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Optically Active Transition-Metal Complexes. 103[1].

Configurational Stability of New Planar Chiral Indenyl Iron Complexes

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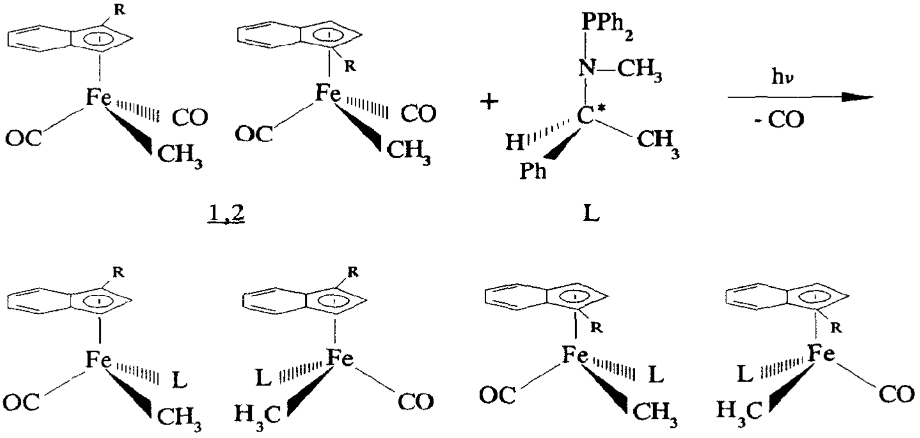
Abstract: 1-Me and 1-^{t}Bu substituted π-indenyl iron complexes of the type IndFe(CO)(CH_3)L have been prepared. Due to the planar chirality and the central chirality at Fe, they consist of 4 stereoisomers. The introduction of the optically active phosphine L = (S)-(+)-$(C_6H_5)_2P$-N(CH_3)-CH(CH_3)C_6H_5 into the complexes allows ^{1}H nmr differentiation of the four diastereoisomers of each series. Some of the diastereoisomers can be isolated by preparative liquid chromatography. Whereas the diastereoisomers epimerize with respect to the chiral iron atom, they do not change their configuration with respect to the planar chirality neither in boiling toluene solution, nor in the solid state at 60 kbar pressure up to temperatures of 400°C, and in the presence of electron transfer reagents.

Planar chiral ferrocene derivatives are generally characterised by a high configurational stability[2-4], exceptions being scarce[5,6]. In the present paper, we tested the configurational stability of 1-Me and 1-^{t}Bu substituted π-indenyl Fe half-sandwich complexes, which in principle can change configuration with respect to the planar chirality by i) reversible decomplexation, ii) 1,3-migration of the alkyl group in the five-membered ring, iii) insertion of Fe in one of the C-C bonds of the five-membered ring, giving a ferra-benzene.

In the photochemical reaction of (R-Ind)Fe$(CO)_2(CH_3)$, 1 and 2, with the optically active (S)-aminophosphine L = (S)-(+)-$(C_6H_5)_2P$-$N(CH_3)$-$CH(CH_3)C_6H_5$, the complexes [(R-Ind)Fe(CO)(CH_3)L], 3 and 4 [R = methyl (3), tert-butyl (4)], are formed. In the course of the substitution of one of the diastereotopic carbonyl groups in 1 or 2, the iron atom becomes a stereogenic centre. Due to the planar chirality and the central chirality at Fe, the complexes 3 and 4 form a mixture of 4 diastereoisomers (Figure 1).

Figure 1



3 (a,b,c,d) (R = methyl); 4 (a,b,c,d) (R = tert-butyl)

The diastereoisomers of the compounds 3 and 4 can be differentiated by their Fe-CH_3 and their indenyl alkyl resonances in the ^1H nmr spectrum. The high field Fe-CH_3 resonance is the best probe for the determination of the diastereomeric purity.

By fractional crystallisation from petroleum ether/ether mixtures, no significant enrichment of the components could be achieved. Preparative liquid chromatography on silica gel with petroleum ether/ether 10/1 as an eluent, however, allows the isolation of optically pure epimers of each compound. The configurational stability of two of these, arbitrarily designated as 3b and 4b was investigated by ^1H nmr spectroscopy. Attempts were made to induce a change in the planar chirality of 3b and 4b by thermal treatment of the compounds in solution, by application of high temperatures under high pressure, and by the use of electron transfer reagents.

In the solid state the diastereoisomers 3b and 4b are configurationally stable. Heating 3b and 4b, respectively, in benzene-d_6 solution to 70°C for 24 hours led to epimerisation with respect to the configuration at the iron atom, but the planar chirality remained unchanged. At higher temperatures considerable decomposition took place in solution. The temperatures required to induce epimerisation at the asymmetric iron center in 3 and 4 are comparable to those found for the unsubstituted indenyl complex[7].

Compounds, which tend to decompose at higher temperatures under atmospheric pressure can be stabilized by application of high pressure. Thus, the compounds 3b and 4b withstood a thermal treatment up to 400°C for 30 minutes under a pressure of 60 kbar and could be reisolated without any decomposition. Surprisingly, the planar chiral configuration of 3b and 4b was unaffected even under these conditions.

The increased reactivity of organometallic compounds induced by reducing or oxidizing agents is well known[8]. The rate enhancement of the epimerization of optically active iron complexes of the type $Cp'Fe(CO)(CH_3)L$ (Cp' = cyclopentadienyl, indenyl) with electron transfer reagents such as Cp_2FePF_6 or Na-amalgam was described in a previous study[7]. 3b and 4b show similar cyclovoltammograms as the $Cp'Fe(CO)(CH_3)L$ complexes. Treatment of 3b and 4b with ferricinium hexafluorophosphate or sodium amalgam led to the expected epimerisation at the chiral iron atom, but not to a change of the planar chirality.

(Me-Ind)Fe(CO)(CH_3)L (3)

2.15 g of (Me-Ind)$Fe(CO)_2(CH_3)$ 1 and 3.20 g of L = (S)-(+)-$(C_6H_5)_2P$-$N(CH_3)$-$CH(CH_3)C_6H_5$ were dissolved in 200 ml of methylenechloride/petroleum ether 1/1 and photolysed for 4 h with a high-pressure mercury lamp. The initially yellow brown solution turned redbrown. The progress of the reaction was monitored by IR. Removal of the solvent gave a brown solid, which was chromatographed on a 20 cm column of alumina. Elution with petroleum ether separated unreacted starting material as a yellow band. Development of the column with petroleum ether/ether 4/1 eluted 3 as a brown band. A red-brown powder remained after evaporation of the solvent. Yield: 3.45 g (75%). IR (CH_2Cl_2): 1905 cm^{-1} (CO). ^1H nmr (C_6D_6 , i-TMS, 250 MHz): δ = -0.96 (d, Fe-CH_3, 3a), -0.94 (d, Fe-CH_3, 3b), -0.04 (d, Fe-CH_3, 3c), 0.03 (d, Fe-CH_3, 3d), 1.39 (d, C-CH_3, 3b), 2.12 (d, N-CH_3, 3b), 2.16 (s, Ind-CH_3, 3b). MS (FD): m/e = 547 (M^+), 319 (L^+).

Compound 4 was prepared analogously from 2.00 g of (^{t}Bu-Ind)$Fe(CO)_2(CH_3)$ 2 and 2.50 g of L. Yield: 3.10 g (78%). IR (CH_2Cl_2): 1900 cm^{-1} (CO). ^1H nmr (C_6D_6, i-TMS, 250 MHz): δ = -0.97 (d, Fe-CH_3, 4a), -0.95 (d, Fe-CH_3, 4b), 0.17 (d, Fe-CH_3, 4c), 0.22 (d, Fe-CH_3, 4d), 1.47 (d, C-CH_3, 4a), 1.40 (d, C-CH_3, 4b), 2.17 (d, N-CH_3, 4a), 2.09 (d, N-CH_3, 4b), 1.58 (s, 9H, Ind-^{t}Butyl (4a), 1.56 (s, Ind-^{t}Butyl, 4b), 1.55 (s, Ind-^{t}Butyl, 4c). MS (FD): m/e = 589 (M^+), 319 (L^+).

Diastereoisomer separation (representatively described for complex 4):

After isolation of the complexes 3 and 4 the diastereoisomers 3a, 3b, 4a and 4b are the predominant components in the reaction mixtures. They could be separated from the c- and d-diastereoisomers via chromatography on a 50 cm alumina column. As shown for 4a and 4b, they can be separated as follows.

400 mg of the diastereomer mixture of 4a and 4b were dissolved in a minimum amount of petroleum ether/ether 10/1 and chromatographed on Merck Lobar columns, size B (25*2.5 cm), with petroleum ether/ether 10/1. The chromatography was carried out under nitrogen atmosphere, using a pressure of 1.5 bar. After passing the complex through 4 columns[9,10], the brown band split into 2 bands of equal intensity. The bands were collected separately and the solutions evaporated. This procedure left brown solids of the optically pure epimers with respect to the planar chirality.

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