Cage Effect

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Change of the Fe Configuration in Chiral Half-Sandwich Complexes Within the Solvent Cage**

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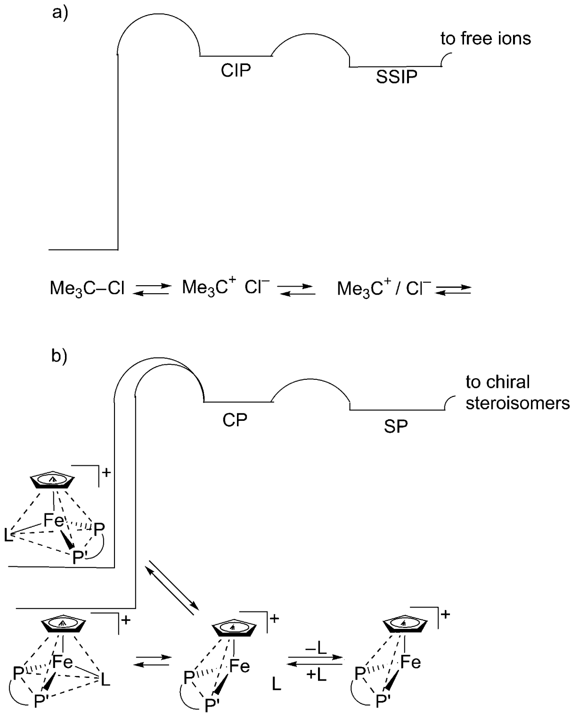
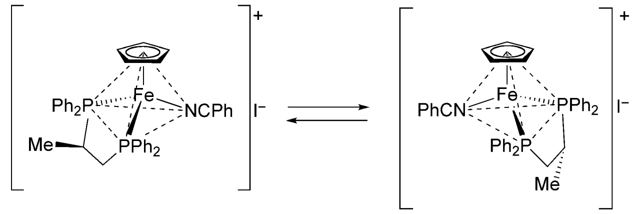
Dedicated to Professor Michael P. Doyle on the occasion of his 70th birthday

Cage effects are a challenge since in the development of the S_N1 mechanism, contact ion pairs and solvent separated ion pairs were differentiated. According to the classical S_N1 mechanism *tert*-butyl chloride dissociates to the contact ion pair (CIP). In competition with recombination, this contact pair transforms to the solvent separated ion pair (SSIP) and to the free ions (Scheme 1 a).[1,2] Formally similar, in a ligand dissociation from a complex, a contact pair (CP) is formed, the parts of which can recombine or separate to individually solvated species (Scheme 1 b). The following discussion concerns the contact pair, the solvent separated and solvated species are both termed SP. The recombination of CIP and CP to the starting material and the separation to SSIP and SP can be followed by calculation,[3–6] experimental monitoring, however, is difficult. Herein, we present systems in which the contact pair not only has the double reactivity choice of the S_N1 mechanism in Scheme 1 a, but three reaction pathways as in Scheme 1 b. Two of these pathways can easily be differentiated at ambient temperature by conventional $^{31}P\{^1H\}$ NMR spectroscopy.

The half-sandwich complex (S_{Fe},R_C)/(R_{Fe},R_C)-[CpFe(Prophos)NCPh]I (**1**; Cp = C_5H_5) was prepared by reaction of benzonitrile with (S_{Fe},R_C)/(R_{Fe},R_C)-[CpFe(Prophos)I],[7] (Prophos = (R_C)-propane-1,2-diylbis(diphenylphosphane)).[8] Diastereomer separation was carried out by fractional crystallization from hexane/dichloromethane. In $CDCl_3$ solution the diastereomerically pure benzonitrile complex (S_{Fe},R_C)-**1** epimerized at ambient temperature by change of the Fe configuration (Scheme 2) as described for the analogous acetonitrile complex (S_{Fe},R_C)-[CpFe(Prophos)NCMe]I.[9] The diastereomer equilibrium (S_{Fe},R_C)-**1**/(R_{Fe},R_C)-**1** = 91:9 was attained in a first-order reaction with a half-life of 320 min at 20 °C.



Scheme 1. S_N1 mechanisms for a) dissociation of Me_3CCl and b) dissociation of $[CpFe(P\text{-}P')L]^+$.



(S_{Fe},R_C)-[CpFe(Prophos)NCPh]I
(S_{Fe},R_C)-**1** major diastereomer

(R_{Fe},R_C)-[CpFe(Prophos)NCPh]I
(R_{Fe},R_C)-**1** minor diastereomer

Scheme 2. Epimerization equilibrium (S_{Fe},R_C)-**1**/(R_{Fe},R_C)-**1**.

The rate-determining step in the epimerization reaction of (S_{Fe},R_C)-**1** is the cleavage of the Fe-NCPh bond. The 16-electron intermediate (S_{Fe},R_C)-$[CpFe(Prophos)]^+$ retains its pyramidal geometry with the vacant site at the remaining

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Supporting information for this article (synthesis and characterization of new compounds and crystallographic data, including the CCDC numbers for (S_{Fe},R_C)-**1**, (S_{Fe},R_C)-[CpFe(Prophos)NCPh]PF_6, (S_{Fe},R_C)-[^{Me}CpFe(Prophos)NCMe]PF_6), and (S_{Fe},R_C)-[^{Me}CpFe(Prophos)NCPh]PF_6) is available on the WWW under http://dx.doi.org/10.1002/anie.201104960.

coordination position.[10–12] Pyramidal inversion to $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-[CpFe(Prophos)]$^+$ and re-association of the intermediates with PhCN establish the $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-**1**/$(R_{\mathrm{Fe}},R_{\mathrm{C}})$-**1** equilibrium. The $^{\mathrm{Me}}$Cp compound $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-[$^{\mathrm{Me}}$CpFe(Prophos)NCMe]I ($S_{\mathrm{Fe}},R_{\mathrm{C}}$-**2**; $^{\mathrm{Me}}$Cp = MeC$_5$H$_4$) containing the acetonitrile ligand, was synthesized analogously.

In the cross-over experiment with $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-**1** and $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-**2**, exchange of ligands NCPh and NCMe competes with pyramidal inversion. Ligand exchange must proceed via individual species in the bulk solution, whereas pyramidal inversion may occur within the contact pair. A demonstration that the change of the Fe configuration is faster than ligand exchange would show that pyramidal inversion takes place within the solvent cage prior to transition to the bulk solution.

We dissolved the diastereomerically pure salts $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-**1** and $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-**2** in CDCl$_3$ at 0 °C. The ^{31}P{^{1}H} NMR spectra in Figure 1, measured after warming the solutions to 27 °C, show that the signals of the major diastereomers of the starting materials and the ligand exchange products overlap appreciably. Diagnostically more valuable are the signals of the minor diastereomers. In the area $\delta = 97$–94 ppm all four of them are clearly visible and between $\delta = 108$ and 106 ppm three of them are visible. The assignment is $\delta = 96.6$ ppm = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-**1**, 96.2 ppm = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-[CpFe(Prophos)NCMe]I, 94.8 ppm = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-[$^{\mathrm{Me}}$CpFe(Prophos)NCPh]I, and 94.2 ppm = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-**2**.

Spectrum 1 in Figure 1, measured after 5 min at 27 °C, shows that the two starting compounds $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-**1** and $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-**2** are diastereomerically pure. In spectrum 2 after 15 min the signals of the minor diastereomers of the starting materials are clearly seen, but not those of the minor diastereomers of the cross-over products. In addition, the signals of the major diastereomers of the cross-over products are still very small. Even in spectrum 3 (Figure 1) taken after 45 min, the signals of the minor diastereomers of the ligand-exchange products do not appear. They are only present in spectrum 4, measured after 280 min.

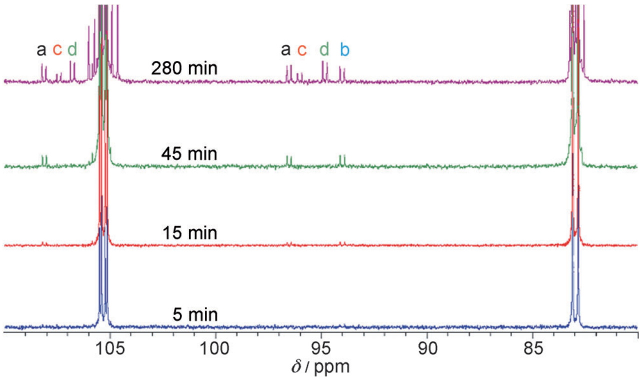


Figure 1. Time-dependent ^{31}P{^{1}H} NMR spectra of the cross-over experiment $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-**1**/$(S_{\mathrm{Fe}},R_{\mathrm{C}})$-**2** in CDCl$_3$ at 27 °C. Signal assignment: a = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-**1**, b = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-**2**, c = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-[CpFe(Prophos)NCMe]I, d = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-[$^{\mathrm{Me}}$CpFe(Prophos)NCPh]I.

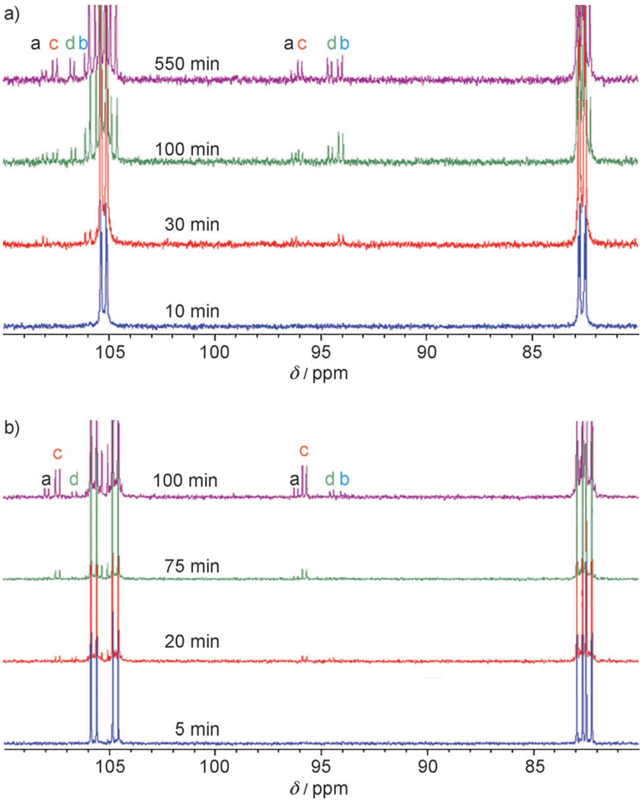
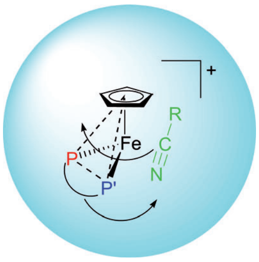


Figure 2. Time-dependent ^{31}P{^{1}H} NMR spectra of the cross-over experiment a) $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-[CpFe(Prophos)NCPh]PF$_6$/$(S_{\mathrm{Fe}},R_{\mathrm{C}})$-[$^{\mathrm{Me}}$CpFe(Prophos)NCMe]PF$_6$ in CDCl$_3$ at 27 °C and b) $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-[CpFe(Prophos)NCMe]PF$_6$/$(S_{\mathrm{Fe}},R_{\mathrm{C}})$/[$^{\mathrm{Me}}$CpFe(Prophos)NCPh]PF$_6$ in CDCl$_3$ at 27 °C. Signal assignment: a = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-[CpFe(Prophos)NCPh]PF$_6$, b = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-[$^{\mathrm{Me}}$CpFe(Prophos)NCMe]PF$_6$, c = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-[CpFe(Prophos)NCMe]PF$_6$, d = $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-[$^{\mathrm{Me}}$CpFe(Prophos)NCPh]PF$_6$.

Figure 2 shows the spectra of the same cross-over experiment and an alternative cross-over experiment with the corresponding PF$_6$ salts. The first spectra in both series again demonstrate that the starting compounds are diastereomerically pure. In the second spectra (Figure 2) the signals of the minor diastereomers of the starting materials appear, but those of the minor diastereomers of the ligand-exchange products are absent. They come in only at later stages. The cross-over experiments with the PF$_6$ salts are particularly conclusive, because the ligand-exchange equilibrium is approached from two different sides.

The spectra in Figure 1 and 2 show that the rates of the change of the Fe configuration are faster than the rates of the nitrile exchange in compounds of the type $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-[Cp′Fe(Prophos)NCR]X (Cp′ = Cp, $^{\mathrm{Me}}$Cp; X = I, PF$_6$). The change of the Fe configuration occurs in the contact pair $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-[Cp′Fe(Prophos)]$^+$/NCR before its parts separate. It must involve at least one pyramidal inversion of the chiral intermediate $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-[Cp′Fe(Prophos)]$^+$ and a migration of the nitrile ligand to its diastereotopic side (Scheme 3). Alignment of the nitrile dipole with the dipole of the intermediate $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-[Cp′Fe(Prophos)]$^+$ may facilitate the pyramidal inversion. Nitriles such as MeCN[13] and PhCN[14] have strong dipole moments of about 4 D, whereas the dipole moment of the solvent CDCl$_3$ is 1.1 D.[13]



Scheme 3. Minimum requirements for the change of the Fe configuration in the contact pair $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-[CpFe(Prophos)]$^+$/NCR within the solvent cage.

Up to now the epimerization at the metal atom in compounds of the type $(S_{\mathrm{Fe}},R_{\mathrm{C}})$-[CpFe(Prophos)-NCR]X (X = I, PF_6) has been discussed on the basis of energy diagrams containing only the pyramidal intermediates $(S_{\mathrm{Fe}},R_{\mathrm{C}})$- and $(R_{\mathrm{Fe}},R_{\mathrm{C}})$-[CpFe(Prophos)]$^+$. The results of the present cross-over experiments enforce an extension according to Figure 3. The rate-determining dissociation of the Fe−NCR bond (k_1/k_1') leads to a contact pair in the solvent cage, indicated by the circles in Figure 3. In this contact pair, the change of the Fe configuration (k_4/k_4') can take place, a process faster than the transfer of its constituents to the bulk solution (k_3/k_3').

The activation energies for the collapse of contact pairs to re-form the starting materials (k_2 and k_2' in Figure 3) and for diffusion of the constituents of contact pairs into the bulk solution (k_3 and k_3') are small.[15] For *tert*-butyl chloride the activation energy for the transformation of the contact ion pair to the solvent separated ion pair has been calculated to be 2 kcal mol^{-1}.[3] Generally, the barriers for diffusion of the constituents of contact pairs into the bulk solution are estimated to the order of 3 kcal mol^{-1}.[16] According to our measurements the barriers for the change of the Fe configuration within the contact pair (k_4 and k_4') are lower than for the separation of the components of the contact pair (k_3 and k_3') to give individually solvated species as shown in Figure 3.

We argue against other mechanisms. As the iodide and PF_6 salts have similar reactivities, a participation of iodide ion can be ruled out. Planarization instead of pyramidal inversion of the 16-electron intermediates [Cp′Fe(Prophos)]$^+$ would not change the argumentation with respect to the cage effect. In this case, the two diastereomeric pyramidal intermediates in the central part of Figure 3 would merge to a planar intermediate which still has two diastereotopic faces. Calculations have shown a pyramidal structure for $[CpFe(CO)_2]^+$, whereas $[CpFe(PH_3)_2]^+$ has been assigned a planar structure.[12] An intramolecular mechanism of the epimerization without ligand dissociation would be compatible with the results. However, it would require a transition state in which the Cp′Fe centroid and the Fe−P and Fe−NCMe bonds would be in one plane which is considered to be as unlikely as the planarization of the central carbon atom in methane derivatives.

In the S_N1 mechanism the contact ion pair as well as the solvent separated and the free ions participate in product formation. The stereochemistry of S_N1 reactions is determined on the level of the contact ion pair. The inversion, sometimes appreciable, in substitution reactions is ascribed to the shielding of the carbenium ion by the leaving nucleophile.[17] A demonstration that a change in configuration may occur in the contact ion pair, as shown here for [Cp′Fe(Prophos)NCR]X, would be a new specification in the classical S_N1 mechanism.

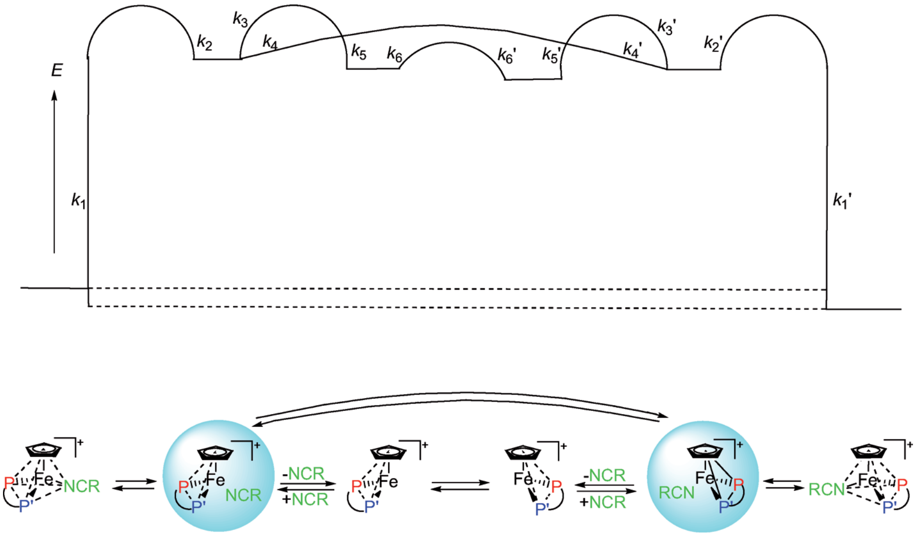


Figure 3. Energy diagram for the epimerization of $(S_{\mathrm{Fe}},R_{\mathrm{C}})/(R_{\mathrm{Fe}},R_{\mathrm{C}})$-[CpFe(Prophos)NCR]$^+$ including contact pairs in solvent cages (encircled).

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