Chiral diiminophosphoranes: a new class of ligands for enantioselective transition metal catalysis

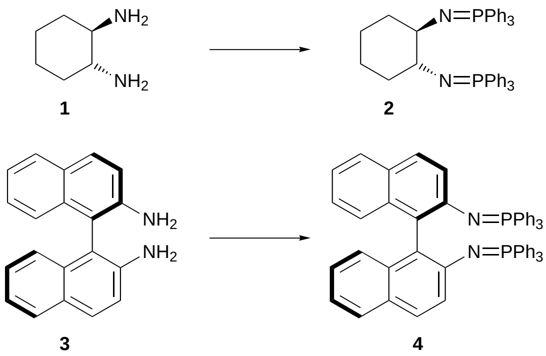
Manfred T. Reetz,*† Edward Bohres and Richard Goddard

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim/Ruhr, Germany

Chiral diamines such as (1*R*,2*R*)-1,2-diaminocyclohexane or *R*-2,2′-diamino-1,1′-binaphthalene can be converted into the corresponding diimino(triphenyl)phosphoranes, which serve as C_2-symmetric ligands for enantioselective transition metal catalyzed reactions such as copper-mediated cyclopropanations.

Chiral nitrogen-containing compounds are gaining increasing importance as ligands in enantioselective transition metal catalyzed reactions.[1] Although iminophosphoranes[2] of the general structure $R_3P{=}NR'$ possess a donor position at the nitrogen function capable of metal complexation,[3] chiral versions have not been prepared to date. Since iminophosphoranes are readily available from the corresponding primary amines $R'NH_2$, we envisioned a simple route to chiral chelating diiminophosphoranes and their possible use as ligands in enantioselective transition metal catalyzed reactions. Here we report the first examples of this concept.

Upon reacting the commercially available diamines **1** and **3** with Ph_3PBr_2 followed by base treatment according to a literature procedure (modified by working in the presence of molecular sieves),[4] compounds **2** and **4** were obtained in yields of 82 and 75%, respectively.



Scheme 1

Ligands **2** and **4** are crystalline compounds, which were characterized by standard methods, including ^{31}P NMR spectroscopy (δ −0.5 and −4.6, respectively, in CD_2Cl_2) and X-ray crystallography‡ (Fig. 1). The effect of the crystal environment appears to have a more significant effect on **2** than **4**, since whereas **4** exhibits exact C_2 symmetry in the crystal [N···N* 3.617(8) Å], even in spite of the presence of solvent of crystallization, in **2** the local C_2 symmetry is restricted to the cyclohexane ring and the two nitrogen atoms [N(1)···N(2) 3.770(2) Å].

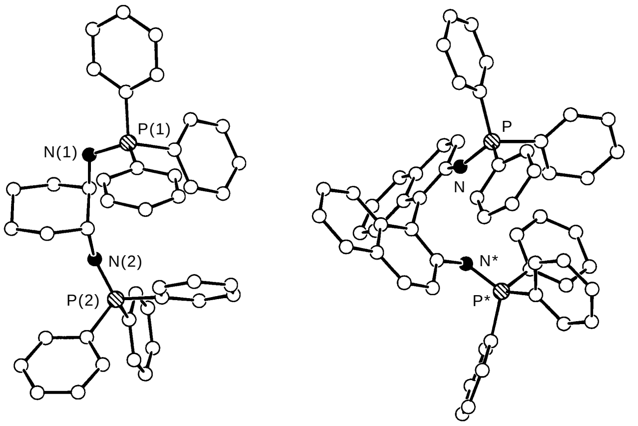


Fig. 1 Molecular structures of **2** (left) and **4** (in **4** the CD_2Cl_2 solvent of crystallization has been removed for clarity)

These two chiral ligands are suitable for preparing a wide variety of new types of transition metal complexes. Indeed, the complexes **2**·Rh(cod)BF_4, **2**·$CoCl_2$ and **4**·CuOTf were readily synthesized in yields of *ca.* 80% by reacting the corresponding ligands with $[RhCl_2(cod)]_2$ (followed by $NaBF_4$), $CoCl_2(thf)_x$ or CuOTf, as appropriate. The crystal structures of **2**·Rh(cod)BF_4 and **2**·$CoCl_2$ confirm the flexibility of the diimino(triphenyl)phosphorane ligand (Fig. 2). Thus, whereas the iminophosphorane groups in the free ligand (**2**) occupy diaxial positions, in the complexed ligand both groups are equatorial, presumably enabling the N atoms to accommodate the metals [**2**·Rh(cod)BF_4 N···N 2.665(6) Å, N–Rh–N 77.3(3)°; **2**·$CoCl_2$ N···N 2.75(2) Å, N–Co–N 85.6(6)°]. In addition, the extent of the C_2 symmetry induced by the ligand strongly depends on the coordination sphere of the metal. In **2**·Rh(cod)BF_4 the approximately square-planar coordinated Rh atom deviates strongly (2.818 Å) from the local C_2 symmetry of the iminocyclohexane ring (dashed line, Fig. 2, left). In **2**·$CoCl_2$, on the other hand, the loss of symmetry is much smaller and distorted tetrahedral Co lies approximately (±0.2 Å) on the local C_2 axis of symmetry (dashed line, Fig. 2, right).

Preliminary studies using these chiral metal complexes for enantioselective catalysis have also been undertaken. Particularly worthy of note is the copper catalyzed cyclopropanation[5] of styrene **5** by ethyl diazoacetate **6** using the complex **4**·CuOTf (1.5 mol%) as the catalyst (Scheme 2). Adducts **7** and **8** were

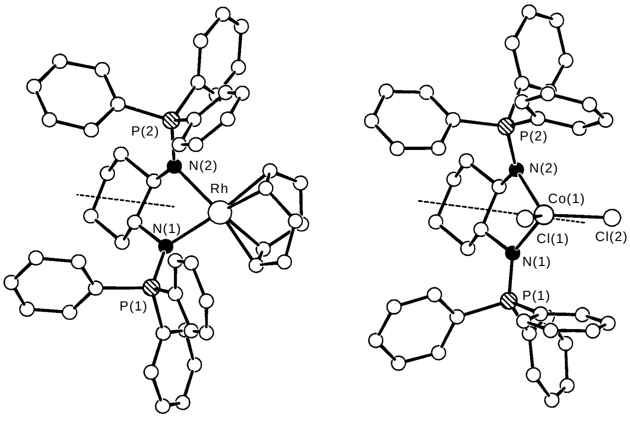
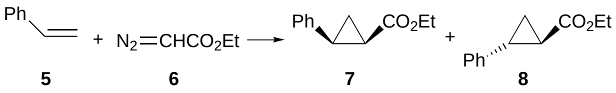


Fig. 2 Molecular structures of the $[\mathbf{2}\cdot Rh(cod)]^+$ cation in **2**·Rh(cod)BF_4 (left) and **2**·$CoCl_2$. Dashed lines indicate local C_2 symmetry.



Scheme 2

formed in equal amounts, each having an enantiomeric excess (ee) of 90 and 74% in favour of the absolute configurations (*S*,*R*) and (*R*,*R*), respectively.§

In summary, we have developed a new and readily accessible class of chiral nitrogen containing ligands for asymmetric transition metal catalysis. The possibility of varying the substituents of phosphorus and/or utilizing other chiral diamines or functionalized amines is currently being explored.

Notes and References

† E-mail: reetz@mpi-muelheim.mpg.de

‡ *Crystal data*: **2**: $C_{42}H_{40}N_2P_2$, $M_r = 634.7$, colourless plate, crystal size $0.32 \times 0.60 \times 0.88$ mm, $a = 11.3778(2)$, $b = 8.7847(2)$, $c = 17.5062(3)$ Å, $\beta = 103.296(1)°$, $U = 1702.85(6)$ Å^3, $T = 100$ K, monoclinic, space group $P2_1$ (no. 4), $Z = 2$, $D_c = 1.24$ g cm^{-3}, $\mu = 0.16$ mm^{-1}. Siemens SMART diffractometer, Mo-Kα X-radiation, $\lambda = 0.71073$ Å. 19124 measured reflections, 9573 unique, 9288 observed [$I > 2.0\sigma(F_o^2)$]. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least squares (SHELXL-97) on F^2 for all data with Chebyshev weights to $R = 0.059$ (obs.), $wR = 0.160$ (all data), $S = 1.05$, H atoms riding, max. shift/error 0.001, residual $\rho_{max} = 0.968$ e Å^{-3}.

4·CD_2Cl_2: $C_{57}H_{42}Cl_2D_2N_2P_2$: $M_r = 889.8$, yellow prism, crystal size $0.28 \times 0.39 \times 0.46$ mm, $a = 10.703(1)$, $b = 18.868(2)$, $c = 22.522(2)$ Å, $U = 4547.9(8)$ Å^3, $T = 100$ K, orthorhombic, space group $C222_1$ (no. 20), $Z = 4$, $D_c = 1.30$ g cm^{-3}, $\mu = 0.26$ mm^{-1}. Enraf-Nonius CAD4 diffractometer, Mo-Kα X-radiation, $\lambda = 0.71069$ Å. 2568 measured reflections, 2051 observed [$I > 2.0\sigma(F_o^2)$]. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least squares (SHELXL-97) on F^2 for all data with Chebyshev weights to $R = 0.074$ (obs.), $wR = 0.231$ (all data), $S = 1.04$, H atoms riding, solvent CD_2Cl_2 disordered over two positions, max. shift/error 0.001, residual $\rho_{max} = 0.633$ e Å^{-3}.

2·Rh(cod)BF_4: $C_{50}H_{52}BF_4N_2P_2Rh$, $M_r = 932.6$, orange prism, crystal size $0.35 \times 0.52 \times 0.59$ mm, $a = 13.732(2)$, $b = 16.915(2)$, $c = 19.222(3)$ Å, $U = 4465(1)$ Å^3, $T = 293$ K, orthorhombic, space group $P2_12_12_1$ (no. 19), $Z = 4$, $D_c = 1.39$ g cm^{-3}, $\mu = 0.51$ mm^{-1}. Enraf-Nonius CAD4 diffractometer, Mo-Kα X-radiation, $\lambda = 0.71069$ Å. 5746 measured reflections, 5619 unique, 5114 observed [$I > 2.0\sigma(F_o^2)$]. Analytical absorption correction (T_{min} 0.7769, T_{max} 0.9805). The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least squares (SHELXL-97) on F^2 for all data with Chebyshev weights to $R = 0.059$ (obs.), $wR = 0.151$ (all data), $S = 1.03$, H atoms riding, max shift/error 0.001, residual $\rho_{max} = 1.681$ e Å^{-3}.

2·$CoCl_2$·$3CH_2Cl_2$: $C_{45}H_{46}Cl_8CoN_2P_2$, $M_r = 1019.3$, blue prism, crystal size $0.35 \times 0.42 \times 0.62$ mm, $a = 24.447(1)$, $b = 9.8142(4)$, $c = 40.257(2)$ Å, $\beta = 99.710(2)°$, $U = 9520.1(8)$ Å^3, $T = 100$ K, monoclinic, space group $C2$ (no. 5), $Z = 8$, $D_c = 1.42$ g cm^{-3}, $\mu = 0.91$ mm^{-1}. Siemens SMART diffractometer, Mo-Kα X-radiation, $\lambda = 0.71073$ Å. 48840 measured reflections, spherical absorption correction, 20400 unique, 13253 observed [$I > 2.0\sigma(F_o^2)$]. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least squares (SHELXL-97) on F^2 for all data (Co, Cl, P anisotropic) with Chebyshev weights to $R = 0.086$ (obs.), $wR = 0.199$ (all data), $S = 1.07$, H atoms riding, max. shift/error 0.001, residual $\rho_{max} = 0.998$ e Å^{-3}. CCDC 182/796.

§ *Procedure*: a catalyst solution of **4**·CuOTf was prepared by mixing 1 equiv. of a copper(I) triflate benzene complex with 1.2 equiv. of ligand **4** in dry CH_2Cl_2 under an atmosphere of argon. A Schlenk tube was charged with 1.0 ml of a 0.015 M catalyst solution, freed from the solvent *in vacuo* and charged with styrene (1.0 ml of a 1.0 M solution in 1,2-dichloroethane). The mixture was cooled to −20 °C and treated with **6** (3 mmol in 3 ml of 1,2-dichloroethane) within 3 h using a syringe pump. The mixture was analyzed by GC (80% conversion).

1 A. Togni and L. M. Venanzi, *Angew. Chem.*, 1994, **106**, 517; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 497; A. Pfaltz, *Acc. Chem. Res.*, 1993, **26**, 339.
2 A. W. Johnson and W. C. Kaska, *Ylides and Imines of Phosphorus*, Wiley, New York, 1993.
3 E. W. Abel and S. A. Mucklejohn, *Inorg. Chim. Acta*, 1979, **37**, 107; P. Imhoff, C. J. Elsevier and C. H. Stam, *Inorg. Chim. Acta*, 1990, **175**, 209; R. W. Reed, B. Santarsiero and R. G. Cavell, *Inorg. Chem.*, 1996, **35**, 4292; R. Appel and P. Volz, *Z. Anorg. Allg. Chem.*, 1975, **413**, 45.
4 K.-W. Lee and L. A. Singer, *J. Org. Chem.*, 1974, **39**, 3780.
5 Recent review: V. K. Singh, A. DattaGupta and G. Sekar, *Synthesis*, 1997, 137.

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