Catalytic and Stoichiometric Synthesis of Ferrocene-Containing Polyazamacrocycles and Chelating Bidentate Nitrogen Ligands

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A series of ferrocene-containing chelating bidentate nitrogen ligands (**1** & **2**) and polyazamacrocycles (**3** & **4**) were prepared in high yields from the reaction of ferrocenecarboxaldehydes with corresponding diamines under various catalytic and stoichiometric reaction conditions. The stoichiometric condensation to form Schiff bases required the presence of MgSO₄ in the reaction mixture as a water-absorbent. Employment of cyclic diamines such as 1,2-diaminocyclohexane and *p*-phenylenediamine in the reaction with 1,1'-ferrocenedicarboxaldehyde resulted in the formation of polymers in stead of the expected macrocycles. All these compounds were characterized by microanalytical and spectroscopic techniques. In one case, the structure of **3a** was confirmed by X-ray crystallography.

Introduction

Ferrocene-containing chelate bidentate phosphines and aminophosphines have served as powerful ligand for transition metal complexes in a number of homogeneous catalytic reactions and asymmetric syntheses.[1,2] From a redox view point, ferrocene-containing macrocycles and cryptands have also attracted considerable attention in recent years due to their potential applications in the fields of chemical sensors, cation transport across membranes, molecular electronics, and even as catalysts either in chemical processes or as mimics for metallo-enzymes.[3,4]

Thus an important challenge in this area is the design and synthesis of potential multielectron redox mediators which could also function as ligand in homogeneous catalysis. Our interest in this field has led us to synthesize a series of ferrocene-containing polyazamacrocycles and chelate bidentate Schiff bases and to explore their complex formation with metal ions in order to investigate their catalytic activities in comparison with those incorporating the well-known ferrocenyl-phosphines and aminophosphines. In fact, we have recently demonstrated that some rhodium(I) and iridium(I) complexes incoporating a chelate Schiff base such as N,N'-ethylenebis((ferrocenylmethyl)imine) (**1a**) are excellent catalysts for the synthesis of high-molecular weight polyphenylacetylenes[5] and for the cyclization of alkynoic acids to give lactones.[6] In the present paper, we report the synthesis and characterization of the ferrocene-containing nitrogen donors **1-4** (Schemes 1 and 2). It should be noted, however, that although the compounds **1a**, **2a**, **3a**, and **4a** are already known[12,14] the synthetic routes described in this work are rather comprehensive and general giving higher yields. In particular, the one-pot bimetallic catalytic synthesis of amines from aldehyde and primary diamines is the first example of the kind in the literature.

Experimental Section

Reagents and Instrumentals
All the chemicals were purchased from Aldrich Chemical Co. and Strem Chemical Co. unless otherwise mentioned. 1, 1'-ferrocenedicarboxaldehyde,[7] 1,1'-bis(diphenylphosphino) ferrocene (dppf),[8] [Rh(COD)(dppf)]ClO₄,[9] and Ru(PPh₃)₃Cl₂[10] were prepared according to the literature methods. All manipulations were carried out under an argon atmosphere using a double manifold vacuum system and Schlenk techniques. Solvents were purified by standard methods[11] and were freshly distilled prior to use. Microanalysis were performed by the Center for Instrumental Analysis, Kyungpook National University. ¹H and ³¹P NMR spectra were recorded on a Varian Unity Plus 300 spectrometer operating at 300 and 121.5 MHz, respectively. IR spectra were recorded on a Mattson FT-IR Galaxy 6030E spectrophotometer and Nicolet Magna-IR 550 spectrometer. UV-Vis spectra were measured on a HP 8452A Diode-Array spectrophotometer.

Typical Procedure for the Synthesis of Ferrocenyl Diimines 1
Synthesis of 1a
Stoichiometric Reaction (Route a). The title compound was prepared according to the literature method[12] with slight modification. Namely, a mixture of ferrocenecarboxaldehyde (1.0 g, 4.7 mmol), ethylenediamine (0.20 mL, 2.9 mmol), and anhydrous MgSO₄ (0.30 g) in diethyl ether was stirred at ambient temperature for 20 h. The solid suspension was removed by filtration, and the resulting orange solution was evaporated to dryness and the oily residue was recrystallized from diethyl ether to give yellow solid (0.84 g, yield 76%).

Catalytic Reaction (Route b). To a solution of ferrocenecarboxaldehyde (1.0 g, 4.7 mmol) and ethylenediamine (0.20 mL, 2.9 mmol) in dioxane (50 mL) was added a catalytic amount of RuCl₂(PPh₃)₃ (0.20 g, 2 mol%). The mixture was stirred for 5 h at ambient temperature, after which time diethyl ether was added, and the orange precipitate was separated by filtration. The crude product was purified by recrystallization from CH₂Cl₂/diethyl ether (1.0 g, yield 91%). Anal. Calcd (found) for C₂₄H₂₄N₂Fe₂: C, 63.80 (63.40); H, 5.40 (5.62); N, 6.20 (6.40). IR (KBr/Nujol, cm⁻¹): 1639 ($v_{C=N}$, vs). ¹H NMR (CDCl₃, d): 3.76 (s,

4H, NCH$_2$CH$_2$N), 4.14 (s, 10H, C$_5$H$_5$), 4.33 (s)/4.62 (s) (8H, C$_5$H$_4$), 8.16 (s, 2H, HC=N).

Synthesis of 1b

This was prepared by the same manner as described above for **1a** and obtained as orange solid (yield 87%). Anal. Calcd (found) for C$_{25}$H$_{26}$N$_2$Fe$_2$: C, 64.40 (64.66); H, 5.62 (5.62); N, 6.15 (6.01). ^{1}H NMR (CDCl$_3$, δ): 2.02 (qnt, 2H, CCH$_2$C, $^3J_{H-H}$=7.0 Hz), 3.55 (t, 4H, =NCH$_2$, $^2J_{H-H}$=7.0 Hz), 4.12 (s, 10H, C$_5$H$_5$), 4.38 (s)/4.66 (s) (8H, C$_5$H$_4$), 8.17 (s, 2H, HC=N).

Synthesis of 1c

This was obtained as an orange oil (yield 73%). ^{1}H NMR (CDCl$_3$, δ): 1.71 (bs, 1H, NH), 2.59-2.85 (m, 4H, H$_2$CNH), 3.51 (bs, 4H, =NCH$_2$), 4.09 (s, 10H, C$_5$H$_5$), 4.27 (s)/4.54 (s) (8H, C$_5$H$_4$), 8.08 (s, 2H, HC=N); MS m/z 495 (M$^+$), 452, 430, 323, 299, 269, 227, 199, 162, 121. HRMS calcd for C$_{26}$H$_{29}$N$_3$Fe$_2$ 495.1061, found 495.1043.

Synthesis of 1d

This was obtained as orange solid (yield 92%). Anal. Calcd (found) for C$_{28}$H$_{30}$N$_2$Fe$_2$: C, 66.43 (66.45); H, 5.97 (6.10); N, 5.53 (5.62). ^{1}H NMR (CDCl$_3$, δ): 1.35 (m, 8H, Cyclohexyl), 1.52 (s, 2H, HC=N), 4.02 (s)/4.15 (s) (8H, C$_5$H$_4$), 4.17 (s, 10H, C$_5$H$_5$), 8.11 (s, 2H, HC=N).

Synthesis of 1e

This was obtained as orange solid (yield 86%). Anal. Calcd (found) for C$_{28}$H$_{24}$N$_2$Fe$_2$: C, 67.23 (67.42); H, 4.84 (4.70); N, 5.62 (5.78). ^{1}H NMR (CDCl$_3$, δ): 4.26 (s, 10H, C$_5$H$_5$), 4.49 (s)/4.81 (s) (8H, C$_5$H$_4$), 7.18-7.26 (m, 4H, phenyl), 8.38 (s, 2H, HC=N).

Typical Procedure for the Synthesis of Ferrocenyl Diamines 2.

Synthesis of 2a.

Stoichiometric Reduction by KHFe(CO)$_4$ (Route c). The title compound was prepared as follows. KHFe(CO)$_4$ was prepared from Fe(CO)$_5$ (0.27 mL, 2.1 mmol) in an 1 N alcoholic KOH solution according to the literature procedure.[13] To this solution was added ferrocencarboxaldehyde (0.43 g, 2 mmol) in ethanol (20 mL) and ethylenediamine (0.07 mL, 1 mmol). The reaction mixture was stirred vigorously for 2 days at room temperature under an atmosphere of carbon monoxide. The solution was then filtered and the filtrate was evaporated to dryness under vacuum to yield an oily residue. Recrystallization from CH$_2$Cl$_2$/isooctane gave orange solid (0.12 g, yield 75%).

Stoichiometric Reduction by LiAlH$_4$ (Route d). The same product was obtained by simple reduction of the corresponding Schiff base by LiAlH$_4$ as described in the literature.[12]

Catalytic Hydrogenation (Route e). In a 50 mL autoclave were placed **1a** (2.3 g, 5 mmol), a catalytic amount of [Rh(COD)(dppf)]ClO$_4$ (2 mol%), and dioxane (20 mL) under a stream of argon, along with a stirring bar. After being flushed with H$_2$, the reactor was then pressurized to 1 atmosphere of hydrogen and placed in a thermostatic oil bath (120 °C) for 9 h. Diethyl ether was added to the resulting reaction solution, and the orange precipitate was separated by filtration which was recrystallized from CH$_2$Cl$_2$/diethyl ether to give **2a** as orange powder (1.7 g, 72%). Anal. Calcd (found) for C$_{24}$H$_{28}$N$_2$Fe$_2$: C, 63.20 (63.10); H, 6.10 (5.87); N, 6.10 (5.98). ^{1}H NMR (CDCl$_3$, δ): 1.77 (b, 2H,

NH), 2.73 (s, 4H, NCH$_2$CH$_2$N), 3.53 (s, 4H, =CCH$_2$N), 4.09 (s)/4.18 (s) (8H, C$_5$H$_4$), 4.12 (s, 10H, C$_5$H$_5$).

Synthesis of 2b

This was obtained as orange oil (yield 63%). Anal. Calcd (found) for C$_{25}$H$_{30}$N$_2$Fe$_2$: C, 63.85 (62.95); H, 6.43 (6.98); N, 5.95 (5.18). ^{1}H NMR (CDCl$_3$, δ): 1.43 (b, 2H, NH), 1.84 (m, 2H, CCH$_2$C), 2.68 (s, 4H, NCH$_2$C), 3.50 (s, 4H, CpCH$_2$N), 4.09 (s, 10H, C$_5$H$_5$), 4.16 (s)/4. 17 (s) (8H, C$_5$H$_4$).

Synthesis of 2c

This was obtained as an orange oil (yield 67%). Anal. Calcd (found) for C$_{26}$H$_{30}$N$_3$Fe$_2$: C, 62.54 (62.50); H, 6.66 (7.47); N, 8.41 (7.90). ^{1}H NMR (CDCl$_3$, δ): 1.11 (b, 2H, β-NH to Cp), 1.19 (b, 1H, NH), 2.67 (m, 4H, CH$_2$), 2.70 (m, 4H, CH$_2$), 3.47 (s, 4H, CpCH$_2$), 4.04 (m, 18H, (C$_5$H$_4$)Fe(C$_5$H$_5$)).

Synthesis of 2d

This was obtained as an orange oil (yield 71%). Anal. Calcd (found) for C$_{28}$H$_{32}$N$_2$Fe$_2$: C, 65.91 (65.97); H, 6.72 (7.11); N, 5.49 (5.58). ^{1}H NMR (CDCl$_3$, δ): 1.23 (m, 8H, cyclohexyl), 1.46 (b, 2H, NH), 2.09 (m, 2H, CH), 3.53 (s, 4H, CpCH$_2$), 4.15 (s, 10H, C$_5$H$_5$), 4.18 (s)/4.19 (s) (8H, C$_5$H$_4$).

Synthesis of 2e

This was obtained as orange solid (yield 75%). Anal. Calcd (found) for C$_{28}$H$_{28}$N$_2$Fe$_2$: C, 66.69 (66.58); H, 5.60 (5.83); N, 5.55 (5.25). ^{1}H NMR (CDCl$_3$, δ): 3.47 (b, 2H, NH), 3.92 (s, 4H, CpCH$_2$), 4.17 (s, 10H, C$_5$H$_5$), 4.23 (s)/4.24 (s) (8H, C$_5$H$_4$), 6.63 (m, 4H, C$_6$H$_4$).

Typical Procedure for the Synthesis of Ferrocenyl Macrocyclic Tetraimines 3.

Synthesis of 3a.

Stoichiometric Reaction (Route f). This compound was prepared essentially using the same method for the preparation of **1a** replacing the ferrocenemonocarboxaldehyde by the corresponding 1,1'-ferrocenedicarboxaldehyde. A mixture of ferrocenedicarboxaldehyde (2.4 g, 10.0 mmol), ethylenediamine (0.68 mL, 10.0 mmol), and anhydrous MgSO$_4$ (2.0 g) in diethyl ether was stirred at ambient temperature for 24 h. The solid suspension was removed by filtration, and the resulting orange solution was evaporated to dryness and the oily residue was recrystallized from diethyl ether to give yellow solid (2.3 g, yield 72%).

Catalytic Reaction (Route g). To a solution of ferrocenecarboxaldehyde (2.4 g, 10.0 mmol) and ethylenediamine (0.68 mL, 10.0 mmol) in dioxane (50 mL) was added a catalytic amount of RuCl$_2$(PPh$_3$)$_3$ (0.20 g, 2 mol%). The mixture was stirred for 5 h at ambient temperature, after which time diethyl ether was added, and the orange precipitate was separated by filtration. The crude product was purified by recrystallization from CH$_2$Cl$_2$/diethyl ether (2.6 g, yield 85%). Anal. Calcd (found) for C$_{28}$H$_{28}$N$_4$Fe$_2$: C, 63.20 (63.40); H, 5.30 (5.40); N, 10.30 (10.40). IR (KBr/Nujol, cm^{-1}): 1639 (ν$_{C=N}$, vs). ^{1}H NMR (CDCl$_3$, δ): 3.79 (t, 8H, CH$_2$, $^3J_{H-H}$=8.7 Hz), 4.17 (s)/4.34 (s)/4.15 (s)/4.56 (s) (16H, C$_5$H$_4$), 8.08 (s)/8.21 (s) (4H, HC=N).

Synthesis of 3b

This was obtained as orange solid (yield 81%). Anal. Calcd (found) for C$_{30}$H$_{24}$N$_4$Fe$_2$: C, 64.31 (64.10); H, 5.80 (5.90); N, 9.99 (9.73). ^{1}H NMR (CDCl$_3$, δ): 2.63 (b, 4H, NC̲H$_2$CH$_2$CH$_2$N), 3.61 (s, 8H, CH$_2$N=), 4.41 (s)/4.42 (s)/4.43

(s)/4.60 (s) (16H, C_5H_4), 7.30 (s, 4H, HC=N).

Synthesis of 3c

This was obtained as orange solid (yield 82%). Anal. Calcd (found) for $C_{32}H_{20}N_6Fe_2$: C, 65.10 (65.00); H, 6.49 (6.30); N, 9.50 (9.80). ^1H NMR (CDCl$_3$, δ): 2.85 (t, 8H, =NCH$_2$, $^3J_{H-H}$=5 Hz), 3.57 (t, 8H, CH$_2$N=C, $^3J_{H-H}$=5 Hz), 4.36 (s)/4.72 (s) (16H, C_5H_4), 7.95 (s, 4H, HC=N).

Typical Procedure for the Synthesis of Ferrocenyl Macrocyclic Tetraamines 4.

Synthesis of 4a.

Stoichiometric Reduction by KHFe(CO)₄ (Route h). This compound was prepared essentially using the same method for the preparation of 2a via route (c) replacing the ferrocenemonocarboxaldehyde by the corresponding 1,1'-ferrocenedicarboxaldehyde. The product was obtained as red solid (yield 72%).

Stoichiometric Reduction by LiAlH₄ (Route i). The same procedure as route (d) by employing the corresponding dialdehyde gave the same product (yield 75%).

Catalytic Hydrogenation (Route j). The same reaction conditions as described in route (e) was employed (yield 70%). Anal. Calcd (found) for $C_{28}H_{28}N_4Fe_2$: C, 62.24 (62.35); H, 6.72 (6.18); N, 10.37 (10.18). ^1H NMR (CDCl$_3$, δ): 1.80 (b, 4H, NH), 3.47 (t)/3.84 (t) (8H, CH$_2$, $^3J_{H-H}$=9.7 Hz), 3.75 (s, 8H, CpCH$_2$), 4.16 (s)/4.18 (s)/4.33 (s)/4.37 (s) (16H, C_5H_4).

Synthesis of 4b

This was obtained as an orange oil; yield 60%; Anal. Calcd (found) for $C_{30}H_{40}N_4Fe_2$: C, 63.39 (63.10); H, 7.09 (7.14); N, 9.86 (9.37). ^1H NMR (CDCl$_3$, δ): 2.02 (b, 4H, NCH$_2$CH$_2$CH$_2$N), 2.61 (b, 8H, CpCH$_2$), 3.58 (b, 8H, NCH$_2$CH$_2$CH$_2$N), 4.39 (s)/4.57 (s) (16H, C_5H_4).

Synthesis of 4c

This was obtained as an orange oil (yield 60%). Anal. Calcd (found) for $C_{32}H_{44}N_4Fe_2$: C, 61.35 (61.69); H, 7.40 (7.78); N, 13.42 (13.78). ^1H NMR (CDCl$_3$, δ): 2.17 (b, 6H, NH), 2.57-2.67 (m, 8H, CH$_2$N), 3.14 (b, 8H, CpCH$_2$), 3.40-3.55 (m, 8H, CH$_2$N), 3.99-4.44 (m, 16H, C_5H_4).

Crystal Structure Determination of 3a[14]

An orange, single crystal, 0.45×0.40×0.40 mm, was mounted in a thin-walled glass capillary on an Enraf-Nonius CAD-4 diffractometer with Mo-K$_α$ radiation (λ=0.71073 Å), unit cell parameters were determined by least-squares analysis of 25 reflections (10°<θ<13°). Intensity data were collected with θ range of 2.16-24.97° in ω/2θ scan mode for the range −35≤h≤34, 0≤k≤11, 0≤l≤9.2016 independent reflections were observable, of which 1667 with I>2σ(I). Three standard reflections were monitored every 1 h during data collection. the data were corrected for Lorentz-polarization effects and decay. Empirical absorpotion corrections with X scans were applied to the data (the range of correction; 0.73 to 1.00). The crystals of 3a belong to the monoclinic system. The space group is C2/c (No. 15) with cell dimension a=29.640(3), b=9.935(1), c=8.111(1) Å, β= 96.76(2)°, V=2371.9(5) Å^3, Z=4, D_c=1.49 g/cm^3, μ=1.248 mm^{-1}.

The structure was solved by using Patterson method and refined by full-matrix least-squares techniques on F^2 using SHELXS-8615 and SHELXS-93.[16] All non-hydrogen atoms

were refined anisotropically, and all hydrogen atoms were positioned geometrically and refined using riding model. The final cycle of the refinement converged with R$_1$=0.034 and wR$_2$=0.081 [w=1/[σ^2(F$_0^2$)+(0.0444×P)^2+0.48×P, where P is Max (F$_0^2$, 0)+2×F$_c^2$)/3]. Goodness-of-fit on F^2 is 1.13. In the last cycle of refinement, shifts of all parameters were less than 0.1% of their estimated standard deviations. Inspection of the last Fourier difference map showed a maximum residual electron density of 0.41 e/Å^3.

## Results and Discussion

Synthesis

The synthesis of ferrocene-containing ligands can in principle be carried out under various reaction conditions depending upon the starting ferrocenyl groups. For instance, some chelate bidentate ferrocenyl Schiff bases are known to form from the reaction of ferrocenylamines with an appropriate aldehyde[17] or from the reaction of ferrocene carboxaldehydes with corresponding amines.[18]

In this connection, we wish to report some simple and convenient methods for the formation of a series of ferrocene-containing polyazamacrocycles as well as their chelate bidentate analogues (e.g., amines & imines) in high yields from the condensation of ferrocenecarboxaldehydes and with corresponding diamines (i.e., ethylenediamine, propylenediamine, diethylenetriamine, 1,2-diaminocyclohexane, and p-diaminobenzene)ˉ under various reaction conditions described in Schemes 1 and 2.

Scheme 1 shows various routes leading to the selective
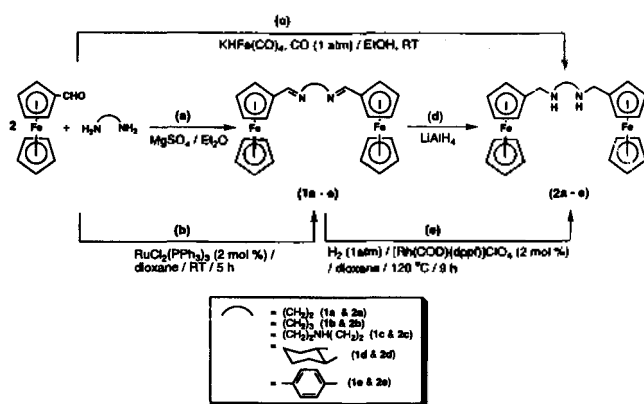
Scheme 1.
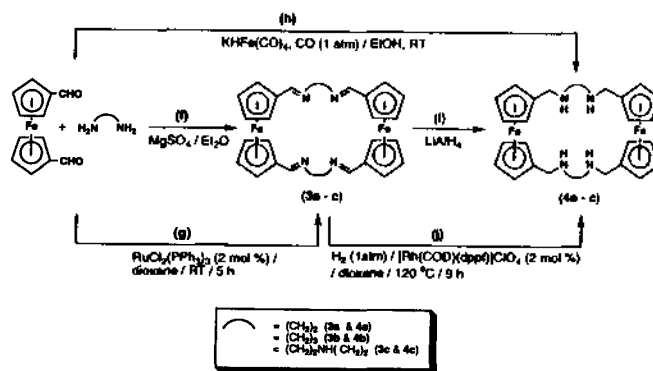
Scheme 2.

formation of chelate bidentate Schiff bases (**1a-e**) and their reduction counterparts (**2a-e**) depending upon the reaction conditions. The preparation of **1a** and **2a** has recently been reported by others from simple azeotropic condensation of ferrocenecarboxaldehyde with ethylenediamine followed by the LiAlH₄ reduction.[12] In our hands, however, this method did not give us **1a** in an any significant amount, and we found that the addition of MgSO₄ into the reaction mixtures was essential to form **1a-e** in high yields (route a). Still better yields were achieved through homogeneous ruthenium catalysis (route b) which gave nearly 100% conversion in all cases examined under very mild reaction conditions. RuCl₂(PPh₃)₃ is now a well-known catalyst for the high yield synthesis of Schiff bases from the reaction of alcohols with primary amines.[19-21] The ruthenium catalysis may involve as key steps coordination of aldehyde to the ruthenium center followed by nucleophilic attack of the amine to form the ruthenium-Schiff base intermediate as proposed in the left circle of Scheme 3.

Ferrocenyl diamines (**2a-e**) were prepared essentially in two different ways, namely either stoichiometrically or catalytically as represented by routes c, d, and e. The direct one-pot synthesis of secondary amines from the reaction of aldehyde and primary amines in the presence of KHFe(CO)₄ is now a well-established procedure,[22] and was employed for the present purposes as described in route c. This reaction is thought to proceed via initial formation of Schiff base and immonium salt followed by the reduction of the carbon-nitrogen double bond.[13,22] One can see that this method eliminates the necessity of isolating the intermediate Schiff base.

The second method involves the catalytic or stoichiometric reduction of the Schiff base (routes d & e). Both routes resulted in the products in high yields. Although the stoichiometric reduction of imines to secondary amines using borohydride-type derivatives is well known,[23] as is catalytic reduction using heterogeneous platinum metals and dihydrogen,[24] it is only recent to be known that homogeneous rhodium-phosphine and iridium-phosphine systems can also hydrogenate the same functional group.[25] We have employed for the present purposes [Rh(COD)(dppf)]ClO₄ which is a well-known catalyst for the hydrogenation of a number of carbon-carbon double bonds.[9,24] The reactions went to nearly 100% conversion in most cases under the conditions described in the scheme.

Of two possible reaction mechanisms for the catalytic hy-

drogenation of carbon-carbon double bond, the hydride route may be preferred, which is an adaption of the scheme proposed by Longley *et al.*[25f] and Cullen *et al.*[25b] for the similar catalytic systems. According to this route, the initial imine binding to rhodium takes place via the nitrogen lone pair. It is also implied that vacant coordination sites have been created at the metal center prior to the initial imine-metal binding, that a Rhᴵᴵᴵ(H)₂ species is first formed, and that the function of the solvent is to facilitate η²- (C=N) bonding. The overall catalytic cycle is proposed in Scheme 3 (the right circle).

In connection with the catalytic hydrogenation of imines, it is worth noting that the ruthenium catalysis ended up with giving the intermediate imines (**1**) even under hydrogenation conditions with the hydrogen pressure of up to 5 atm at 100 °C. Addition of a pre-formed ruthenium hydride such as H₂Ru(PPh₃)₄ into the reaction mixture would not give any hydrogenated products. Nevertheless, as expected, the combination of routes (b) and (e) has provided us with the final diamine derivatives, thus putting a new entry into a bicatalytic tool for the direct one- pot synthesis of secondary amines from the reaction of aldehyde with primary amine. This system is perferred to KHFe(CO)₄ obtaining the same product (route c) in that the reaction can be done in a neat and simple way.

Scheme 2 shows that the synthetic methods described in Scheme 1 can also be applied in the same manner for the synthesis of ferrocene-containing polyazamacrocycles by simply substituting the ferrocenecarboxaldehyde with the corresponding dialdehyde. The results are exactly as expected from those observed in Scheme 1.

An interesting exception, however, was the observations that employment of cyclic diamines such as 1,2-diaminocyclohexane *p*-phenylenediamine resulted in the formation of polymers in stead of the expected macrocycles **5** and **6**, respectively, as shown below.
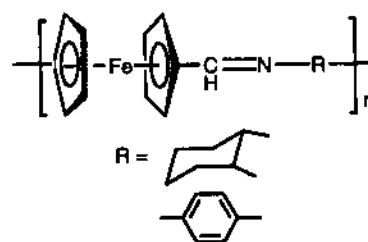

The molecular weight (M�w) of the polymer (**5**) incorporating 1,2-diaminocyclohexane was determined to be 5, 900. On the other hand, the polymer (**6**) incorporating p-phenylenediamine is black powder insoluble in any organic solvent, and thus prevented from molecular weight determination and NMR characterization. Yet the presence of the imine group in addition to the ferrocene and benzene units was confirmed by its IR bands. Microanalytical data for both compounds were consistent well with the above formulation: Anal. Calcd (found) for **5**: C, 67.77 (67.52); H, 6.90 (6.30); N, 8.88 (8.75), and for **6**: C, 68.81 (67.42); H, 4.49 (4.78); N, 8.92 (9.37).

Finally, as for the reaction of ferrocene-1,1'-dicarboxaldehyde, other possible product such as a ferrocenophane (*vide infra*) did not form, indicating that the distance

Scheme 3.

Ferrocene-Containing Polyazamacrocycles
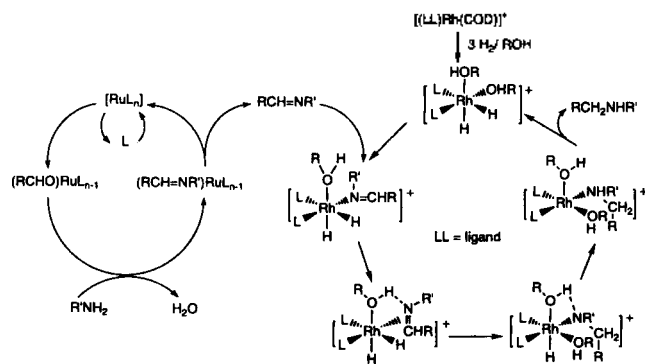
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between the two cyclopentadienyl rings may contribute as an important factor for this ring closure.
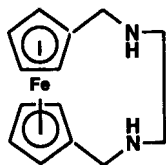
Characterization

The formation of all these ligands have been confirmed by their analytic and spectroscopic techniques, and in one case by X-ray crystallography. One of the most characteristic features of the imine derivatives (**1 & 3**) in ^{1}H NMR spectra is the presence of the aldehydic imine proton (HC=N-) signals that appear as a singlet near 8-9 ppm except for the case of **3a** which gives rise to a pair of singlets (Figure 1). This is because in **3a** the four aldehydic protons exist as two pairs of diastereotopic protons as confirmed by its crystal structure as shown in Figure 2,[14] while in other imines all aldehydic protons are equivalent intrinsically or become equivalent on the NMR time scale due to the conformational fluctuation. The Cp ring pattern also gives a good clue about the numbers of ring substitution. Namely, the macrocycles exhibit a simple AB quart or doublet due to the symmetric 1,1'-disubstituted ferrocene moiety, while the chelate bidendate derivatives give a sharp singlet due to the unsubstituted Cp ring in addition to the AB pattern for the monosubstituted Cp ring (Figure 1).

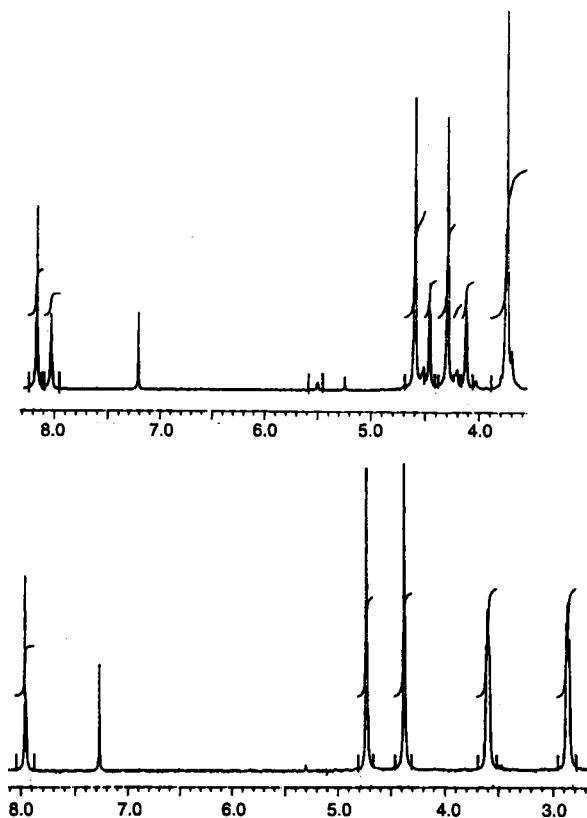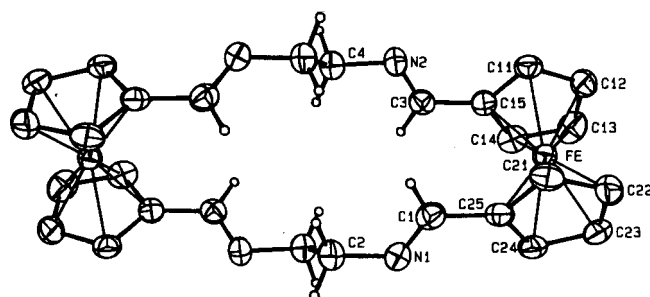Reduction of the imine group to the corresponding amine

Figure 2. X-ray crystal structure of **3a**.

group can be monitored by disappearance of the aldehydic signal with concomitant appearance of a new broad signal for the N-proton in the region 1-2 ppm. Furthermore, for instance, the ν(C=N) imine stretching band which appears as a strong absorption at 1639 cm^{-1} in the spectrum of **1a**, is lacking for **2a** that gives rise to several ν(N-H) stretching vibration in the region 3300-3100 cm^{-1} in stead.

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Figure 1. ^{1}H NMR spectra of **3a** (upper) and **3c** (bottom).

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New Device for Addition of Modifier to Supercritical Fluid Carbon Dioxide Mobile Phase

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A new device to accurately deliver small amount of modifier into supercritical carbon dioxide fluid is described. Carbon dioxide, the most widely used mobile phase in supercritical fluid chromatography, is a relatively non-polar fluid, and hence the addition of small amount of polar modifiers could be necessary to migrate polar solutes. In this work, supercritical CO_2 and modifier are delivered from the pump to a 100 μL mixing chamber in which a small magnetic bar is rotating. After passing through the mixing chamber, supercritical CO_2 is changed to a new mobile phase with different polarity. The amount of modifier added into supercritical CO_2 is measured by an amperometric microsensor, which is prepared from a thin film of perfluorosulfonate ionomer.

Introduction

In 1962, the idea of using dense gases for the transport of nonvolatile substances through a chromatographic column

was conceived and reduced to practice by Klesper *et al.*[1] in a simple chromatographic apparatus using porphyrins as the eluates. Many developments have been made since then, especially during the 1980s, supercritical fluid chromato-