Mechanistic Studies on a Facile Ring-Flipping Process in Planar Chiral Ferrocenes under Ambient and High Pressure and Its Relevance to Asymmetric Catalysis

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The bis-planar chiral ferrocenyldiphosphine bis(1-(diphenylphosphino)-η^5-indenyl)iron(II) is observed to undergo an isomerization from the *meso* isomer to the *rac* isomer in THF solvent at ambient temperature. This process requires ring flipping of one of the indenyl ligands. The isomerization is slowed by the addition of the noncoordinating solvent chloroform and is accelerated by addition of salts such as LiCl and $LiClO_4$. Rate and activation parameters have been determined for the spontaneous isomerization: $k_{obs} = 1.6 \times 10^{-5}$ s^{-1} at 23 °C, $\Delta H^{\ddagger} = 58 \pm 4$ kJ mol^{-1}, $\Delta S^{\ddagger} = -140 \pm 15$ J mol^{-1} K^{-1}, and $\Delta V^{\ddagger} = -12.9 \pm 0.8$ cm^3 mol^{-1}. Labeling of the ferrocene with deuterium in the 3- and 3′-positions followed by isomerization showed no incorporation of deuterium into the 2- or 2′-positions, thus ruling out 1,2-hydrogen-shift mechanisms. Attempted crossover experiments with dideuterated and nondeuterated ferrocenes gave no monodeuterated products of crossover, thus ruling out ligand dissociative mechanisms. The proposed isomerization mechanism involves coordination of two THF ligands with ring slippage of one indenide and then displacement of that indenide and coordination through the phosphine. Coordination of the indenide by the other face in the reverse process then leads to the other isomer.

Introduction

Phosphine-functionalized ferrocenes continue to be intensively investigated for their utility in homogeneous catalysis; chiral derivatives are of particular interest for asymmetric catalysis.[1] The introduction of a chiral substituent or the generation of planar chirality is usually used to create the chirality. Despite the many planar chiral ferrocenyl phosphines that have been reported and used in asymmetric catalysis, no racemization has been observed in these systems. Compounds containing two planar chiral units may exhibit *rac* and *meso* isomers. The conversion of one isomer to the other requires one of the rings to flip over and coordinate to the iron atom by the other face. To the best of our knowledge, this has not been observed in any ferrocenyl phosphine, although racemization of acylferrocenes in nitroalkane solvents in the presence of strong acids, such as $HClO_4$ and $AlCl_3$, has been reported.[2] Other processes resulting in the flipping over of a cyclopentadienyl ligand have been observed in metallocene systems of the lanthanide,[3] group 3,[4] and group 4[5] metals. A number of the group 4 ring-flipping processes are photochemically initiated.[5a−g] Also of particular note, Hollis and Fu have independently described group 4 diphosphametallocenes in which a phosphole flips over via a proposed intermediate in which the phosphole is coordinated by only the phosphorus atom.[6] Herberich and co-workers have described systems in which cyclopentadienyl rings are exchanged between metal centers

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via triple-decker sandwich intermediates and which result in coordination of the rings by the other face. This involves an intermolecular exchange process.[7] That such a process could occur in some ferrocene systems is evidenced by the cyclopentadienyl-exchange reactions between ferrocenes, using the Lewis acid $AlCl_3$,[8] and the synthesis of $[Cp_3Fe_2]^+$ by Kudinov.[9] Other examples of cyclopentadienyl-transfer reactions from ferrocenes include transfer of acylferrocenes to Re,[10] a redistribution reaction between ferrocene and 1,1′-dimethylferrocene at 250 °C after 3 days,[11] and the synthesis of ruthenocene from ferrocene and $RuCl_3$ at 250 °C.[12]

We have previously reported the preparation of the diindenyl analogue of 1,1′-bis(diphenylphosphino)-ferrocene (dppf), bis(1-diphenylphosphino-η^5-indenyl)-iron(II) (**1**), and the characterization of its *rac* and *meso* isomers by X-ray crystallographic studies of their tetracarbonylmolybdenum complexes.[13] We now report on the remarkable ring-flipping *meso* to *rac* isomerization process of **1** and detailed mechanistic studies that we have carried out to elucidate the mechanism of this process. Our studies also indicate the type of conditions under which ring-flipping processes are most likely to occur and thus need to be considered; this is particularly important in the application of such complexes for asymmetric homogeneous catalysis in which, until now, ring-flipping processes have not been thought to be important. A preliminary report on some of this work has been communicated.[14]

Results and Discussion

The reaction of lithium 1-(diphenylphosphino)indenide (**2**) (prepared by deprotonation of 3-(diphenylphosphino)indene (**3**) with BuLi) with ferrous chloride initially produces a 1:1 mixture of two phosphorus-containing compounds, as shown by peaks in the ^{31}P NMR spectrum at −22.26 and −26.53 ppm. Overnight, the peak at −26.53 ppm almost disappears, leaving essentially only one product (Scheme 1). Crystals of this compound were obtained by recrystallization from dichloromethane/diethyl ether and shown by X-ray crystallography to be the *rac* isomer of **1**.[14] If the reaction is stopped after 2 h by removal of solvent, the *rac*/*meso* product mixture can be isolated.

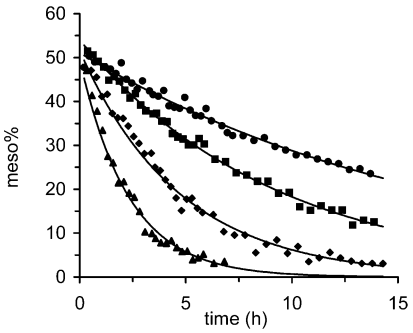

Figure 1. Conversion of *meso*-**1** to *rac*-**1** in THF at various temperatures (top to bottom: 23, 30, 40, 50 °C).

Scheme 1. Synthesis and Isomerization of 1

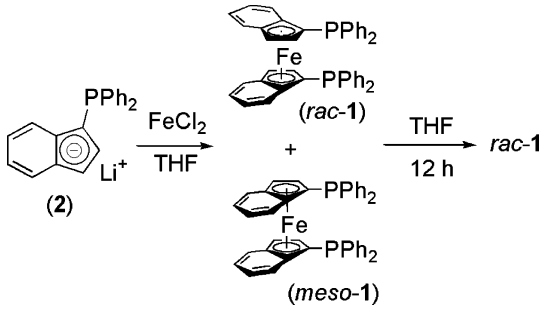

Table 1. Rate of Isomerization for *meso*-1 to *rac*-1 under Various Conditions

T^a (K)	k_{obs} (10^{-5} s^{-1})	[LiCl]^b (mol L^{-1})	k_{obs} (10^{-5} s^{-1})	$CDCl_3$ in THF^c (%)	k_{obs} (10^{-5} s^{-1})
296	1.59(3)	0	3.01(9)	0	3.01(9)
303	3.01(9)	0.019	3.58(20)	25	1.26(3)
308	4.89(14)	0.038	6.83(20)	40	0.87(3)
313	5.89(16)	0.076	35.9(6)	50	0.62(2)
323	12.0(4)				

[a] In THF solvent. [b] In THF solvent at 303 K. [c] At 303 K.

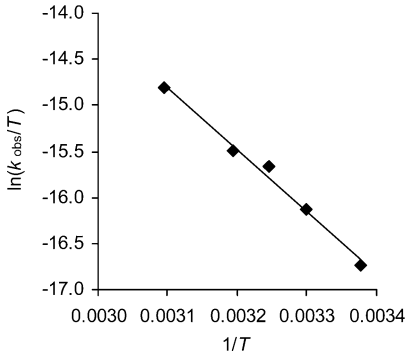

Figure 2. Plot of $\ln(k_{obs}/T)$ versus $1/T$ for the isomerization of *meso*-**1** to *rac*-**1**.

The isomerization of *meso*-**1** to *rac*-**1** was followed by ^{31}P NMR spectroscopy as a function of temperature (Figure 1). The *meso* isomer does not completely disappear, which indicates that the reverse process of *rac* to *meso* isomerization does occur, but with a slower rate constant. Thus, the *meso*/*rac* equilibrium lies on the side of the *rac* isomer. Nonetheless, the isomerization is first order in *meso*-**1** concentration, with the data being fitted to single-exponential functions for the first 4 half-lives to yield k_{obs} (Table 1). A linear plot of $\ln(k_{obs}/T)$ versus $1/T$ (Figure 2) allowed the determination of the enthalpy and entropy activation parameters, which were found to be $\Delta H^{\ddagger} = 58 \pm 4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -140 \pm 15$ J

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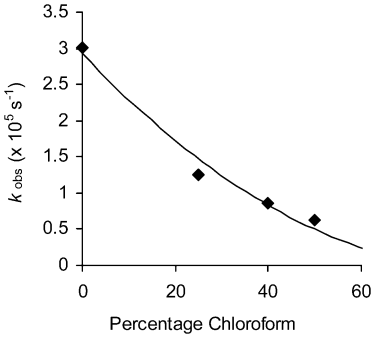


Figure 3. Effect of increasing amount of chloroform solvent in THF, fit to a square function, on the rate of *meso*-**1** to *rac*-**1** isomerization at 30 °C.

mol^{-1} K^{-1}, respectively.[15] In neat THF at 23 °C, the observed rate constant is $[1.59(3)] \times 10^{-5}$ s^{-1}. During the synthesis of **1**, however, the rate was found to be $[3.60(9)] \times 10^{-5}$ s^{-1} ([**1**] = 0.0605 M, T = 23 °C). Extrapolation back to $t = 0$ gives an initial *rac*:*meso* ratio of 55:45. Possible causes of the rate increase include excess indene **3** and dissolved salts. It was found that the rate is independent of the concentration of indene **3**, whereas addition of LiCl increased the rate significantly (see below). LiCl is the major salt present during the synthesis of **1**; thus, it is likely to be the species responsible for the rate enhancement. The equilibrium constant for the conversion of *meso* to *rac*, derived from the *rac*:*meso* ratio at $t = \infty$, is 0.074(5).

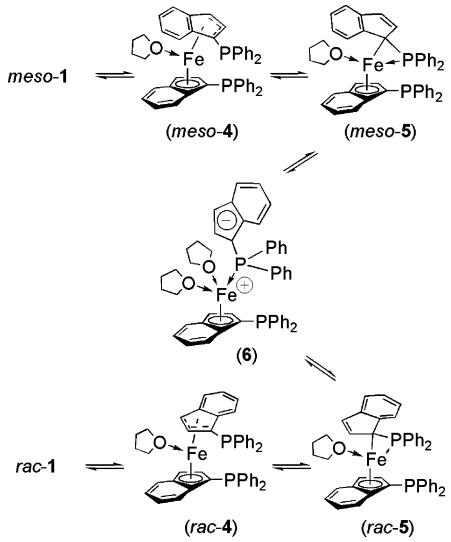
To determine the importance of the solvent, isomerization experiments were performed with varying ratios of THF and the noncoordinating solvent chloroform. Figure 3 shows the effect of increasing the percentage of chloroform on the rate at 30 °C. With a 100% chloroform solution, no isomerization was observed after 1 week. It is found that the rate is approximately proportional to the square of the THF concentration, although one must take into account solvent polarity effects when interpreting this result. Nonetheless, it is clear that a coordinating solvent is required for this isomerization.

Salt effects were investigated by adding LiCl (Table 1), and a significant effect was observed: for [LiCl] = 0.076 M, a greater than 10-fold increase in the rate was observed. This implies an intermediate that is either a salt or highly polar, since *rac*- and *meso*-**1** are of low polarity. To check that the acceleration is not due to chloride acting as a nucleophile, an experiment was run using $LiClO_4$. This gave the same rate acceleration (for $[LiClO_4] = 0.038$ M, $k_{obs} = [6.29(60)] \times 10^5$ s^{-1}), within experimental error, thus ruling out chloride acting as a nucleophile in the isomerization mechanism. Although chloride is generally a better nucleophile than THF, it should be noted that the concentration of THF (12.4 M) is significantly higher than the chloride concentrations we investigated (up to 0.076 M).

On the basis of these observations, our proposed mechanism (Scheme 2) involves coordination of THF (one or two molecules) and slippage of the indenylphosphine ligand until the indenide dechelates and the ligand coordinates by only the phosphorus atom, thus generating the zwitterionic intermediate **6**. This

(15) These activation parameters differ slightly from those given in ref 14, which were calculated from an Arrhenius fit.

Scheme 2. Preferred Ring-Slippage Isomerization Process



zwitterion could be stabilized by the presence of ionic species. Thus, solvent-assisted dechelation of indenide from **5** to **6** is the rate-determining step. Recoordination of the five-membered indenide ring could then occur by either face. The large negative entropy of activation and volume of activation (see below) further support an associative rate-determining step and solvent-stabilized intermediate. In further support of this mechanism, dmpe has been observed to completely displace indenide from $(C_9H_7)Rh(C_2H_4)_2$ to form $[Rh(dmpe)_2][C_9H_7]$.[16]

The effect of pressure on the rate was investigated to determine the volume of activation for the isomerization process. A strong increase in rate with pressure was observed. A significant buildup of free ligand also occurred during these experiments; however, the rate of isomerization was at least twice as fast. Figure 4 shows some of the NMR spectra recorded at 0.5 and 150 MPa, and Figure 5 shows the simulated spectra of the 150 MPa pressure cycle as well as the corresponding difference spectra. Plots of decreasing or increasing integrals versus time for *rac*-**1**, *meso*-**1**, and free ligand could be fitted with single-exponential functions, from which the observed rate constants were obtained. The proposed mechanism involves nucleophilic attack by solvent to give the intermediate **6** in the rate-determining step, which can then either isomerize to the *rac* isomer or hydrolyze to give the free ligand (Scheme 3). Since the nucleophilic attack by the solvent is the rate-determining step, the observed rate constants for the decrease in *meso* concentration and the increase in the concentrations of *rac*-**1** and free ligand should be the same and are equal to $k_1 + k_2$. The ratio of the increase in the *rac*-**1** integral to the increase in the free ligand integral gives k_1/k_2, which then allows the determination of both k_1 and k_2. A plot of $RT \ln(k_1)$ versus pressure reveals a linear dependency (Figure 6). A fit to these data gives a volume of activation, $\Delta V^{\ddagger}$, of -12.9 ± 0.8 cm^3 mol^{-1}. This significantly negative volume of activa-

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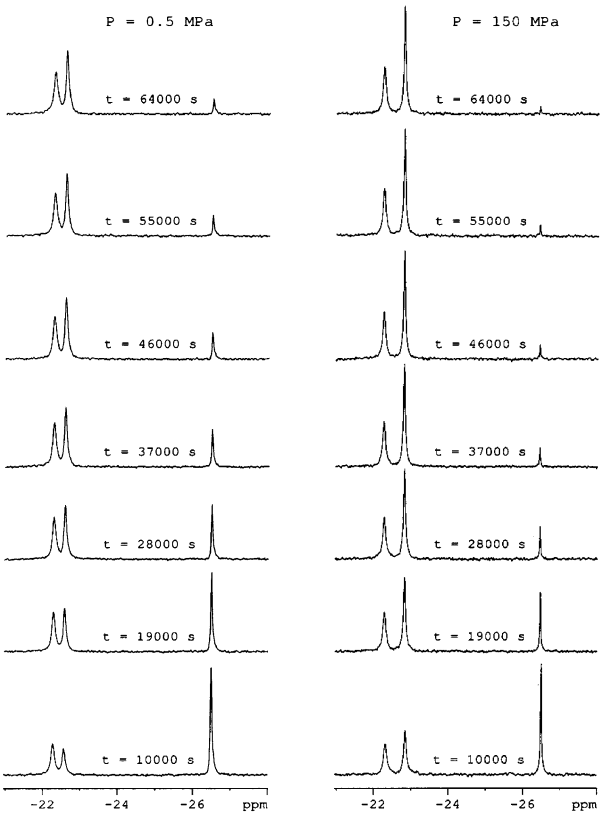


Figure 4. NMR spectra recorded at 0.5 and 150 MPa as a function of reaction time. The absolute times given in the spectra are estimates, since the time of the first spectrum cannot be determined exactly, but the time interval between the spectra can be determined accurately.

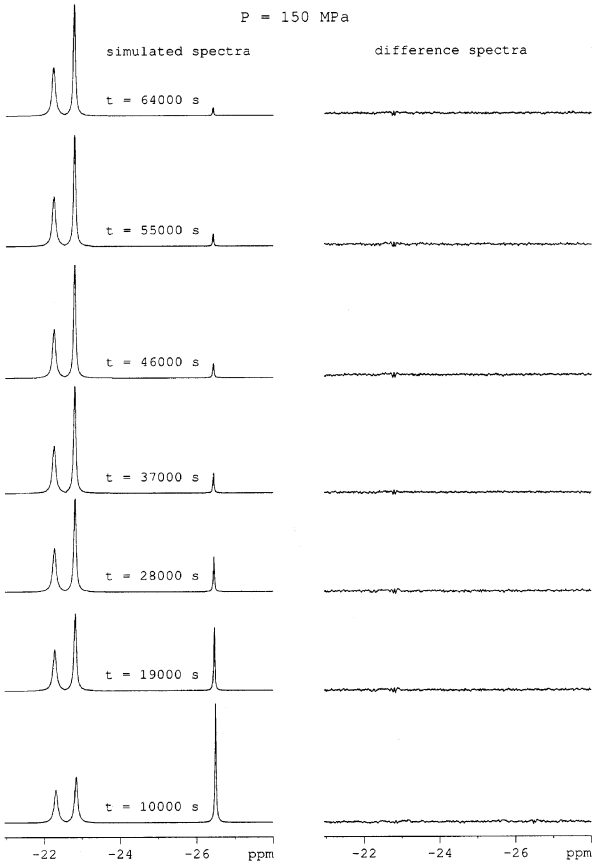


Figure 5. Simulated spectra of the 150 MPa pressure cycle and the corresponding difference spectrum (experimental − simulated spectrum). The integrals of these signals can therefore be determined precisely.

tion is consistent with an associative type of reaction.[17] It is, however, difficult from the size of $\Delta V^{\ddagger}$ to say whether the result is consistent with the addition of two molecules of THF since, according to the suggested mechanism, ring slippage and partial dechelation of indenide will cause an intrinsic volume increase and so partially compensate the volume decrease associated with the binding of THF. In addition, the zwitterionic nature of the intermediate **6** may cause an increase in solvent electrostriction that will also lead to a volume decrease.

A plot of $RT\ \ln(k_2)$ versus pressure gives the activation volume for the hydrolysis of *meso*-**1** to give free ligand (Figure 7). Unfortunately, the kinetic traces for the formation of free ligand were not very good, due to the low conversion and significant scatter in the data points. Nonetheless, the volume of activation was determined to be $-10 \pm 2\ \text{cm}^3\ \text{mol}^{-1}$, which is slightly smaller than for the isomerization process, since there will be a larger contribution from bond cleavage as a result of the dissociation of phosphine in the transition state for the hydrolysis reaction.

It is notable that the rate of hydrolysis of **1** is related to the rate of isomerization and shares a common intermediate, presumably the zwitterion **6**. It is not surprising that a zwitterionic intermediate such as **6** would be much more rapidly protonated at the indenyl ligand than nonpolar **1**. Since *meso*-**1** isomerizes to **6** much more rapidly than *rac*-**1** does, the *meso* isomer also hydrolyzes much more rapidly than the *rac* isomer. Hydrolysis was also observed in the variable-temperature experiments, but to a lesser extent, since the

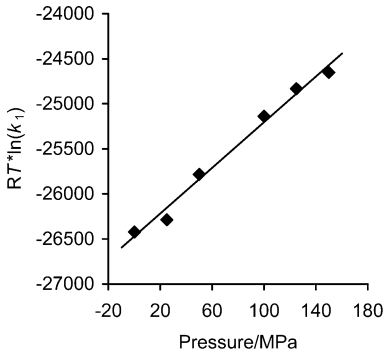
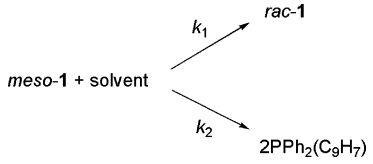


Figure 6. Plot of $RT\ \ln(k_1)$ versus pressure for the isomerization of *meso*-**1** to *rac*-**1** in THF solvent (data taken from Table S1, Supporting Information).

Scheme 3. Reaction Scheme Used To Account for the Observed Kinetic Data



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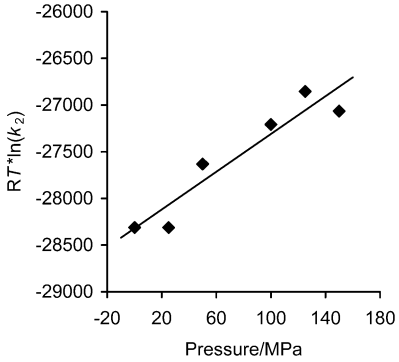
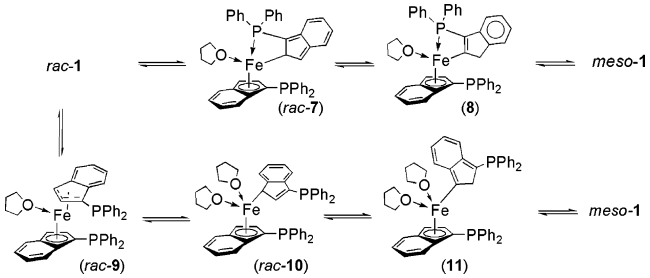


Figure 7. Plot of $RT\ \ln(k_2)$ versus pressure for the hydrolysis of *meso*-**1** in THF solvent (data taken from Table S1, Supporting Information).

Scheme 4. Possible 1,5-Proton-Shift Mechanisms

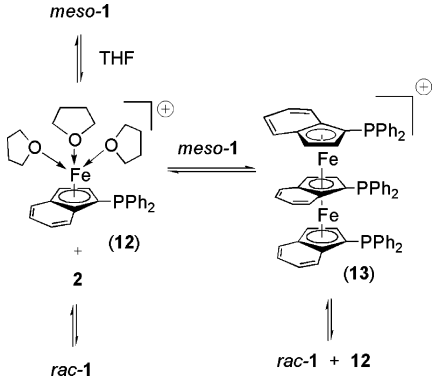


nondeuterated solvent was, presumably, drier. The fate of the iron has yet to be confirmed, but it is probably in the brown precipitate that forms upon hydrolysis as hydrated iron(III) oxide.

There are a number of other possible isomerization mechanisms that must also be considered. Although a 1,3-proton shift could not result in isomerization, a 1,5-proton shift, after ring slippage via **7** (or **9** and **10**) to give an intermediate such as **8** (or **11**), could (Scheme 4). Miyoshi and co-workers have recently isolated a compound similar to **8**, $[Fe(P(OMe)_3)_2(\eta^5{:}\eta^1\text{-}PPhS(C_5H_4)_2)]$, in which one cyclopentadienide group has been ring-slipped from the [1]ferrocenophane $[Fe(\eta^5{:}\eta^5\text{-}PPhS(C_5H_4)_2)]$ and a proton has undergone a 1,2-shift as a result of $P(OMe)_3$ coordination.[18] Nonetheless, these intermediates are not likely to be as energetically favorable as **6**, since their formation involves a loss of aromaticity at some stage (intermediates **7** and **11**) and we would not expect the rate to be significantly affected by salts. Nonetheless, we carried out deuterium labeling studies to confirm that these mechanisms are not operating. 1,1-Dideuterio-3-(diphenylphosphino)indene (**3**-d_2) is readily prepared by addition of D_2O/OD^- to a THF solution of the indenide. The corresponding ferrocene was then prepared by the usual method, and ^1H and ^2H NMR spectroscopy confirmed that the deuterium is present in only the 1- and 1′-positions of both isomers. After the solution was stirred overnight, only the *rac* isomer was found to be present and, again, deuterium was only found in the 1- and 1′-positions. These findings rule out any possibility of 1,5-proton shifts occurring during the isomerization process.

Dissociative mechanisms may also lead to *rac*/*meso* isomerization. Two possibilities are shown in Scheme

Scheme 5. Possible Dissociative Mechanisms



5. Coordination of three THF molecules with complete displacement of indenide from the *meso* isomer would give the monocationic piano-stool complex **12**. Related species containing three solvent molecules and a Cp ligand are well-known.[19] Complex **12** could then either recoordinate an indenide by the other face to give the *rac* isomer or react with another *meso* molecule to give the monocationic triple-decker sandwich complex **13**. Complex **13** could then react with THF at the other Fe center to generate the *rac* isomer and another molecule of **12**. Two experiments were carried out to test these mechanisms. First, a nondeuterated *rac*-**1**/*meso*-**1** mixture was allowed to isomerize in the presence of 1-deuterio-3-(diphenylphosphino)indenide (**2**-*d*) and found to give *rac*-**1** with no incorporation of deuterium, as shown by mass spectrometry and the proton integrals of 1.0 for both H2 and H3 in the ^1H NMR spectrum. Second, a crossover experiment was attempted by carrying out the isomerization of a 1:1 mixture of nondeuterated and dideuterated **1** and found to give only the *rac* isomer of **1** with no increase in the amount of monodeuterated **1**, as shown by mass spectrometry. The lack of incorporation of deuterium into **1** in the first experiment rules out both indenide dissociative mechanisms, since a triple-decker mechanism would most certainly also allow the indenide recoordination mechanism. The second experiment rules out more explicitly a triple-decker intermediate species.

The question of why this isomerization has not been observed in other ferrocenylphosphines needs to be addressed: indenyl ligands generally undergo more facile ring-slippage reactions than cyclopentadienyl ligands, and the usual explanation for this is generation of aromaticity in the six-membered ring upon ring slippage of the indenyl ligand.[20] In our proposed mechanism, intermediates **4** and **5** contain aromatic six-membered rings and the intermediate **6** contains an aromatic five-membered ring. Thus, aromaticity is not lost at any stage. In analogous cyclopentadienyl sys-

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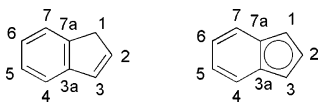
tems, however, aromaticity would be lost upon formation of the analogues of **4** and **5**. This suggests that the initial ring-slipping process prior to indenide dechelation is important in facilitating this isomerization.

Conclusions

We have reported an unprecedented and facile *meso* to *rac* isomerization of the ferrocenyldiphosphine **1** of relevance to the chemistry of other planar chiral ferrocenes with phosphine substituents. The solvent and salt effects, along with the various activation parameters we have measured, are all consistent with an associative solvent-mediated ring-slipping process resulting in dechelation of the indenide and coordination of the phosphine in the key intermediate species. With respect to other planar chiral phosphine-functionalized ferrocene systems, many of which are used in homogeneous asymmetric catalysis, one can no longer simply assume the stability of the ferrocenyl unit with respect to ring flipping and racemization. In particular, it is clear from our studies that highly nucleophilic solvents or reagents, high salt concentrations, and elevated temperatures may all serve to promote racemization via ring-flipping processes. Although this will generally not be important in analogous cyclopentadienyl systems, one should certainly now be aware of the possibility. The structural details of this and related systems, as well as the relative stabilities of the *rac* and *meso* isomers, will be addressed in a forthcoming paper.

Experimental Section

General Considerations. All manipulations and reactions were carried out under an inert atmosphere (Ar or N_2) by use of standard Schlenk techniques. Reagent-grade solvents were dried and distilled prior to use: diethyl ether and THF from Na/benzophenone and dichloromethane from CaH_2. 3-(Diphenylphosphino)indene[21] and bis(1-(diphenylphosphino)-η^5-indenyl)iron(II)[14] were prepared by published procedures. All other reagents were purchased from Aldrich or Sigma Chemical Co. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopic data were collected on a Varian Unity-300 spectrometer operating at 300, 75, and 121 MHz, respectively. Spectra were measured at ambient temperature with residue solvent peaks as internal standard for ^1H and $^{13}C\{^1H\}$ spectroscopy. $^{31}P\{^1H\}$ NMR chemical shifts were reported relative to external 85% H_3PO_4, positive shifts representing deshielding. The atom-numbering scheme is as follows:



EI mass spectra were collected on a Kratos MS80RFA mass spectrometer.

Preparation of 1,1-Dideuterio-3-(diphenylphosphino)-indene (3-d_2). To a solution of indene **3** (5.576 g, 18.57 mmol) in THF (100 mL) at −80 °C was added a solution of *n*-BuLi (11.61 mL, 1.6 M, 18.57 mmol). The solution was warmed to ambient temperature, and the reaction mixture was stirred for 1 h. To the solution was added deoxygenated D_2O (3.865 mL, 0.214 mol), and the mixture was stirred for a further 16 h. To the resulting purple solution was added DCl (37%, 1.57 mL, 0.186 mol). After the mixture was stirred for 1 h, the aqueous layer was removed and the diethyl ether fraction was dried over $MgSO_4$. The solution was filtered and the solvent removed in vacuo to produce a yellow powder. Analysis of the isotope pattern from EI-MS indicates that the product contains 80% 1,1′-dideuterio-3-(diphenylphosphino)indene (**3**-d_2), 18% 1-deuterio-3-(diphenylphosphino)indene (**3**-*d*), and 2% **3**. ^1H NMR ($CDCl_3$): δ 7.16−7.52 (m, 14H, H-4−H-7 and Ph), 6.22 (d, $^3J_{PH}$ = 3.4 Hz, 1H, H-2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.6 (d, $^1J_{PC}$ = 20 Hz, C-3), 144.2 (d, $^3J_{PC}$ = 5 Hz, C-7a), 141.8 (d, $^2J_{PC}$ = 12 Hz, C-3a), 141.2 (d, $^2J_{PC}$ = 5 Hz, C-2), 135.5 (d, $^1J_{PC}$ = 8 Hz, *ipso*-Ph), 133.9 (d, $^2J_{PC}$ = 18 Hz, *o*-Ph), 128.9 (s, *p*-Ph), 128.5 (d, $^3J_{PC}$ = 8 Hz, *m*-Ph), 126.2 (s, C-5), 124.9 (s, C-6), 123.7 (s, C-7), 121.4 (d, $^3J_{PC}$ = 5 Hz, C-4), 39.5 (m, C-1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −22.27 (s). $^2H\{^1H\}$ NMR ($CHCl_3$): δ 3.48 (s).

Preparation of Bis(1-deuterio-3-(diphenylphosphino)-η^5-indenyl)iron(II) (1-d_2). To a solution of the indene **3**-d_2 (1.0 g, 3.31 mmol) in THF (30 mL) at −80 °C was added a solution of *n*-BuLi (2.07 mL, 1.6 M, 3.31 mmol). After 2 h, $FeCl_2$ (0.21 g, 1.66 mmol) was added and the reaction mixture stirred for 2 h at ambient temperature. The solvent was removed in vacuo, and the residue was loaded onto a Celite column and washed with diethyl ether (to remove unreacted **3**-d_2). Subsequent washing with dichloromethane yielded 0.66 g (61%) of **1**-d_2 as a 60:40 mixture of *rac* and *meso* diastereomers. Stirring of the reaction mixture for a period of 12 h after the addition of $FeCl_2$ produces exclusively the *rac* isomer. Analysis of the isotope pattern from EI-MS and the integrals from ^1H NMR indicates the product contains 85% **1**-d_2 and 15% **1**-*d*. *meso* isomer: ^1H NMR ($CDCl_3$) δ 7.56−6.84 (m, 28H, H-4−H-7 and Ph), 3.82 (s, 2H, H-2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −26.51 (s); $^2H\{^1H\}$ NMR ($CHCl_3$) δ 3.83 (s). *rac* isomer: ^1H NMR ($CDCl_3$) δ 7.54−6.48 (m, 28H, H-4−H-7 and Ph), 3.17 (s, 2H, H-2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 139.8 (d, $^1J_{PC}$ = 10 Hz, *ipso*-Ph), 136.7 (d, $^1J_{PC}$ = 7 Hz, *ipso*-Ph), 135.2 (d, $^2J_{PC}$ = 22 Hz, *o*-Ph), 131.7 (d, $^2J_{PC}$ = 18 Hz, *o*-Ph), 129.3 (s, *p*-Ph), 128.3 (d, $^3J_{PC}$ = 8 Hz, *m*-Ph), 128.0 (d, $^3J_{PC}$ = 5 Hz, *m*-Ph), 127.6 (s, *p*-Ph), 124.2 (d, $^3J_{PC}$ = 8 Hz, C-4), 123.6 (s, C-7), 122.9 (s, C-6), 122.4 (s, C-5), 90.9 (d, $^2J_{PC}$ = 25 Hz, C-3a), 89.6 (d, $^3J_{PC}$ = 5 Hz, C-7a), 72.0 (s, C-2), 68.1 (d, $^1J_{PC}$ = 9 Hz, C-3), 66.1 (m, C-1); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −22.59 (s); $^2H\{^1H\}$ NMR ($CHCl_3$) δ 5.07 (s).

Attempted Crossover Experiment of 1 with 1-d_2. To a solution containing a 55:45 mixture of *rac*- and *meso*-**1** (0.075 g, 0.115 mmol) in THF (25 mL) was added a 60:40 mixture of *rac*- and *meso*-**1**-d_2 (0.075 g, 0.115 mmol, d_2:d_1:d_0 = 85:15:0). After the mixture was stirred for 3 days at ambient temperature, the solvent was removed in vacuo and the residue dissolved in dichloromethane (15 mL). After the mixture was filtered through Celite, the solvent was removed in vacuo to yield a green powder (0.141 g, 94%). Analysis of the isotope pattern using the peak heights from EI-MS indicates the product contains 39% **1**-d_2, 12% **1**-*d*, and 49% **1** (expected 42.5% **1**-d_2, 7.5% **1**-*d*, and 50% **1** if crossover is not occurring compared to 21:50:29 for complete crossover and 34:25:41 if only the molecules isomerizing from *meso* to *rac* crossover). Analysis of the integrals from the ^1H NMR spectrum indicates that the product contains 40% **1**-d_2, 10% **1**-*d*, and 50% **1**.

Isomerization of 1 in the Presence of 1-Deuterio-3-(diphenylphosphino)indenide (2-*d*). To a solution of **3**-d_2 (0.05 g, 0.166 mmol) in THF (20 mL) at −80 °C was added a solution of *n*-BuLi (0.1 mL, 1.6 M, 0.166 mmol). After the mixture was stirred at ambient temperature for 2 h, a 55:45 mixture of *rac*- and *meso*-**1** (0.108 g, 0.166 mmol) was added and the solution stirred for 3 days. The solvent was removed in vacuo and the residue dissolved in dichloromethane (20 mL). After the solution was filtered through Celite, the solvent was removed in vacuo to yield a green powder. Analysis of the isotope pattern from EI-MS and the integrals from the ^1H NMR spectrum indicates the product contains only nondeuterated **1**.

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Isomerization Studies: General Considerations. Under an argon atmosphere, a 5 mm NMR tube was charged with 5.0 mg of a 55:45 mixture of *rac*- and *meso*-**1**. THF (0.4 mL) was introduced, and an external D_2O lock standard was inserted. The sample was immediately inserted into the thermostated probe of a Varian Unity-300 NMR instrument, and an initial $^{31}P\{^1H\}$ NMR spectrum was recorded. The ^{31}P 90° pulse width was 13 μs, and a sweep width of approximately 2400 Hz was used. A relaxation time of 3 s was applied, with 130 transients being collected for each experiment. Using these parameters, a single experiment takes approximately 10 min. For each isomerization study, up to 40 spectra were collected over a period of 14 h. Three signals were observed: a peak at −26.66 corresponding to the *meso* isomer was observed to decrease over time, a peak at −22.74 ppm corresponding to the *rac* isomer increased over time, and a peak at −22.37 ppm corresponding to the free ligand initially remained constant but began to increase at longer times as air slowly entered the NMR tube. The integrals of each signal were obtained, and the corresponding plots of integrals versus time were analyzed with a single-exponential function. The plot of $\ln(X_{t=0}/X_{t=t})$, where X is the mole fraction of *meso*-**1**, versus time, afforded k_{obs} from the slope.

Isomerization Studies in the Presence of Salts. Under an argon atmosphere, a 5 mm NMR tube was charged with 5.0 mg of a 55:45 mixture of *rac*- and *meso*-**1**. To this was added the desired amount of either LiCl or $LiClO_4$. THF (0.4 mL) was introduced to give a concentration of **1** of 0.019 M, and an external D_2O lock standard was inserted. The sample was immediately inserted into the thermostated probe of a Varian Unity-300 NMR instrument at 30 °C. Experiment and analysis are as described above. Table 1 presents the results of the LiCl experiments. For $[LiClO_4] = 0.038$ M, the observed rate was $[6.29(60)] \times 10^5\ s^{-1}$.

Isomerization Studies with Mixed THF/$CDCl_3$ Solvent. Under an argon atmosphere, a 5 mm NMR tube was charged with 5.0 mg of a 55:45 mixture of *rac*- and *meso*-**1**. To this was added a mixed-solvent system containing varying ratios of THF and $CDCl_3$ (total volume of 0.4 mL). An external D_2O lock standard was inserted, and the sample was immediately inserted into the thermostated probe of a Varian Unity-300 NMR instrument at 30 °C. Experiment and analysis are as described above.

High-Pressure NMR Measurements. To perform the high-pressure NMR measurements, we used a specially designed home-built high-pressure NMR probe,[22] which is a modification of an earlier developed high-pressure probe.[23] With this probe we were able to detect ^{31}P spectra at 161.98 MHz while performing inverse gated decoupling on the proton resonance at 400.13 MHz. We dissolved 17 mg of the sample in 0.65 mL of THF-d_8. Each sample was sealed in a cutoff 5 mm o.d. commercial NMR tube (58 mm length) with a floating Teflon piston. Sample temperature was monitored through a Pt-100 resistor and was held constant (±0.5 °C) with circulating fluid. A temperature of 308 K was chosen for the pressure cycles. The samples were measured at selected pressures in the range 1−150 MPa with a Bruker AVANCE DRX-400 spectrometer equipped with a wide-bore magnet. Field homogeneities better than 6×10^{-9} can be achieved by shimming on the ^1H FID with the BOSS I shim system. The ^{31}P 90° pulse width was 35 μs, and a sweep width of about 13 000 Hz was used. A relaxation delay of 2 s was applied with accumulation of up to 548 scans. Using these parameters, a single experiment takes about 30 min. For one pressure cycle up to 40 spectra were accumulated, and in that way the reaction was followed over 20 h, which corresponds to at least 3 half-lives of the reaction. The pressure remained constant during this time, since no pressure leakage of the high-pressure vessel could be observed.

Three main signals could be detected: first, the signal of the *meso* form (−26.49 ppm), which decreases with time, and then that of the free ligand (−22.28 ppm) and the *rac* form (−22.58 ppm), which increase with time. For the *rac* signal, a high-field shift of −0.2 ppm could be observed on increasing the pressure from 0.5 to 150 MPa. It turned out that the conversion rate from *meso* to *rac* is at least twice as fast as the buildup of the free ligand. The integrals of each signal were determined by Lorentzian line-shape analysis. The corresponding plots of decreasing or increasing integrals versus time were analyzed with single-exponential functions, from which the observed rate constants were obtained and k_1 and k_2 for the isomerization and hydrolysis reactions, respectively, could then be determined. Rate constants k_1 and k_2 were then analyzed as a function of pressure, and the slope of the straight line obtained on plotting $RT \ln(k_{1\text{ or }2})$ versus pressure represents the activation volume.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft.

Supporting Information Available: Tables of rate constants and species distribution as a function of pressure, as determined by ^{31}P NMR spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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