Tetrahedron: Asymmetry Vol. 2, No. 7, pp. 593-596, 1991
Printed in Great Britain

0957-4166/91 $3.00+.00
Pergamon Press plc

A Trans-Chelating Chiral Diphosphine Ligand: Synthesis of 2,2''-Bis[1-(diphenylphosphino)ethyl]-1,1''-biferrocene and Its Complexes with Platinum(II) and Palladium(II)

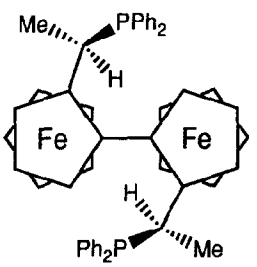
Masaya Sawamura, Hitoshi Hamashima and Yoshihiko Ito*

Department of Synthetic Chemistry, Kyoto University, Kyoto 606-01, Japan

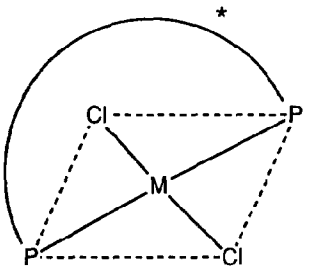
(*Received* 30 *April* 1991)

Abstract: A new chiral diphosphine ligand, (*R,R*)-(*S,S*)-2,2''-bis[1-(diphenylphosphino)ethyl]-1,1''-biferrocene, which possesses both central and planar elements of chirality, was synthesized. The NMR studies and molecular weight determination indicated that the ligand chelates to platinum(II) and palladium(II) in *trans*-manner.

Although many kinds of chiral diphosphines have been developed as a chiral ligands for catalytic asymmetric synthesis promoted by transition metal complexes in the last two decades,[1] only one example of the *chiral* diphosphine ligand which chelates to metals in *trans*-manner has been reported.[2,3] It may be true that a *cis*-chelated phosphine complex has a wider range of use than a *trans*-complex, but we have a deep interest in the potential of *trans*-complex for new asymmetric catalysis. Recently, we have undertaken works on applications of C_2 symmetric biferrocenes for asymmetric synthesis.[4] This paper describes synthesis of a new chiral diphosphine bearing a C_2 symmetric biferrocene framework, 2,2''-bis[1-(diphenylphosphino)ethyl]-1,1''-biferrocene (**1**), which possesses both central and planar elements of chirality, and its platinum(II) and palladium(II) complexes (**2**), in which the chiral diphosphine chelates to central metals in *trans*-manner.



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

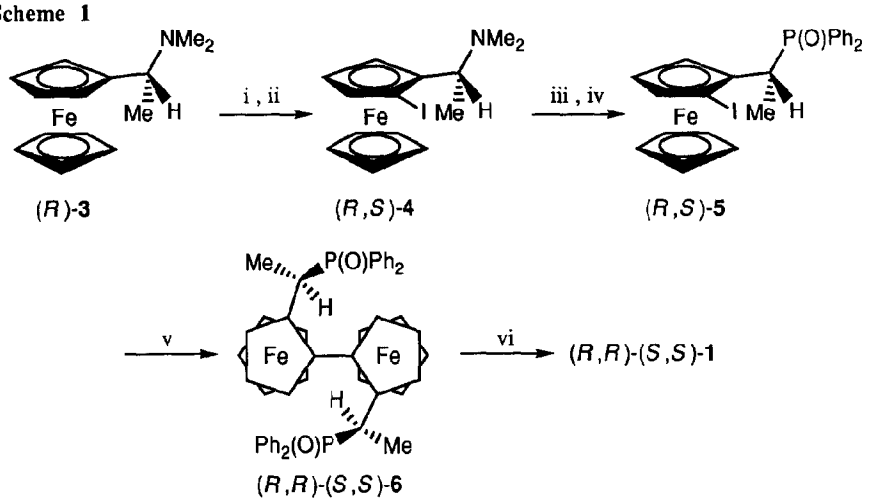


2a (M = Pt)
2b (M = Pd)

P P = **1**

The synthesis of ligand **1** starts from optically resolved amine (*R*)-**3**[5] (Scheme 1), which was converted to iodide **4**[6] *via* stereoselective *ortho*-lithiation [(*R*)-(*S*)/(*R*)-(*R*) = 10/1]. The dimethylamino group of **4** was quarternized, and then substituted by diphenylphosphinyl group with complete retention of configuration by the reaction with lithium diphenylphosphinylide in DME. The homocoupling of **5** promoted by in situ-generated Ni(0) complex[7] produced biferrocene (*R*,*R*)-(*S*,*S*)-**6** {$[\alpha]_D^{25}$ -130 (*c* 1.02, $CHCl_3$), mp 245-250 °C (dec)},[8] which was separated from the epimeric isomer derived from (*R*)-(*R*)-**4** at the stage by column chromatography (silica gel, AcOEt/benzene). Finally, reduction of phosphinyl group of **6** with trichlorosilane/triethylamine[9] afforded diphosphine (*R*,*R*)-(*S*,*S*)-**1** {$[\alpha]_D^{25}$ -426 (*c* 0.51, $CHCl_3$), mp 99-103 °C}.[10]

Scheme 1



i) *n*-BuLi / Hexane (1.2 eq), Et_2O, rt, 2 h. ii) I_2 (1.1 eq), -30 °C, 10 min. (55%).

iii) CH_3I (10 eq), Acetone, rt, 30 min. (90%).

iv) $Ph_2P(O)H$ (1.0 eq), *n*-BuLi / Hexane (1.0 eq), DME, reflux, 3 h. (78%).

v) $NiBr_2(PPh_3)_2$ (0.5 eq), Zn (1.5 eq), Et_4NI (1.0 eq), DMF, 120 °C, 12 h. (50%).

vi) $HSiCl_3$ (5.0 eq), Et_3N (6.0 eq), Benzene, 100 °C (in sealed tube), 12 h. (83%).

The coordinating properties of the diphosphine ligand **1** were first examined with a platinum complex, because the isomeric structures (*trans* or *cis*) are easily determined by the magnitude of $J_{^{195}Pt\text{-}^{31}P}$.[11] Thus, the treatment of (*R*,*R*)-(*S*,*S*)-**1** with 1 eq of *trans*-$PtCl_2(MeCN)_2$ in chloroform at 40 °C for 12 h gave two platinum species in a ratio of 20:1. The $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$, 85% H_3PO_4) of the major product (δ 21.41) was accompanied by its ^{195}Pt satellite with $J_{^{195}Pt\text{-}^{31}P}$ value of 2612 Hz, indicating the *trans* geometry of two phosphorus atoms. On the other hand, the minor product was deduced to have a *cis* geometry from larger $J_{^{195}Pt\text{-}^{31}P}$ value (3668 Hz) (Figure 1). The ^1H and $^{13}C\{^1H\}$ NMR spectra were also in agreement with the assignments.[12] After a chromatographic separation (silica gel, CH_2Cl_2, Rf 0.94 for *trans*; 0.20 for *cis*), the chelated mononuclear structure of the *trans*-complex (**2a**) {$[\alpha]_D^{20}$ -571 (*c* 0.57, $CHCl_3$), mp 240-245 °C(dec)} was concluded from FAB-Mass spectra and a molecular weight determination by VPO analysis (MW calcd 1060.5, obsd 1120 in $CHCl_3$).

Similar reaction of (*R*,*R*)-(*S*,*S*)-**1** with $PdCl_2(MeCN)_2$ was complete within a few minutes at room temperature giving *trans*-chelated palladium complex **2b** {$[\alpha]_D^{20}$ -726 (*c* 0.55, $CHCl_3$), mp 230-235 °C(dec)} without formation of *cis* palladium species.[13]

As previously demonstrated with an achiral version of *trans*-chelating diphosphine ligand by Venanzi et al.,[3] the pre-organization of free ligand is very important for the preferential formation of *trans*-chelated complex. From molecular modeling examinations of **1**, the angle between the planes of two substituted cyclopentadienyl rings is roughly estimated to have a range between 90° and 180° for stable conformations (Figure 2), and each Ph_2P-group on asymmetric carbon center should be fixed to sterically less crowded exo region of ferrocene, as dialkylamino groups of a series of ferrocenylphosphines and their metal complexes thus far reported are so.[14,15] In such a conformation, the lone pairs of the two P atoms are easy to converge with appropriate distances for chelation to transition metals in *trans*-manner.

Currently, our intention is to explore the new catalytic asymmetric reaction by the use of the *trans*-chelating diphosphine as a chiral ligand.

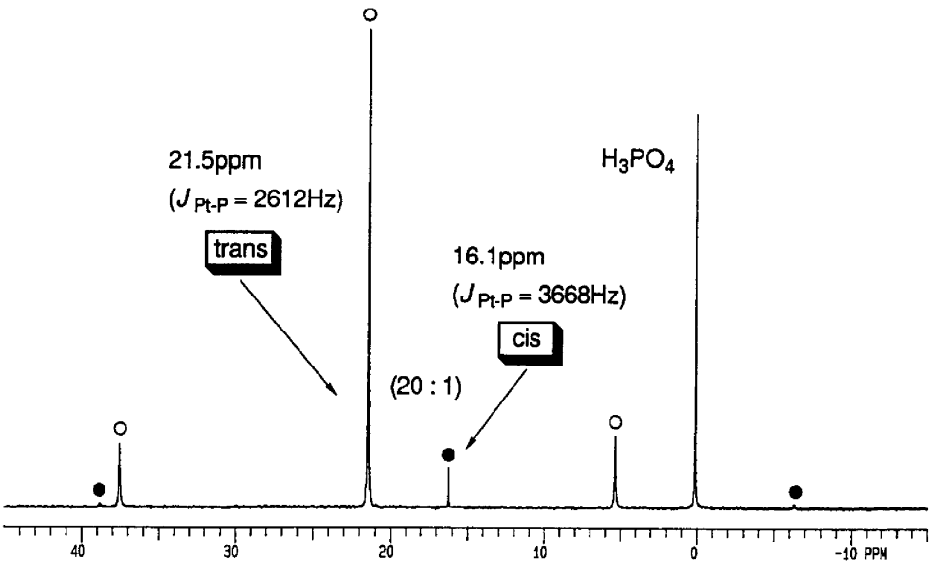


Figure 1. The $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$, 85% H_3PO_4, 81 MHz) of the solution which was prepared from the reaction of (*R*,*R*)-(*S*,*S*)-**1** with $PtCl_2(MeCN)_2$ in $CDCl_3$ at 40 °C for 12 h.

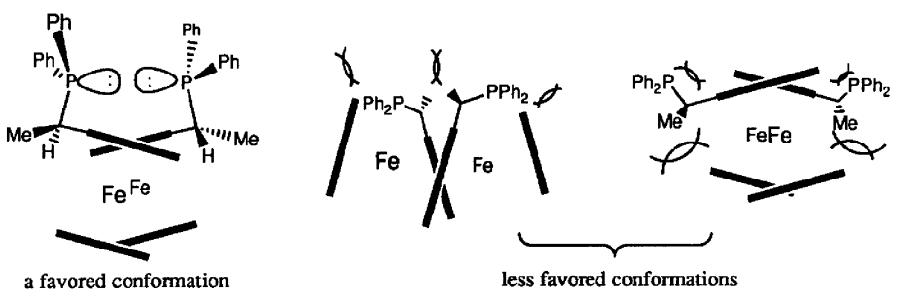


Figure 2. Three possible conformations of (*R*,*R*)-(*S*,*S*)-**1**.

References and Notes

1 For reviews, see: (a) I. Ojima, N. Clos, C. Bastos, *Tetrahedron* **45**, 6901 (1989). (b) R. Noyori, M. Kitamura, In *Modern Synthetic Methods*: R. Scheffold, Ed.; Springer-Verlag: 1989; Vol. 5, p 115.

2 (a) J. M. Brown, P. A. Chaloner, G. Descotes, R. Glaser, D. Lafont, D. Sinou, *J. Chem. Soc. Chem. Commun.* 611 (1979). (b) G. Descotes, D. Lafont, D. Sinou, J. M. Brown, P. A. Chaloner, D. Parker, *Nouveau J. Chim.* **5**, 167 (1981).

3 For achiral *trans*-chelating diphosphine, 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene and its derivatives, see: (a) N. J. DeStefano, D. K. Johnson, L. M. Venanzi, *Angew. Chem. internat. Edit.* **13**, 133 (1974). (b) H-B. Bürgi, J. Murray-Rust, M. Camalli, F. Caruso, L. M. Venanzi, *Helv. Chim. Acta* **72**, 1293 (1989), and references cited therein.

4 The synthesis of a chiral *cis*-chelating diphosphine, 2,2"-bis(diphenylphosphino)-1,1"-biferrocene (BIFEP), and its palladium(II) complex was reported: *J. Chem. Soc. Chem. Commun.* in press.

5 D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, I. Ugi, *J. Am. Chem. Soc.* **92**, 5389 (1970).

6 Optically pure (*R*)-(*S*)-**4** has been reported. See: M. Watanabe, S. Araki, Y. Butsugan, M. Uemura, *Chemistry Express* **4**, 825 (1989).

7 M. Iyoda, H. Otsuka, K. Sato, N. Nisato, M. Oda, *Bull. Chem. Soc. Jpn.* **63**, 80 (1990).

8 The optical purity of (*R*,*R*)-(*S*,*S*)-**6** was confirmed to be 100% by HPLC analysis on chiral stationary phase column (Sumitomo Chemical Co., SUMICHIRAL OA-4100, hexane/dichloroethane/ethanol).

9 K. Naumann, G. Zon, K. Mislow, *J. Am. Chem. Soc.* **91**, 7012 (1969).

10 The NMR spectra for **1** are as follows: ^{1}H NMR (200MHz, $CDCl_3$, TMS) δ 1.35 (m, 6 H), 3.49 (q, J = 7.0 Hz, 2 H), 3.79 (m, 2 H), 4.12 (m, 2 H), 4.30 (s, 10 H), 4.55 (m, 2 H), 7.1-7.3 (m, 20 H). $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$, TMS) δ 17.03, 29.25 (m), 65.35, 68.05 (t), 69.32, 71.66, 84.36 (t), 93.08 (t), 127.18, 127.45 (t), 127.99 (t), 128.31, 132.13 (t), 135.10 (t), 136.14 (m), 139.00 (m). $^{31}P\{^{1}H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 2.19.

11 J. A. Rahn, L. Baltusis, J. H. Nelson, *Inorg. Chem.* **29**, 750 (1990), and references cited therein.

12 (a) D. A. Redfield, L. W. Cary, J. H. Nelson, *Inorg. Chem.* **14**, 50 (1975). (b) The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for **2a** are as follows: ^{1}H NMR (200MHz, $CDCl_3$, TMS) δ 1.66 (dt, $|^{3}J_{H\text{-}H}|$ = 6.6 Hz, $|^{3}J_{P\text{-}H} + {}^{5}J_{P\text{-}H}|$ = 12.2 Hz, 6 H), 3.76 (m, 2 H), 4.06 (m, $|^{2}J_{P\text{-}H} + {}^{4}J_{P\text{-}H}|$ = 4.0 Hz, 2 H), 4.31 (s, 10 H), 4.39 (m, 2 H), 4.64 (m, 2 H), 7.2-7.4 (m, 16 H), 7.8-7.9 (m, 4 H). $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$, TMS) δ 19.96 (t, $|^{3}J_{Pt\text{-}C}|$ = 22 Hz), 30.85 (quint, $|^{1}J_{P\text{-}C} + {}^{3}J_{P\text{-}C}|$ = 27 Hz), 67.10, 67.85, 69.71, 72.55, 86.63, 91.62 (t, $|^{3}J_{P\text{-}C} + {}^{5}J_{P\text{-}C}|$ = 8 Hz), 126.97 (t, $|^{1}J_{P\text{-}C} + {}^{3}J_{P\text{-}C}|$ = 46 Hz, ipso), 127.05 (t, $|^{3}J_{P\text{-}C} + {}^{5}J_{P\text{-}C}|$ = 10 Hz, meta), 127.24 (t, $|^{3}J_{P\text{-}C} + {}^{5}J_{P\text{-}C}|$ = 9 Hz, meta), 129.19 (para), 129.90 (t, $|^{1}J_{P\text{-}C} + {}^{3}J_{P\text{-}C}|$ = 50 Hz, ipso), 130.60 (para), 133.48 (t, $|^{2}J_{P\text{-}C} + {}^{4}J_{P\text{-}C}|$ = 9 Hz, ortho), 137.53 (t, $|^{2}J_{P\text{-}C} + {}^{4}J_{P\text{-}C}|$ = 11 Hz, ortho).

13 The structure of the *trans*-chelated palladium complex was identified on the basis of the spectroscopic data, which are similar to those of the platinum complex except for the coupling between ^{31}P and ^{195}Pt. The ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra for **2b** are as follows: ^{1}H NMR (200MHz, $CDCl_3$, TMS) δ 1.65 (dt, $|^{3}J_{H\text{-}H}|$ = 6.6 Hz, $|^{3}J_{P\text{-}H} + {}^{5}J_{P\text{-}H}|$ = 13.0 Hz, 6 H), 3.72 (m, 2 H), 4.08 (m, 2 H), 4.31 (s, 10 H), 4.40 (m, 2 H), 4.67 (m, 2 H), 7.2-7.4 (m, 16 H), 7.9-8.0 (m, 4 H). $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$, TMS) δ 19.88, 30.90 (t, $|^{2}J_{P\text{-}C} + {}^{4}J_{P\text{-}C}|$ = 18 Hz), 67.61, 68.06, 70.14, 72.74, 86.68, 91.71 (t, $|^{2}J_{P\text{-}C} + {}^{4}J_{P\text{-}C}|$ = 10 Hz), 127.08 (t, $|^{3}J_{P\text{-}C} + {}^{5}J_{P\text{-}C}|$ = 9 Hz, meta), 127.23 (t, $|^{3}J_{P\text{-}C} + {}^{5}J_{P\text{-}C}|$ = 7 Hz, meta), 127.93 (t, $|^{1}J_{P\text{-}C} + {}^{3}J_{P\text{-}C}|$ = 38 Hz, ipso), 129.12 (para), 130.59 (para), 130.94 (t, $|^{1}J_{P\text{-}C} + {}^{3}J_{P\text{-}C}|$ = 43 Hz, ipso), 133.46 (t, $|^{2}J_{P\text{-}C} + {}^{4}J_{P\text{-}C}|$ = 9 Hz, ortho), 137.80 (t, $|^{2}J_{P\text{-}C} + {}^{4}J_{P\text{-}C}|$ = 11 Hz, ortho). $^{31}P\{^{1}H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 25.11.

14 For the conformations in solution, see: (a) M. Sawamura, Y. Ito, T. Hayashi, *Tetrahedron Lett.* **31**, 2723 (1990). (b) A. Togni, S. D. Pastor, *J. Org. Chem.* **55**, 1649 (1990). (c) N. Deus, G. Hübener, R. Herrmann, *J. Organomet. Chem.* **384**, 155 (1990).

15 For the crystal structures, see: (a) T. Hayashi, M. Kumada, T. Higuchi, K. Hirotsu, *J. Organomet. Chem.* **334**, 195 (1987). (b) T. Hayashi, A. Yamamoto, Y. Ito, E. Nishioka, H. Miura, K. Yanagi, *J. Am. Chem. Soc.* **111**, 6301 (1989). (c) T. Hayashi, A. Yamamoto, M. Hojo, K. Kishi, Y. Ito, E. Nishioka, H. Miura, K. Yanagi, *J. Organomet. Chem.* **370**, 129 (1989).