Synthesis and molecular structure of a chiral ferrocenylphosphine

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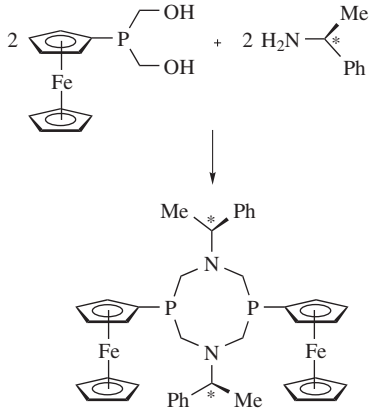
DOI: 10.1070/MC2005v015n03ABEH002119

The first chiral (aminomethyl)ferrocenylphosphine (*S*,*S*)-1,5-bis(α-methylbenzyl)-3,7-bisferrocenyl-1,5-diaza-3,7-diphosphacyclooctane was obtained *via* a condensation reaction of bis(hydroxymethyl)ferrocenylphosphine with chiral (*S*)-α-methylbenzylamine.

Ferrocenylphosphines are widely used ligands with applications ranging from catalysis to materials science.[1] Chiral ferrocenylphosphines[2] with inherent special electronic properties of the ferrocenyl fragment[3] are of paramount importance for asymmetric catalysis, which is one of the most interesting and challenging technologies.[4] A wide variety of planar chiral ferrocenylphosphines and/or ferrocenylphosphines that are chiral due to a stereogenic carbon centre have been reported, and their high effectivity in asymmetric catalysis was demonstrated.[2] However, the Mannich-type condensation of hydroxymethylphosphines with primary or secondary amines, which is a powerful method of constructing chiral tertiary phosphines with predicted properties,[5] has only recently been employed in ferrocenylphosphine chemistry.[6] Although the synthesis of bis(hydroxymethyl)ferrocenylphosphine was described,[7] there are only a few examples of aminomethyl(ferrocenyl)phosphines.[6] Here we report the synthesis and molecular structure of the first chiral heterocyclic bis(phosphine) containing two ferrocenylphosphino groups, namely, (*S*,*S*)-1,5-bis(α-methylbenzyl)-3,7-bisferrocenyl-1,5-diaza-3,7-diphosphacyclooctane **1**.



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Scheme 1

Optically active (*S*)-α-methylbenzylamine reacts with bis(hydroxymethyl)ferrocenylphosphine in a condensation reaction to give chiral (*S*,*S*)-1,5-bis(α-methylbenzyl)-3,7-bisferrocenyl-1,5-diaza-3,7-diphosphacyclooctane **1** in a good yield (Scheme 1).† Compound **1** is an air-stable yellow crystalline solid soluble in common organic solvents ($CHCl_3$, CH_2Cl_2), in contrast to 1,5-diaza-3,7-diphosphacyclooctanes described previously,[5(j)] due to the presence of the α-methylbenzyl substituents at the nitrogen atoms.[5(d)] The ^{31}P, ^1H NMR and elemental analysis data are in good agreement with the proposed structure.

As was observed before for 1,5-diaza-3,7-diphosphacyclooctanes with chiral exocyclic substituents,[5(d)] the ring methylene groups are inequivalent in the ^1H NMR spectrum of **1** due to the presence of asymmetric substituents at the 1- and 5-positions of the heterocycle. They are detected as two (AA′)X spin systems. The asymmetric substituents at the nitrogen atoms are equivalent.

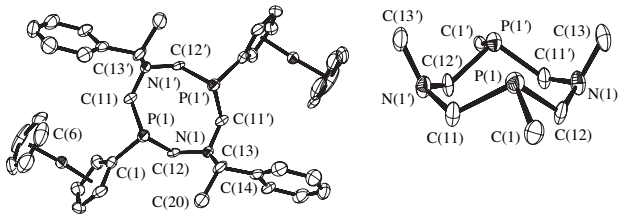

Figure 1 An ORTEP view of **1** (left) and the eight-membered central ring with *ipso*-C atoms (right). Hydrogen atoms are omitted for clarity; ellipsoids are shown with 50% probability. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.817(8), P(1)–C(11) 1.878(8), P(1)–C(12) 1.913(8); C(1)–P(1)–C(11) 98.4(4), C(1)–P(1)–C(12) 93.1(4), C(11)–P(1)–C(12) 101.2(4), C(11′)–N(1)–C(12) 112.6(6), C(11′)–N(1)–C(13) 113.6(7), C(12)–N(1)–C(13) 116.5(6), N(1′)–C(11)–P(1) 119.4(6), N(1)–C(12)–P(1) 119.7(6).

The protons of the CH and Me groups of the α-methylbenzyl moieties appear as a broad quartet and a doublet, respectively. The signals of the cyclopentadienyl rings are rather broad, as are the signals in the ^{31}P NMR spectrum, which could be due to the hindered rotation of the ferrocenyl groups around the P–C bonds.

X-ray crystallography‡ confirmed the formation of chiral (*S*,*S*)-1,5-bis(α-methylbenzyl)-3,7-bisferrocenyl-1,5-diaza-3,7-diphosphacyclooctane **1** (Figure 1). The molecule has a chair–chair conformation of the bis(phosphine) heterocycle with nearly parallel lone electron pairs at the phosphorus atoms (the P–P–lone pair angle is about 77.5°). The P···P distance of 3.54 Å is noticeably longer than those of similar heterocycles with phenyl substituents at the phosphorus atoms (P···P 3.128–3.279 Å).[5(d)] The increase in the P···P distance is explained by an increase of the endocyclic P–C–N bond angle from 116° in previously

† All manipulations were carried out using standard high-vacuum and dry-nitrogen techniques. NMR spectra: Avance DRX 400 (Bruker), standards: C_6H_6, TMS for ^1H NMR (400 MHz); external 85% H_3PO_4 for ^{31}P NMR (162 MHz). Specific rotation was determined on a Perkin–Elmer Model 341 polarimeter at 589 nm. Cyclic voltammograms were recorded at a glassy carbon electrode (working surface area of 3.14 mm^2) in a thermostatically controlled (20 °C) three-electrode electrochemical cell under an argon atmosphere in the presence of $(NBu_4)BF_4$ (0.1 M). Curves were recorded at a constant potential scan rate of 50 mV s^{-1}.

(S,S)-1,5-bis(α-methylbenzyl)-3,7-bisferrocenyl-1,5-diaza-3,7-diphosphacyclooctane **1**. A solution of bis(hydroxymethyl)ferrocenylphosphine (0.71 g, 2.6 mmol) and (*S*)-α-methylbenzylamine (0.31 g, 2.6 mmol) in 15 ml of ethanol was refluxed for 5 h. Yellow crystals were collected by filtration, washed with ethanol and dried in a vacuum. Yield 0.58 g (62%); mp 176–178 °C, $[\alpha] = -40.5$ (*c* 0.01, C_6H_6). ^1H NMR (C_6D_6) δ: 1.51 (d, 3H, Me, $^3J_{HH}$ 6.4 Hz), 3.37 (br. d, 1H, PCH_2^AN, $^2J_{HH}$ 13.2 Hz), 3.44 (br. d, 1H, PCH_2^AN, $^2J_{HH}$ 13.7 Hz), 3.71 (br. d, 1H, PCH_2^BN, $^2J_{HH}$ 13.2 Hz), 3.80 (br. d, 1H, PCH_2^BN, $^2J_{HH}$ 13.7 Hz), 3.91 (s, 5H, C_5H_5), 3.93 (br. s, 2H, C_5H_4), 4.01 (br. s, 2H, C_5H_4), 4.77 (br. q, 1H, C*H, $^3J_{HH}$ 6.4 Hz), 7.08 (br. t, 2H, *m*-H in Ph, $^3J_{HH}$ 7.3 Hz, $^3J_{HH}$ 6.8 Hz), 7.22 (br. t, 1H, *p*-H in Ph, $^3J_{HH}$ 6.8 Hz), 7.55 (br. d, 2H, *o*-H in Ph, $^3J_{HH}$ 7.3 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: –71.6 (br. s). Found (%): C, 65.7; H, 6.0; N, 3.6; P, 8.6%. Calc. for $C_{40}H_{44}Fe_2N_2P_2$ (726.41) (%): C, 66.11; H, 6.06; N, 3.86; P, 8.54.

described compounds[5(d)] to 120° in **1**. The lone electron pairs of the nitrogen atoms are situated in equatorial positions. Thus, in the conformation that exists in the solid state, the lone pairs of electrons of the phosphorus atoms are situated in positions suitable for coordination to soft transition metals in a chelating fashion (Figure 1).

In DMF, the ferrocenyl groups in **1** can be quasireversibly electrochemically oxidised [E_p^{ox} = +0.53 V (2.0 μA), E_p^{red} = = +0.30 V (1.3 μA), ref. $Ag/AgNO_3$, 0.01 M in MeCN] in the range characteristic of ferrocenylphosphines.[8] The observed two-electron process was the result of the consecutive oxidation and further reduction of the two ferrocenyl fragments of **1**.

The high solubility of **1** in organic solvents provides an opportunity to prepare chiral complexes of transition metals and catalysts, in which the donor ability of the phosphine can be determined electrochemically.

This work was supported by DFG-RFBR (grant nos. 436RUS113/724/0-1 and 03-03-04003, respectively) and the President of the Russian Federation (grant no. 1985.2003.3 for support of leading scientific schools). A. A. K. thanks the Russian Science support Foundation.

References

1 (*a*) K. S. Gan and T. S. A. Hor, in *Ferrocenes. Homogeneous Catalysis, Organic Synthesis and Material Science*, eds. A. Togni and T. Hayashi, VCH, Weinheim, 1995, Ch. 1 and references therein; (*b*) I. R. Butler, M. G. B. Drew, A. G. Caballero, P. Gerner and C. H. Greenwell, *J. Organomet. Chem*., 2003, **679**, 59.

2 (*a*) S.-L. You, X.-L. Hou and L.-X. Dai, *J. Organomet. Chem*., 2001, **637–639**, 762; (*b*) G. Argouarch, O. Samuel, O. Riant, J.-C. Daran and H. B. Kagan, *Eur. J. Org. Chem*., 2000, 2893.

3 (*a*) *Ferrocenes. Homogeneous Catalysis, Organic Synthesis and Material Science*, eds. T. Hayashi and A. Togni, VCH, Weinheim, Germany, 1995; (*b*) C. J. Richards and A. J. Locke, *Tetrahedron: Asymmetry*, 1998, **9**, 2377.

4 (*a*) R. Noyori and M. Kitamamura, in *Modern Synthetic Methods*, ed. R. Scheffold, Springer, Berlin, 1989, p. 155; (*b*) I. Ojima, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, VCH, New York, 1993; (*c*) J. Seyden-Penne, in *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*, ed. J. Seyden-Penne, Wiley, New York, 1995.

5 (*a*) C. R. Landis, W. Jin, J. S. Owen and T. P. Clark, *Angew. Chem., Int. Ed. Engl*., 2001, **40**, 3432; (*b*) A. A. Karasik, I. O. Georgiev, R. I. Vasiliev and O. G. Sinyashin, *Mendeleev Commun*., 1998, 140; (*c*) D. E. Berning, K. V. Katti, C. L. Barnes and W. A. Volkert, *J. Am. Chem. Soc*., 1999, **121**, 1658; (*d*) A. A. Karasik, R. N. Naumov, O. G. Sinyashin, G. P. Belov, H. V. Novikova, P. Lönnecke and E. Hey-Hawkins, *Dalton Trans*., 2003, 2209; (*e*) P. A. T. Hoye, R. D. W. Kemmitt and D. L. Law, *Appl. Organomet. Chem*., 1993, **7**, 513; (*f*) K. Raghuraman, K. K. Katti, L. J. Barbour, N. Pillarsetty, C. L. Barnes and K. V. Katti, *J. Am. Chem. Soc*., 2003, **125**, 6955; (*g*) M.-L. Lartigue, A.-M. Caminade and J. P. Majoral, *Tetrahedron: Asymmetry*, 1997, **8**, 2697; (*h*) T. Novak, P. Bako, G. Keglevich, A. Dobo, K. Vekey and L. Toke, *J. Inclusion Phenom. Macrocycl. Chem*., 2001, **40**, 207; (*i*) M. T. Reetz and C. Frombgen, *Synthesis*, 1999, 1555; (*j*) B. A. Arbuzov and G. N. Nikonov, *Adv. Heterocycl. Chem*., 1994, **61**, 60.

6 A. A. Karasik, R. N. Naumov, R. Sommer, O. G. Sinyashin and E. Hey-Hawkins, *Polyhedron*, 2002, **2**, 2251.

7 (*a*) W. Henderson and S. R. Alley, *J. Organomet. Chem*., 2002, **658**, 181; (*b*) S. R. Alley and W. Henderson, *Inorg. Chem. Commun*., 2001, **4**, 741.

8 (*a*) A. J. Downard, N. J. Goodwin and W. Henderson, *J. Organomet. Chem*., 2003, **676**, 62; (*b*) E. M. Barranco, O. Crespo, M. C. Gimeno, A. Laguna, P. G. Jones and B. Ahrens, *Inorg. Chem*., 2000, **39**, 680; (*c*) R. D. Eagling, J. E. Bateman, N. J. Goodwin, W. Henderson, B. R. Horrocks and A. Houlton, *J. Chem. Soc., Dalton Trans*., 1998, 1273.

9 G. M. Sheldrick, *SADABS, Program for Scaling and Correction of Area-Detector Data*, Göttingen, 1997.

10 G. M. Sheldrick, *SHELXS97 and SHELXL97 – Programs for Crystal Structure Analysis*, University of Göttingen, 1998.

‡ *Crystallographic data for* **1**: $C_{40}H_{44}Fe_2N_2P_2$, M = 726.41, at 210 K, monoclinic, space group $C2$, a = 20.073(4), b = 5.7144(10) and c = = 15.455(3) Å, β = 99.062(6)°, V = 1750.7(6) Å^3, Z = 2, d_{calc} = 1.378 g cm^{-3}, μ(MoKα) = 0.951 mm^{-1}, collected 3415 reflections, 2333 independent reflections (R_{int} = 0.0445), final R indices [$I > 2\sigma(I)$]: R_1 = 0.0550, wR_2 = 0.1355; absolute structure parameter 0.04(5).

X-ray diffraction data were collected on a Siemens SMART CCD diffractometer (MoKα radiation; λ = 71.073 pm). Absorption correction was performed with the SADABS program.[9] The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically (SHELXL97).[10]

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 259723. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

Received: 12th January 2005; Com. 05/2442