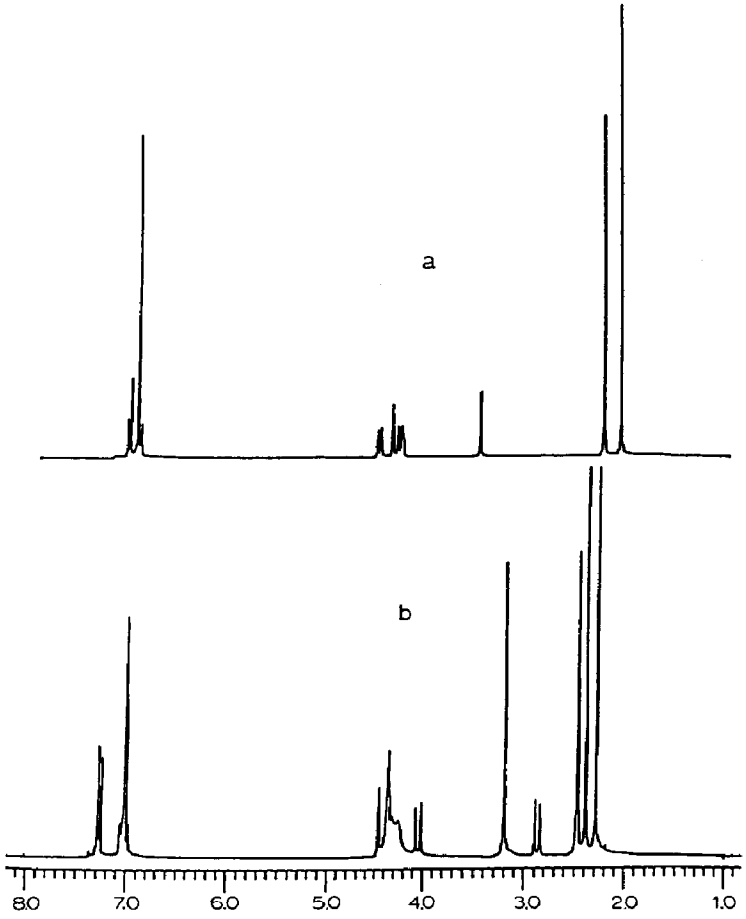
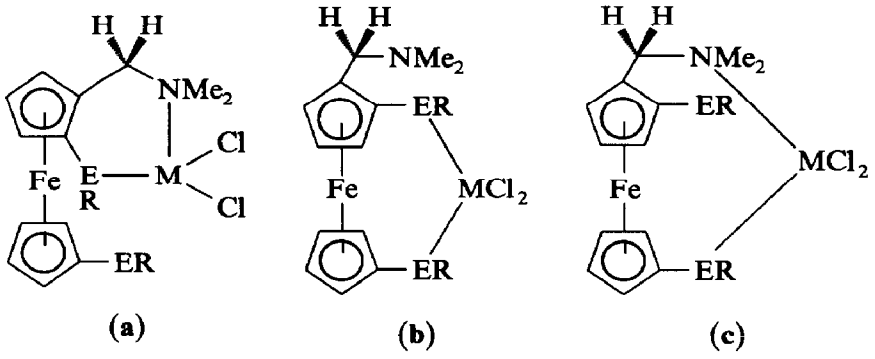


Fig. 1. (a) 250 MHz, ^1H NMR spectrum of ligand [S-(4-tolyl)]$C_5H_4FeC_5H_3[CH_2NMe_2]$[S-(4-tolyl)] (**4c**). (b) 250 MHz, ^1H NMR spectrum of complex [S-(4-tolyl)]$C_5H_4FeC_5H_3[CH_2NMe_2]$[S-(4-tolyl)][$PdCl_2$ (**6g**).



Scheme 3

Structure of complexes

Ligands **2a–2g** and **4a–4g** (Scheme 1) have three coordination sites, N atoms and two S atoms (or Se atoms), as a result, there are 3 possible structures for the palladium and platinum complexes (Scheme 3). Cullen and co-workers investigated the structures of different rhodium-ferrocenyl amine phosphine complexes. They found that there are two different structures for $[PR_2]C_5H_4FeC_5H_3$-$[CHMeNMe_2][PR_2][RhNBD]^+$, depending on the group attached to the phosphorus. When R = Ph, Rh is coordinated to the two phosphorus atoms, but when R = t-Bu, Rh is coordinated to the nitrogen and phosphorus of the same cyclopentadienyl group [4b]. The structure of $PdCl_2$[(*S*,*R*)-BPPFA] (BPPFA = racemic (*S*)-*N*,*N*-dimethyl-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine has been reported (Fig. 2) [15]. The palladium-BPPFA complex has square planar geometry with two *cis*-phosphorus and two chlorine atoms. The nitrogen atom is not coordinated to the palladium. The structure of ferrocenylamine sulfide and selenide analogs is different, however. Non-isochronicity of the two methyl groups of NMe_2 (Fig. 1b) is strong evidence for coordination of that group to the metal. Therefore, the complexes have structure **a** or **c** (Scheme 3). Complex **6a** (Scheme 2) was recrystallized from acetone and was used for an X-ray structure determination. Regrettably, all the crystals were twins, therefore, the results are not as good as is expected. Nevertheless, this study unambiguously revealed that compound **6a** has structured **a** (Scheme 3). A drawing showing the atom labeling and thermal ellipsoid of complex **6a** is given in Fig. 3. Atomic parameters, bond angles, and bond distances are given in the supplementary material. The carbon–carbon distances in the cyclopentadienyl ring vary from 1.35(2) to 1.48(3) Å averaging at 1.41(3) Å. This is a typical value for ferrocene derivatives. The bond angles within the two Cp-rings (C–C–C) vary from 105(2) to 111(2)° with an average of 108(2)°, the ideal value

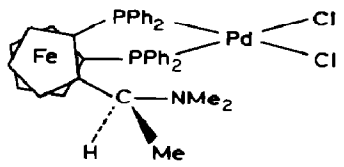


Fig. 2. Structure of $PdCl_2$[(*S*), (*R*)-BPPFA].

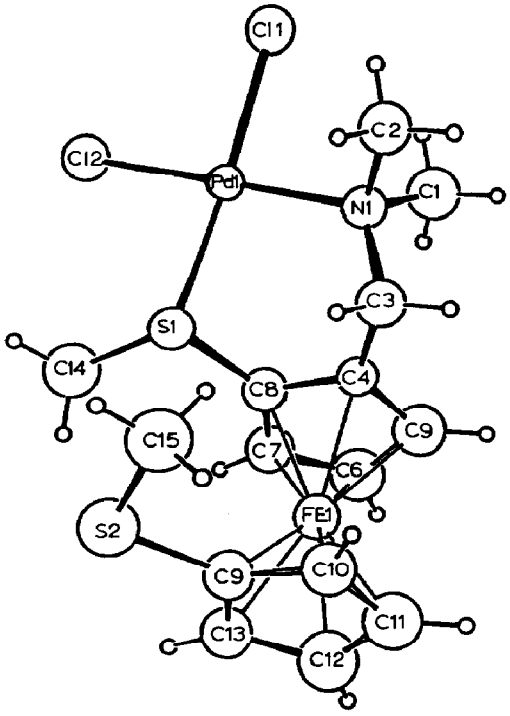


Fig. 3. The molecular structure and the numbering of the atoms of complex [SMe]$C_5H_4FeC_5H_3$[CH_2N-Me_2][SMe][$PdCl_2$] (**6a**).

for the angle of a regular planar pentagon. The bond lengths to Pd closely approximate the sum of the Pauling covalent radii [16]. Pd–S observed at 2.277(4) Å is compared with 2.35 Å; Pd–Cl observed average 2.320(4) Å, compared with 2.31 Å and Pd–N observed at 2.164(12) Å.

The two cyclopentadienyl rings are eclipsed and are almost parallel; the dihedral angle between the two Cp rings is 1.54°.

The most striking feature of the structure of complex **6a** is the coordination of the Pd atom to S and N atoms of the same Cp ring (structure **a**, Scheme 3). The difference between the structure of palladium ferrocenyl amine sulfides and the phosphine analogs is very interesting and it can be one of the reasons for the differences in the catalytic activities of these two classes of complexes.

Existence of two peaks in the ^1H NMR spectra for methyl groups of NMe_2 in all palladium ferrocenyl amine sulfide and selenide complexes reported here, clearly point out that changing groups attached to S or Se does not affect the structure of the complexes; therefore, in this respect, these compounds behave differently from cataionic Rh complexes reported by Cullene and co-workers [4b].

Selective hydrogenation of conjugated double bonds

Selective hydrogenation of dienes to olefins has been achieved by the use of different catalytic systems such as [$PdCl(PPh_3)(\eta^3$-allyl)] [17], [$Co(CN)_5^{3-}$] [18], ruthenium(0) polyolefin complexes [19], and $Ni(acac)_2$ in the presence of $Al_2Et_3Cl_3$ and PPh_3 [20]. Novel homogeneous and mineral supported, nitrogen containing

Table 3

Selective hydrogenation of 1,3-cyclooctadiene (7.45×10^{-3} mol) with various complexes in acetone (9 ml) at room temperature and 104 p.s.i. initial H_2 pressure

Catalyst [a]	Conversion (%)	Induction time (h)	Turnover rate (mol/mol cat.h)	Products	
				Cyclooctene (%)	Cyclooctane (%)
$[SR]C_5H_4FeC_5H_3[CHMeNMe_2][SR][PdCl_2]$					
R = Me (**5a**)	100	42.5	17.26	96.67	3.33
R = Ph (**5b**)	96.2	0	114.46	84.5	11.7
R = 4-tolyl (**5d**)	98.6	0	464.75	91.88	6.75
R = 4-ClPh (**5e**)	100	0	684.17	96.75	3.25
$[SPh]C_5H_4FeC_5H_3$ $[CHMeNMe_2]$ $[SPh][PtCl_2]$ (**5f**)	No hydrogen uptake				
$[SePh]C_5H_4FeC_5H_3$ $[CHMeNMe_2]$ [Se(4-ClPh)] $[PdCl_2]$ (**5i**)	No hydrogen uptake				
$[SR]C_5H_4FeC_5H_3[CH_2NMe_2][SR][PdCl_2]$					
R = Ph (**6e**)	100	0	363.4	93.8	6.2
R = Bz (**6f**)	100	0	79.3	92.80	7.20
R = 4-tolyl (**6g**)	100	0	390.3	88.60	11.40
R = 4-ClPh (**6h**)	100	0	722.4	96.81	3.19

[a] 2.0×10^{-5} mol of catalyst.

palladium compounds were also used as catalysts in this process [21,22]. Colloidal palladium in poly(*N*-vinyl-2-pyrrolidone) at 30 °C and atmospheric H_2 pressure [23], zirconium(III) complexes containing chelated $\overline{ZrCH_2PPh_3}$ [24], and untreated or prereduced copper chromite [25] are among the other catalytic systems used for selective reduction of conjugated dienes. Selective hydrogenation of polyenes is of practical importance and has been the subject of many patents [26].

Table 3 shows the results of the hydrogenation of 1,3-cyclooctadiene by using some of the new ferrocenyl amine sulfide complexes. When complexes **5f** with Pt–S bond and **5i** with Pd–Se bond were used no hydrogen uptake was observed. On the other hand, hydrogenation reactions were easily performed when complexes **5a, 5b, 5d, 5e, 6e, 6f, 6g,** and **6h** (Scheme 2) were used. The latter complexes all have Pd–S bonds. Cullen and Woollins found that similar system with P–M bonds (M = Pd, Rh) are active catalysts for hydrogenation of ketones, while analogous As–M complexes are inactive [4b]. High turnover rate, excellent selectivity and high conversion (for most of the cases 100%) are characteristics of all hydrogenation reactions when different palladium ferrocenyl amine sulfide catalysts were used. The best result was obtained when the hydrogenation reaction was performed in the presence of catalyst $[S(4\text{-ClPh})]C_5H_4FeC_5H_3[CH_2NMe_2][S((4\text{-ClPh})][PdCl_2]$ (**6h**). In this case the conversion and selectivity were 100 and 96.8% respectively with an initial turnover rate of 722.4 mol (mol cat)$^{-1}$ h^{-1}. This catalyst is comparable with the other state of the art catalysts for selective hydrogenation of 1,3-cyclooctadiene

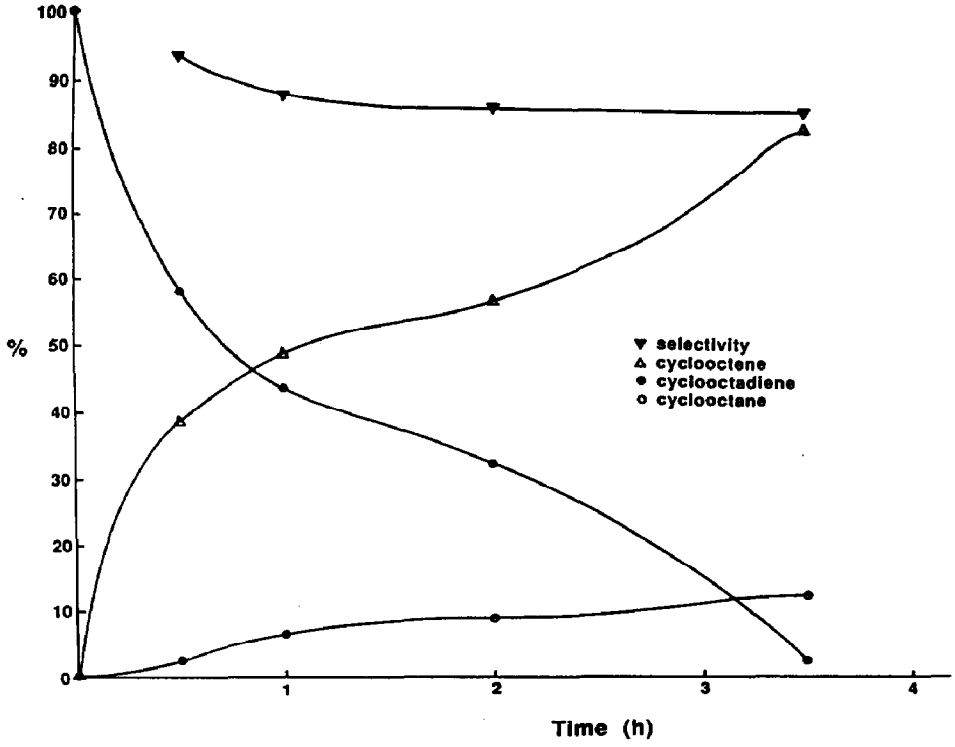


Fig. 4. Variation of selectivity and percentage of different products by time during the hydrogenation of 1,3-cyclooctadiene at room temperature and 104 p.s.i. initial pressure by using complex $[SPh]C_5H_4FeC_5H_3[CHMeNMe_2][SPh][PdCl_2]$ (**5b**).

to cyclooctene. When catalyst **5b** $[SPh]C_5H_4FeC_5H_3[CHMeNMe_2][SPh][PdCl_2]$ was used the conversion was 96.2% and selectivity was 86.8%. Figure 4 shows how the selectivity of the reaction changes with time. It is interesting that both cyclooctene and cyclooctane are formed in the beginning of the reaction but the rate of the production of cyclooctene is much faster than that of cyclooctane. The selectivity gradually decreases and after a while it remains almost constant. Table 4 shows the effect of different solvents on the hydrogenation of 1,3-cyclooctadiene when com-

Table 4

Effect of solvents in selective hydrogenation of 1,3-cyclooctadiene (7.45×10^{-3} mol) with $[S(4\text{-}ClPh)]C_5H_4FeC_5H_2[CH_2NMe_2]$ (**6h**) (2×10^{-5} mol) as catalyst at room temperature and 104 p.s.i. initial H_2 pressure

Solvent (ml)	Conversion (%)	Turnover rate (mol/mol cat. h)	Products	
			Cyclooctene (%)	Cyclooctane (%)
acetone (g)	100	722.4	96.8	3.19
THF (g)	62.8	383.8	60.4	2.13
CH_2Cl_2 (g)	80.0	178.7	79.5	0.47
acetone/water (g/2)	82.0	141.8	76.5	5.50

plex **6h** was used as a catalyst. These data clearly point out that hydrogenation reactions are solvent dependent. The best results were obtained when acetone was used as the solvent. Lower turnover rate and conversion were observed when THF, CH_2Cl_2 and a mixture of 9 ml acetone and 2 ml water were used as solvents. The selectivities for all the cases were very high. Homogeneous mixtures were obtained in the case of acetone, THF, and CH_2Cl_2. When a mixture of water and acetone was used the catalyst precipitated and the reaction was performed under heterogeneous conditions.

A reasonable explanation for the observed solvent effect is the different coordination ability of solvents. Upon dissolving the palladium catalyst in a solvent, the Pd–S bond may dissociate and the solvent coordinate to the Pd followed by the introduction of substrate to the metal center of the complex-solvent intermediate and then H_2 uptake starts to induce the hydrogenation [9,12]. Acetone has the optimum coordination ability for this process. As shown in the Table 4, a hydrogenation reaction in the presence of CH_2Cl_2, a solvent with very limited coordination ability, gives lower conversion and turnover rate in comparison with acetone. It was demonstrated that the use of pyridine, a better coordinating solvent than acetone, resulted in poor conversion (7.2%) and low turnover rate (82.1 mol (mol cat)$^{-1}$ h^{-1}) when (*R*,*S*)-[S(4-ClPh)]C_5H_4Fe[CHMeNMe_2][S(4-ClPh)] was used [11]. The conversion and turnover rate for this catalyst in the presence of acetone was 100% and 645.1 mol (mol cat)$^{-1}$ h^{-1}, respectively. The hydrogenation reaction may be initiated by breakage of the Pd–Cl bond when the solvent is a mixture of acetone and water.

Table 5 shows the results of hydrogenation of 1,3-cyclohexadiene by use of catalysts **5b, 5e, 6e**, and **6h** (Scheme 2) in the presence of acetone as solvent. In all cases, the conversions are 100% and there is no induction time. Turnover rates are fairly high between 152.8 to 665.2 mol (mol cat)$^{-1}$ h^{-1}. The selectivities are high and in the case of catalyst **5b** 96.7% selectivity has been achieved. A comparison between the hydrogenation reactions catalyzed by complexes **5b** with two phenylthio substituents and **5e** with two 4-chlorophenylthio substituents, reveals that the turnover rate is higher in the latter reaction while the selectivity is higher in the

Table 5

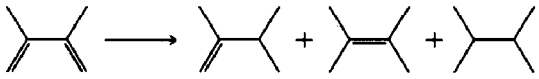
Selective hydrogenation of 1,3-cyclohexadiene (7.45×10^{-3} mol) with various complexes in acetone (9 ml) at room temperature and 104 p.s.i. initial H_2 pressure

Catalyst [a]	Conversion (%)	Induction time (h)	Turnover rate (mol/mol cat. h)	Products	
				Cyclohexene (%)	Cyclohexane (%)
[SR]$C_5H_4FeC_5H_3$[CHMeNMe_2][SR][$PdCl_2$]					
R = Ph (**5b**)	100	0	152.8	96.7	3.3
R = 4-ClPh (**5e**)	100	0	544.2	89.2	10.8
[SR]$C_5H_4FeC_5H_3$[CH_2NMe_2][SR][$PdCl_2$]					
R = Ph (**6e**)	100	0	475.53	95.9	4.1
R = 4-ClPh (**6h**)	100	0	665.17	94.8	5.6

[a] 2.0×10^{-5} mol of catalyst.

former case. Also, the turnover rate is higher for catalyst **6h** with two 4-chlorophenylthio substituents than for **6e** with two phenylthio substituents while the selectivities are almost equal for both catalysts. Comparison of data in Tables 3 and 5 shows that the results of hydrogenation reactions not only depend on catalyst and solvent, but they also depend on the substrate.

Because the new palladium ferrocenyl amine sulfides are active catalysts for the selective hydrogenation of cyclic conjugated substrates, the hydrogenation reaction of an acyclic substrate, 2,3-dimethyl-1,3-butadiene, was carried out. Catalyst **5e** (S,R)-[S-(4-ClPh)]$C_5H_4FeC_5H_3$[CHMeNMe$_2$][S-(4-ClPh)][$PdCl_2$] was used and the results are given in eq. 1.



(24.9%) (73.3%) (0.9%) (1)

The initial H_2 pressure was 80 p.s.i., 4.5 ml acetone was used as solvent, and the amount of substrate was 2.37×10^{-3} mol (0.24 ml). Initial turnover rate, induction time and conversion were 160.8 mol (mol cat)$^{-1}$ h^{-1}, 6 min, and 99.1%, respectively. Interestingly, two olefin isomers were obtained and this shows that during this reaction isomerization occurred. In order to evaluate catalytic activities of the new Pd complexes, they were compared with some known palladium catalysts. The results are summarized in Table 6. Comparison of entries 1–5 with entry 6 ($PdCl_2$ complexed by undecyl amine, reduced by diisobutylaluminum hydride and hydrolyzed) [27] and with the catalyst in entry 7, ($PdCl_2$ treated with tertiary amines) [28] shows the same order of magnitude for hydrogenation of different substrates. However, the new catalysts are faster than chelating bis(phosphine)palladium catalysts by three orders of magnitude (entry 8) [29].

Table 6

Comparison of the catalytic activities of new complexes with known palladium catalysts for selective hydrogenation of dienes to olefins

Entry	Initial rate mol/mol of Pd/h p.s.i.	Substrate	T (°C)	Solvent	Additive	Ref
1	6.58	1,3-Cyclooctadiene	27	acetone	–	This work [a]
2	5.23	1,3-Cyclohexadiene	27	acetone	–	This work [a]
3	6.94	1,3-Cyclooctadiene	27	acetone	–	This work [b]
4	6.39	1,3-Cyclohexadiene	27	acetone	–	This work [b]
5	2.01	2,3-Dimethyl-1,3--butadiene	27	acetone	–	This work [a]
6	8.99	1,3-Cyclooctadiene	22	toluene	water	27
7	3.45–5.52	Isoprene	22	toluene	–	28
8	0.0011	1,4-Cyclohexadiene	65	toluene	–	29

[a] (S,R)-[S(4-ClPh)]$C_5H_3FeC_5H_3$[CHMeNMe$_2$][S(4-ClPh)]. [b] [S(4-ClPh)]$C_5H_4FeC_5H_3$[CH_2NMe$_2$][S(4-ClPh)].

Asymmetric Grignard cross coupling reactions

Asymmetric carbon–carbon bond formation is of great interest for the preparation of chiral molecules and frequently novel chiral transition-metal catalysts have been used for this purpose [30]. In 1973, the first asymmetric Grignard cross-coupling reaction catalyzed by a nickel complex was reported [31].

Reaction of $NiCl_2$ with chiral ligands (*S*,*R*)-[SR]$C_5H_4FeC_5H_3$[CHMeNMe$_2$][SR], R = Et [10], s-Bu [10], Ph, 4-ClPh produced in situ nickel complexes which are active catalysts for asymmetric Grignard cross-coupling reactions between allylmagnesium chloride and 1-phenyl-1-chloroethane.

$$\underset{\displaystyle CH_3}{\underset{|}{PhCHCl}} + ClMgCH_2CH{=}CH_2 \xrightarrow[Et_2O,\ THF]{Catalyst} \underset{\displaystyle CH_3}{\underset{|}{PhCHCH_2CH{=}CH_2}} \quad (> 95\%) \qquad (2)$$

Table 7 shows the chemical and optical yields of these reactions. The chemical yields were very high for all four complexes (96–97.5%). Fairly good optical yields were also achieved (21.2–27.7%). The yields are much higher than those reported by Kellog [32] and slightly better than those reported by Okoroafor [8]. In all cases, the resulting products have the *R* configuration, the configuration of ferrocene chirality. However, we cannot deduce any conclusion from the observation.

It has been shown that the optical rotation of the 4-phenyl-1-pentene was strongly affected by small amounts of impurities [33]. Moreover, products were racemized and it was difficult to determine the optical purity by use of a polarimeter. The enantiomeric excess of the product was determined by use of ^{1}H NMR spectroscopy in the presence of a chiral shift reagent, tris(*d*,*d*-dicamphorylmethanato)europium(III) (Eu(dcm)$_3$), after the alkene was converted into the methyl ester [34]. At room temperature and without addition of the chiral shift reagent there is only one singlet for the methyl protons of the methyl ester. However, the signal separates into two distinct singlets after addition of the shift reagent. It has been reported [33] that the signal of (*S*)-methyl-3-phenyl propionate appears at a higher field than that of the *R* enantiomer.

Conclusion

Two new series of ferrocenyl amine sulfide ligands and their palladium and platinum chloride complexes have been synthesized. The structure of these heterobi-

Table 7
Asymmetric Grignard cross-coupling reactions using chiral nickel ferrocenyl amine sulfide catalysts

Catalyst	Chemical yield (%)	e.e. (%)	Configuration
(*S*,*R*)-[SR]$C_5H_4FeC_5H_3$[CHMeNMe$_2$][SR]/$NiCl_2$			
R = Et	97.5	21.2	*R*
R = s-Bu	96	23.2	*R*
R = Ph	96	22.5	*R*
R = 4-ClPh	96.5	27.7	*R*

metallic complexes was studied by use of ^1H NMR and X-ray structure determination. It was found that palladium is coordinated to a nitrogen and a sulfur or selenium atom of the same Cp ring as is shown in **a** (Scheme 3). This structure is different from palladium ferrocenylaminephosphine analogs. The new palladium complexes are effective catalysts for hydrogenation of dienes to olefins. These catalysts are easy to synthesize and are air-stable. The hydrogenation reactions were performed under low initial H_2 pressures (ca. 5–7 atm) and at room temperature. These complexes are very effective and selective catalysts for the reduction of carbon–carbon double bonds of α–β unsaturated carboxylic acids, esters, nitriles, ketones, aldehydes, and lactones [35]. Because of these advantages, these palladium complexes are attractive alternatives to other transition metal-based catalysts for the selective reduction of double bonds.

Nickel ferrocenylamine sulfide complexes obtained in situ from the reaction of $NiCl_2$ and ferrocenyl sulfide ligands are effective catalysts for asymmetric Grignard cross-coupling reactions.

Experimental

General. Air sensitive reagents were manipulated in a prepurified argon atmosphere. Standard Schlenk-ware techniques and a vacuum line were employed. Where necessary an argon filled glove box was used for transfers.

Infrared spectra (IR) were obtained by use of a Perkin Elmer 457 grating, a Perkin Elmer 599 grating, and a Nicolet 740 FT-IR spectrophotometer by using neat films of liquid samples, Nujol mulls between CsI plates, or in KBr pellets for solid samples. Mass spectra were obtained by means of a Finnigan 4000 instrument with an Incos data system at 70 eV. ^1H and ^{13}C NMR were obtained by use of a Bruker WM-250 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Gas chromatography (GC) was carried out by using a Hewlett–Packard 5880 instrument with a 25m GB-1 capillary column, and a Varian 1400 instrument with 30 m DBWAX MEGABORE column. All melting points were determined by using a Thomas–Hoover capillary melting point apparatus and were uncorrected.

All solvents used were reagent grade and were distilled by standard methods [36]. (*S*)-[1-(Dimethylamino)ethyl]-ferrocene ((*S*)-**1**) was prepared according to Ugi's procedure [37]. [(Dimethylamino)methyl]ferrocene, dialkyl and diaryl disulfides, dimethyl and diaryl diselenides, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were purchased from Aldrich Chemical Co. Bis(benzonitrile) complexes, $[(PhCN)_2MCl_2]$, where M = Pd and Pt were prepared according to published procedures [38].

Preparation of ligands. All the ligands were prepared in a similar way. A representative example (**2a**) is outlined below. Detail of all the analytical data, colors, yields, and melting points are summarized in Table 1.

The amine (*S*)-**1** (1.3 g, 5.1 mmol) was dissolved in 75 ml of dry ether and placed in a 200 ml round-bottomed Schlenk flask equipped with a side arm and rubber septum. The solution was cooled to −78°C and while being stirred, 3.0 ml (8.1 mmol of a 2.7 *M*) solution of n-BuLi in hexane was added dropwise via a syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Then, a solution of freshly distilled TMEDA (0.9, g, 7.5 mmol) and n-BuLi

(3.0 ml, 8.1 mmol) was added to the reaction mixture at −78°C. After being stirred for 8 more h at room temperature, to the reaction mixture was added dropwise, a solution of dimethyl disulfide (1.42 g, 15 mmol) at −78°C. The reaction mixture was allowed to reach room temperature and stirred under Ar for an additional 24 h, after which saturated aqueous $NaHCO_3$ was added to the mixture. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with cold water and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a product mixture that was chromatographed on a silica gel column (hexane/ether) to give a brown oil; yield 90%.

^{1}H NMR (δ ppm), 4.26(m, 1H, H^3, H^4, H^5, C_5H_3); 4.17(m, 4H, C_5H_4); 4.07(m, 2H, H^3, H^4, H^5, C_5H_3); 3.90(q, J 4.4 Hz, 1H, CH_3CH); 2.28(s, 3H, SCH_3); 2.23(s, 3H, SCH_3); 2.09(s, 6H, NMe_2); 1.36(d, J 4.4 Hz, 3H, CH_3CH).

^{13}C NMR (δ ppm), 93.6(s, C^1); 85.9(s, C^2); 84.9(s, C'^1); 73.2 (d, C^5); 77.5(d, C'^3, C'^4); 72.4(d, C'^5); 71.1 (d, C'^2); 69.6(d, C^4); 68.4(d, C^3); 56.2(d, $CHCH_3$); 40.0 (q, NMe_2); 19.7(q, SCH_3); 19.6(q, SCH_3); 10.7(q, CH_3CH).

MS, *m/e* (relative intensity): 349(77, M^+), 334(24, $M^+ - Me$), 304(38, $M^+ - 3Me$), 358(78, $M^+ - SMe-NMe_2$), 72(100, $MeCHNMe_2$), 56(50, Fe), 44(25, NMe_2).

IR (neat, KBr disks) 3095 (ferrocene C–H stretch), 2970–2775 (alkyl C–H stretch), 1452 (ferrocene antisymmetric C–C stretch), 1265, 1249 (C–N stretch), 825 (C–H bend perpendicular to the plane of the Cp ring), 655 (S–C stretch), 491 cm^{-1} (antisymmetric ring–metal stretch).

Preparation of metal complexes. The new complexes (Scheme 2) were prepared from benzene solutions of $(PhCN)_2PdCl_2$ (0.1 g) or $(PhCN)_2PtCl_2$ (0.2 g) and a slight excess of ligand in an approximate 1/1.2 molar ratio. The reaction mixture was stirred for 8 h in the case of Pd complexes, and for 8 days in the case of Pt complexes. The resulting precipitates were collected by filtration, washed with cold benzene and petroleum ether. The pure crystals were obtained by recrystallization from CH_2Cl_2/hexane or acetone.

X-ray structure determination. The crystal structure determination of complex **6a** is summarized in Table 8.

Hydrogenation of 1,3-cyclooctadiene, 1,3-cyclohexadiene, and 2,3-dimethyl-1,3-butadiene. The procedure is identical with that reported before [9]. The initial turnover rate, product analysis and the selectivity were determined at the end of the reactions. Products were analyzed by use of GC and ^{1}H NMR spectroscopy.

Asymmetric Grignard cross-coupling reaction of allymagnesium chloride to 4-phenyl-1-pentene using in situ nickel complexes. $NiCl_2$ (0.0499 mmol, 0.0065 g) was placed in a 100 ml round-bottomed Schlenk flask equipped with a stirring bar and a septum. The vessel was evacuated and filled with Ar several times. 10 ml dry ether was added to the flask to dissolve $NiCl_2$ and then 0.0499 mmol of appropriate ligand was added and the reaction mixture was stirred for 2 h. Upon being cooled to −78°C, 1.41 g (10.0 mmol) 1-phenylethyl chloride in 20 ml dry ether was added dropwise and stirred for 2 h at room temperature before allymagnesium chloride (10 mmol, 5 ml of 2 M solution in THF) was added via syringe at −78°C. The reaction mixture was allowed to warm to 0°C, stirred for 10 h and hydrolyzed with 10% HCl. The organic layer and ether extracts from the aqueous layer were combined, washed with saturated $NaHCO_3$ solution and water, and dried over Na_2SO_4. Evaporation of solvent and chromatography on a silica gel column (hexane/ether) gave 96–97.5% of 4-phenyl-1-pentene.

Table 8

X-ray structure determination for [1-[(dimethylamino)methyl]-2,1′-bis(methylthio)ferrocene]palladium(II) chloride (**6a**)

Formula	$C_{15}H_{21}Cl_2FePdNS_2$
F.W.	512.62
Crystal	
color	deep red
size	0.04×0.36×0.60 mm
mounting	glass capillary, random orientation
density	1.90 g/cm^3 (calc)
Radiation	Mo-K_α, (λ = 0.71073 Å)
Instrument	Nicolet P3F diffractometer
Unit cell	
no. reflns	18
2θ range	$20 < 2\theta < 25$
temperature	24(1) °C
system	monoclinic
space group	$P1_1/c$
a	11.567(2) Å
b	11.675(2) Å
c	13.270(2) Å
β	90.31(1)°
volume	1792.1(4) Å^3
Data collection	
scan type	$\theta-2\theta$
scan rate	3°/min (in 2θ)
scan range (°)	$2.00+(2\theta(K_{\alpha_2})-2\theta(K_{\alpha_1}))$
max. 2θ	50°
total data	3329
unique data	3006
Absorption correction	
coefficient	23.2 cm^{-1} (for Mo-K_α)
type	empirical, based on ψ-scans
range	0.933 to 1.000, average 0.996
Structure solution	
method	Patterson heavy-atom, Pd atom located, other non-H atoms from succeeding difference maps
Structure refinement	
method	full-matrix least-squares
minimization	$\Sigma w(\|F_o\|-\|F_c\|)^2$
weight, w	1.0 for observed reflections
H-atoms	riding on carbon atom
scat. factors	Cromer and Waber [39]
$\Delta f'$ and $\Delta f''$	Cromer [39]
observed data	2742 with $I > 3\sigma(I)$
parameters	200
convergence	largest $\delta/\sigma < 0.37$
R factors	$R_1 = \Sigma\|\|F_o\|-\|F_c\|\|/\|\Sigma F_o\| = 0.084$
	$R_2 = (\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma wF_o^2)^{1/2} = 0.105$
e.s.d.o.u.w. [a]	5.59
computer	VAX 11/750
program system	SDP/VAX [40]

[a] Estimated standard deviation of an observation of unit weight.

Conversion of 4-phenyl-1-pentene to methyl 3-phenylbutyrate. The procedure is identical with that reported [8].

Supplementary material available. Tables of ^{1}H and ^{13}C NMR for ligands **2a–2f** and **4a–4f** (Scheme 1), ^{1}H NMR for complexes **5a–5j** and **6a–6k** (Scheme 2), positional parameters, bond angles, bond distances, temperature factor expressions (U's), least-square planes, torsion angles, hydrogen atom parameters and a list of observed and calculated structure factors for $[SMe]C_5H_4FeC_5H_3[CH_2NMe_2][SMe][PdCl_2]$ (**6a**) (19 pages). Ordering information is available from the authors. (See NAPS document no. 04780 for 19 pages of supplementary material. Order from ASIS/NAPS Microfiche Publications, P.O. Box 3513 Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $0.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. $1.50 for postage of any microfiche orders.)

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