Facile *meso* to *rac* Isomerization of the Bis-Planar Chiral Ferrocenyldiphosphine Bis(1-(diphenylphosphino)-η^5-indenyl)iron(II)

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Summary: The meso isomer of the ferrocenyldiphosphine bis(1-(diphenylphosphino)-η^5-indenyl)iron(II) isomerizes to the rac isomer overnight in tetrahydrofuran at room temperature. The isomerization is accelerated by salts but does not occur in chloroform solvent.

Ferrocenylphosphines 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 large number of planar chiral ferrocenylphosphines 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. We recently 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.[2] Unfortunately, we had been unable to isolate the two isomers. We report here the isolation of the *rac* isomer and the remarkably facile isomerization of the *meso* isomer to the *rac* isomer.

Addition of ferrous chloride to 2 equiv of lithium 1-(diphenylphosphino)indenide in tetrahydrofuran (Scheme 1) initially produces a mixture of two phosphorus-containing compounds, as shown by peaks in the ^{31}P NMR spectrum at −22.26 and −26.53 ppm. After the mixture was stirred overnight, only the peak at −22.26 ppm was observed.[3] Crystals of this compound were obtained and shown by X-ray crystallography[4] to be the *rac* isomer of **1** (Figure 1). If the reaction is stopped after 2 h, the two compounds can be isolated as a mixture.[5] ^{1}H and ^{13}C NMR spectroscopy of the mixture shows the two compounds to have similar spectra, with only minor differences in the chemical shifts. Since the *rac* and *meso* isomers are expected to have similar NMR patterns, it is reasonable to say that the other compound is the *meso* isomer of **1**.

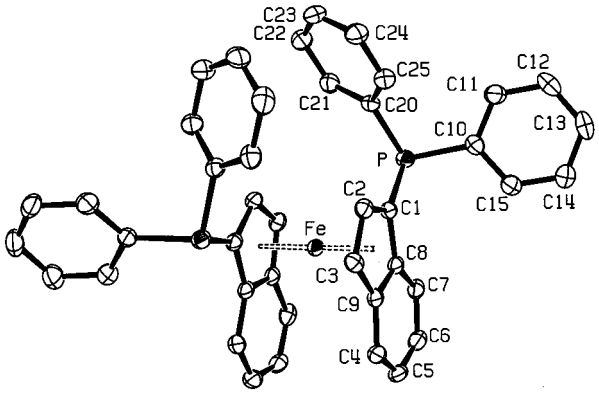
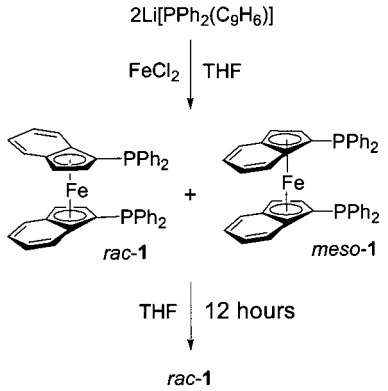


Figure 1. ORTEP drawing of *rac*-**1** indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 50% probability. Selected bond lengths (Å): Fe−CNT = 1.672, Fe−C(1) = 2.062(3), Fe−C(2) = 2.045(3), Fe−C(3) = 2.067(3), Fe−C(8) = 2.090(3), Fe−C(9) = 2.104(3), C(1)−C(2) = 1.446(4), C(1)−C(8) = 1.448(4), C(2)−C(3) = 1.425(4), C(3)−C(9) = 1.432(4), C(4)−C(9) = 1.427(4), C(4)−C(5) = 1.359(5), C(5)−C(6) = 1.441(5), C(6)−C(7) = 1.349(4), C(7)−C(8) = 1.436(4), C(8)−C(9) = 1.447(4), C(1)−P = 1.829(3), P−C(10) = 1.850(3), P−C(20) = 1.833(3). Bond angles (deg): C(1)−P−C(10) = 101.51(15), C(1)−P−C(20) = 100.85(15), C(10)−P−C(20) = 102.37(14), CNT−C(1)−P = 176.07. Dihedral angle (deg): C(1)−CNT−CNT′−C(1′) = 123.07.

Scheme 1. Synthesis and Isomerization of 1



The conversion of the *meso* isomer to the *rac* isomer requires one of the indenyl 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 ferrocenylphosphine, although racemization of acyl-

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ferrocenes in nitroalkane solvents in the presence of strong acids, such as $HClO_4$ or $AlCl_3$, has been reported.[6] Other processes resulting in the flipping over of a cyclopentadienyl ligand have been observed in metallocene systems of the lanthanides[7] and group 3[8] and group 4[9] metals. A number of the group 4 ring-flipping processes are photochemically initiated.[9a−g] Also of particular note, Hollis and Fu have independently described a diphosphazirconocene in which a phosphole flips over via a proposed intermediate in which the phosphole is coordinated by only the P atom.[10]

Herberich and co-workers have described systems in which cyclopentadienyl rings are exchanged between metal centers via triple-decker sandwich intermediates and which result in coordination of the rings by the other face. This involves an intermolecular exchange process.[11] That such a process may occur in some ferrocene systems is evidenced by the cyclopentadienyl-exchange reactions between ferrocenes, using the Lewis acid $AlCl_3$,[12] and the synthesis of $[Cp_3Fe_2]^+$ by Kudinov.[13] Other examples of cyclopentadienyl-transfer reactions from ferrocenes include the following: transfer of acylferrocenes to Re,[14] a redistribution reaction between ferrocene and 1,1′-dimethylferrocene at 250 °C after 3 days,[15] and the synthesis of ruthenocene from ferrocene and $RuCl_3$ at 250 °C.[16]

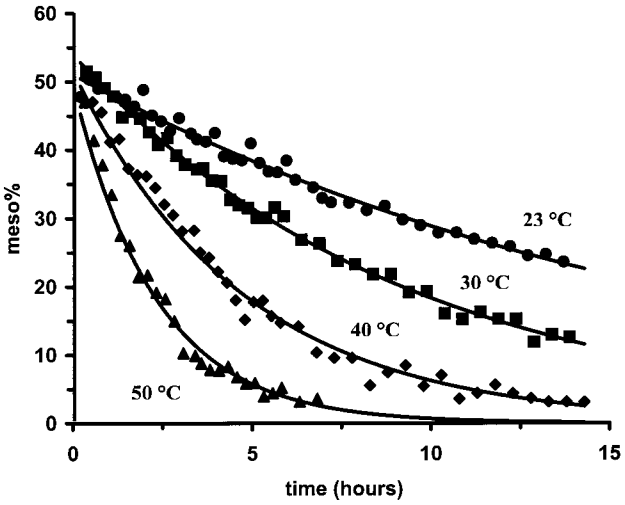

Figure 2. Conversion of *meso*-**1** to *rac*-**1** in tetrahydrofuran at various temperatures: 23 °C, $k_1 = [1.59(3)] \times 10^{-5}$ s^{-1}; 30 °C, $k_1 = [3.01(9)] \times 10^{-5}$ s^{-1}; 40 °C, $k_1 = [5.89(16)] \times 10^{-5}$ s^{-1}; 50 °C, $k_1 = [1.20(4)] \times 10^{-4}$ s^{-1}.

The isomerization of *meso*-**1** to *rac*-**1** was followed by ^{31}P NMR spectroscopy at a variety of temperatures (Figure 2). The isomerization is first order in ferrocene concentration, and the activation parameters were found to be $\Delta H^{\ddagger} = 57 \pm 4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -145 \pm 15$ J mol^{-1} K^{-1}. In neat tetrahydrofuran, the rate is $[1.59(3)] \times 10^{-5}$ s^{-1} at 23 °C. 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* to *meso* ratio of 55:45. Possible causes of the rate increase include excess indenyldiphenylphosphine and dissolved salts. It was found that additional indenyldiphenylphosphine did not increase the rate, whereas addition of LiCl increased the rate significantly (at [LiCl] = 0.081 M and [**1**] = 0.020 M, k_1

(3) To a solution of 1-(diphenylphosphino)indene (1.8 g, 6.0 mmol) in tetrahydrofuran (50 mL) at −80 °C was added a solution of *n*-BuLi (3.75 mL, 1.6 M, 6.0 mmol). After 2 h, $FeCl_2$ (0.38 g, 3 mmol) was added and the reaction mixture was stirred for 12 h at ambient temperature to give a dark green solution. The solvent was removed in vacuo, and the residue was loaded onto a Celite column and washed with diethyl ether (to remove unreacted 1-(diphenylphosphino)indene). Subsequent elution with dichloromethane yielded 1.26 g (64%) of *rac*-**1** as a dark blue powder. Dark blue crystallographic-quality crystals were obtained by recrystallization from CH_2Cl_2/diethyl ether. Data for *rac*-**1**: ^1H NMR ($CDCl_3$) δ 3.07 (d, $^3J_{HH}$ = 2 Hz, 2H, H-2), 4.92 (d, $^3J_{HH}$ = 2 Hz, 2H, H-3), 6.4−7.4 (m, 28H, H4−7 and Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 66.1 (d, $^3J_{PC}$ = 4 Hz, C-3), 68.1 (d, $^1J_{PC}$ = 9 Hz, C-1), 72.0 (d, $^2J_{PC}$ = 4 Hz, C-2), 90.3 (d, $^2J_{PC}$ = 4 Hz, C-9), 91.0 (d, $^3J_{PC}$ = 25 Hz, C-8), 122.5 (s, C-5), 122.9 (s, C-6), 123.6 (s, C-4), 124.1 (d, $^3J_{PC}$ = 9 Hz, C-7), 127.6 (s, *p*-Ph), 128.0 (d, $^3J_{PC}$ = 5 Hz, *m*-Ph), 128.3 (d, $^3J_{PC}$ = 8 Hz, *m*-Ph), 129.3 (s, *p*-Ph), 131.7 (d, $^2J_{PC}$ = 18 Hz, *o*-Ph), 135.2 (d, $^2J_{PC}$ = 22 Hz, *o*-Ph), 136.7 (d, $^1J_{PC}$ = 7 Hz, *ipso*-Ph), 139.8 (d, $^1J_{PC}$ = 10 Hz, *ipso*-Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −22.26 (s).

(4) Crystal data for *rac*-**1**: $C_{42}H_{32}FeP_2$; M_r = 654.47; orthorhombic, *Pbcn*; a = 12.959(6) Å, b = 12.396(5) Å, c = 19.296(8) Å, V = 3100(2) Å^3, Z = 4, $F(000)$ = 1360, D_{calcd} = 1.402 g cm^{-3}, Mo Kα radiation (λ = 0.710 73 Å), μ = 0.6221 mm^{-1}, T = 168(2) K; θ range 2.11−26.44°; 3142 unique reflections, 204 parameters; R1 = 0.0351, wR2 = 0.0783 ($I > 2\sigma(I)$), largest difference peak and hole 0.308 and −0.427 e Å^{-3}. Data were collected on a Siemens P4 Smart CCD area detector; the structure was solved by direct methods and refined by full-matrix least-squares methods on F^2.

(5) The same procedure as for the preparation of *rac*-**1** was used, except that the reaction solution is stirred for only 2 h before the solvent is removed in vacuo. Yields obtained for mixtures do not vary significantly from that obtained for the *rac* isomer. Data for *meso*-**1**: ^1H NMR ($CDCl_3$) δ 3.48 (d, $^3J_{HH}$ = 2 Hz, 2H, H-2), 3.81 (d, $^3J_{HH}$ = 2 Hz, 2H, H-3), 6.88−7.53 (m, 28H, H4−7 and Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 64.4 (s, C-3), 66.9 (d, $^1J_{PC}$ = 13 Hz, C-1), 74.5 (s, C-2), 90.3 (s, C-9), 91.6 (d, $^2J_{PC}$ = 22 Hz, C-8), 124.3 (s, C-5), 124.9 (s, C-6), 127.7 (s, *p*-Ph), 127.9 (s, C-4), 128.0 (d, $^3J_{PC}$ = 3 Hz, *m*-Ph), 128.1 (d, $^3J_{PC}$ = 10 Hz, C-7), 128.2 (d, $^3J_{PC}$ = 8 Hz, *m*-Ph), 129.0 (s, *p*-Ph), 132.4 (d, $^2J_{PC}$ = 20 Hz, *o*-Ph), 135.4 (d, $^2J_{PC}$ = 21 Hz, *o*-Ph), 137.4 (d, $^1J_{PC}$ = 11 Hz, *ipso*-Ph), 139.1 (d, $^1J_{PC}$ = 14 Hz, *ipso*-Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −26.53 (s).

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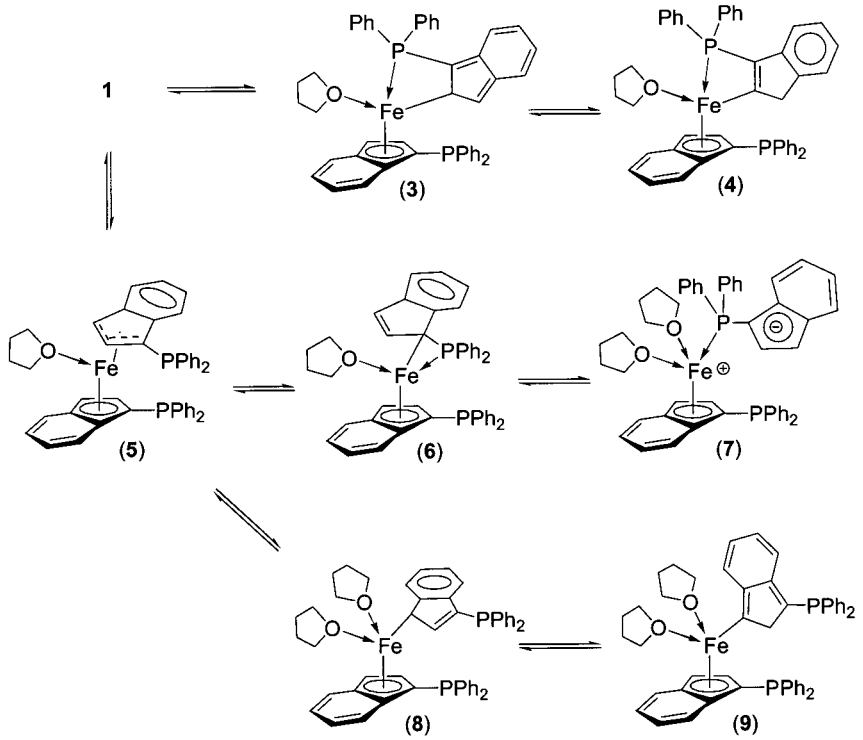
Scheme 2. Some Possible Mechanisms for the Isomerization of 1



= [3.59(14)] × 10^{-4} s^{-1} at 30 °C). LiCl is the major salt present during the synthesis. In the noncoordinating solvent chloroform, no isomerization was observed after 1 week, indicating that the tetrahydrofuran solvent is intimately involved in the mechanism. On the basis of these observations, our proposed mechanism involves coordination of THF (one or two molecules) and slippage of the indenylphosphine ligand until the indenide dissociates and the ligand coordinates by only the phosphorus atom (although we cannot yet rule out complete dissociation of $Ph_2P(C_9H_6)^-$), thus generating the zwitterionic intermediate **7** (Scheme 2), which could be stabilized by the presence of ionic species. Thus, solvent-assisted dissociation of indenide from **6** to **7** is the rate-determining step. Recoordination of the five-membered indenide ring could then occur by either face. The large negative entropy of activation supports 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 $[Rh(dmpe)_2][C_9H_7]$.[17]

Although a 1,3-proton shift could not result in isomerization, a 1,5-proton shift, after ring slippage via **3** or **5** and **8**, to give an intermediate such as **4** or **9** could. However, these intermediates are not likely to be as energetically favorable as **7**, since their formation involves a loss of aromaticity at some stage, and we would not expect the rate to be significantly affected by salts.

The higher stability of the *rac* isomer versus the *meso* isomer may be a result of π stacking between the benzo rings (illustrated by the offset π stacking conformation in the solid-state crystal structure),[18] since this cannot occur in the *meso* isomer without creating significant steric interactions between the diphenylphosphino groups. The question of why this isomerization has not been observed in other ferrocenylphosphines also 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.[19] However, for complete dissociation of an indenyl ligand, to give our proposed intermediate **7**, the six-membered ring does not become aromatic. This suggests that the ring-slipped intermediates **5** and **6**, in which the six-membered ring does become aromatic, are readily formed.

To summarize, we have reported an unprecedented and facile *meso* to *rac* isomerization of the ferrocenyldiphosphine bis(1-(diphenylphosphino)-η^5-indenyl)iron(II) of relevance to the chemistry of other planar chiral ferrocenes with phosphine substituents. In particular, one cannot assume the stability of other planar chiral ferrocenylphosphine systems. Further studies are being carried out to define the mechanism and test its generality.

Supporting Information Available: Tables of crystal data, atomic positional parameters, and bond distances and angles for *rac*-**1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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