Synthesis of 2,2″-Bis(diphenylphosphino)-1,1″-biferrocene, a Planar Chiral Bisphosphine, and its Palladium(II) Complex

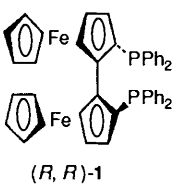
Masaya Sawamura, Akira Yamauchi, Toshiaki Takegawa and Yoshihiko Ito*
Department of Synthetic Chemistry, Kyoto University, Kyoto 606, Japan

A new planar chiral bisphosphine, 2,2″-bis(diphenylphosphino)-1,1″-biferrocene (BIFEP), was synthesized *via* regioselective magnesiation of (diphenylphosphinyl)ferrocene, and converted to its palladium(II) complex.

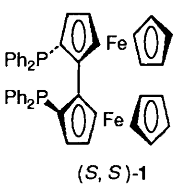
The recent progress of asymmetric synthesis by means of chiral transition-metal catalysts has been mostly prompted by the molecular design and synthesis of new effective chiral phosphine ligands.[1] Herein, we report the synthesis of (*R*,*R*)- and (*S*,*S*)-2,2″-bis(diphenylphosphino)-1,1″-biferrocene **1**, (BIFEP), a new planar chiral bisphosphine, whose complexation with transition-metals may be interestingly compared with that of axially chiral 2,2′-bis(diphenylphosphino)-1,1′-binapthyl (BINAP).[2]

The synthesis of optically active BIFEP is outlined in Scheme 1. The key reaction of the synthesis is the selective magnesiation of (diphenylphosphinyl)ferrocene **2**,[3] which was conveniently prepared *via* monolithiation of ferrocene[4] by Bu^{t}Li. The metalation of **2** with excess *N*,*N*-diisopropylamidomagnesium bromide[5] occurred exclusively on the ferrocenyl part *ortho* to the diphenylphosphinyl group producing ferrocenylmagnesium bromide **3**. The Grignard reagent **3** was stable at least at room temperature, but readily reacted with iodine to give iodoferrocene **4**.† Fortunately, a nickel(0) promoted coupling of the racemic iodide **4** gave no *meso*-biferrocene but only desired (±)-biferrocene **5**,† which was optically resolved to homochiral materials by fractional recrystallization of the complexes with (−)- and (+)-dibenzoyltartaric acid (**5**: dibenzoyltartaric acid = 2 : 1). Finally, resolved phosphine oxide **5** {$[\alpha]_D^{20}$ −498° (*c* 0.53, $CHCl_3$) for (−)-**5**} was reduced to BIFEP {$[\alpha]_D^{20}$ −156° (*c* 0.19, $CHCl_3$), m.p. 226° from (−)-**5**}‡ by the reaction with trichlorosilane.[6] The absolute configuration of **5** and BIFEP are not determined yet.

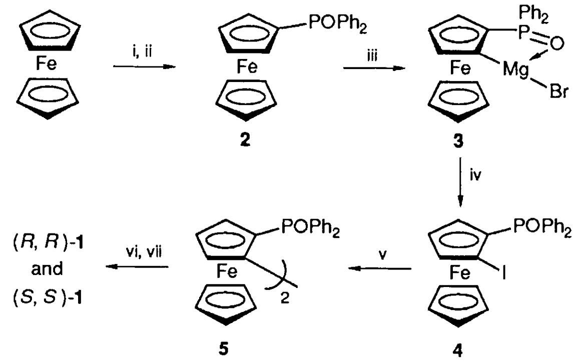
Treating homochiral BIFEP with $PdCl_2(MeCN)_2$ in CH_2Cl_2 gave $PdCl_2$·BIFEP, whose ^{13}C NMR spectra indicated that BIFEP chelates to palladium in a *cis*-fashion.[7]§ The BIFEP



(*R*, *R*)-**1**



(*S*, *S*)-**1**



Scheme 1 *Reagents and conditions* (yields are not optimized): i, Bu^{t}Li–pentane (0.8 equiv.), tetrahydrofuran (THF), 0 °C, 0.5 h; ii, $ClPOPh_2$ (1 equiv.) (61% based on Bu^{t}Li); iii, Pr^i_2NMgBr–THF (4 equiv.), 0 °C, 0.5 h, room temp., 2.5 h; iv, I_2 (3 equiv.), −30 °C, 1 h (70%); v, $Ni(acac)_2$ (2 equiv.), DIBAL (2 equiv.), benzene, reflux, 2 h (55%); vi, (−)- and (+)-dibenzoyltartaric acid, AcOEt; NaOH aq. (80%); vii, $HSiCl_3$ (20 equiv.), Et_3N (20 equiv.), benzene, 100 °C in a sealed tube, 45 h (95%)

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† The structure assignment of **4** and **5** were confirmed by an X-ray crystal structure analysis of (±)-**5**, which has not yet been fully refined.

‡ *NMR spectral data* for BIFEP **1**: ^1H NMR ($CDCl_3$–Me_4Si, 200 MHz) δ 3.94–3.99 (m, 2H), 4.03 (s, 10H), 4.53 (t, *J* 2.5 Hz, 2H), 4.92–4.96 (m, 2H), 6.64–6.70 (m, 8H), 6.75–6.87 (m, 2H), 7.33–7.42 (m, 6H), 7.49–7.58 (m, 4H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2–Me_4Si, 50 MHz) δ 70.09, 70.33, 71.84 (d, J_{C-P} 5.1 Hz), 76.60 (dd, J_{C-P} 8.2 and 4.6 Hz), 78.47 (d, J_{C-P} 11.1 Hz), 91.51 (dd, J_{C-P} 29.9 and 2.6 Hz), 127.22, 127.73 (d, J_{C-P} 5.3 Hz), 128.8 (d, J_{C-P} 8.2 Hz), 129.40, 131.66 (d, J_{C-P} 17.1 Hz), 135.77 (d, J_{C-P} 22.6 Hz), 139.81 (d, J_{C-P} 9.9 Hz), 140.39 (d, J_{C-P} 9.3 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$–85% H_3PO_4, 81 MHz) δ −23.74.

§ $^{13}C\{^1H\}$ resonances of Ph groups split to five-line multiplets or near 1 : 1 : 1 triplets. The computer simulation of an $A[X]_2$ spin system, where A is ^{13}C and X is ^{31}P, has been reported, see ref. 7.

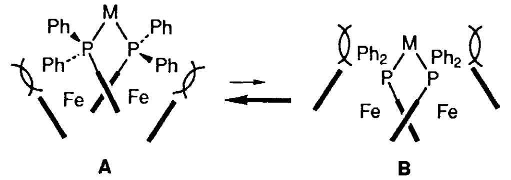

Fig. 1 Illustration of two possible comformations of metal complexes of (*R*,*R*)-BIFEP

does not intrinsically have axial chirality, but can give a $PdCl_2$ complex only in the conformation **A** [for (*R*,*R*)-**1**, Fig. 1], which is similar to that of metal complexes of (*S*)-BINAP, axially chiral bisphosphine. Another possible conformation **B** of $PdCl_2$·BIFEP complex should be excluded because of serious steric repulsion between Ph_2P moieties and unsubstituted Cp rings, as suggested from molecular modelling studies.

The biferrocenyl backbone of BIFEP provides a fairly wide range of chiral environments. The molecular modelling studies of BIFEP–transition metal complexes suggest that there are direct steric interactions between unsubstituted Cp rings and two of the four Ph groups controlling the orientation of the phenyl groups, and that the P–metal–P bite angle is obliged to enlarge to some degree.

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