DALTON
COMMUNICATION

Completely stereoselective synthesis of a chiral tetra(tertiary phosphine). Crystal and molecular structure of [*OC*-6-22-(*R**,*R**)]-(±)-dichloro{1,2-bis[(2-dimethylphosphinophenyl)methylphosphino]benzene-*P*,*P*′,*P*″,*P*‴}cobalt(III) hexafluorophosphate †

Swarup Chatterjee,[a] Roy Doyle,[a] David C. R. Hockless,[b] Geoffrey Salem *[a] and Anthony C. Willis[b]

[a] *Chemistry Department, The Faculties, Australian National University, Canberra, A. C. T. 0200, Australia. E-mail: Geoff.Salem@anu.edu.au*
[b] *Research School of Chemistry, Australian National University, Canberra, A. C. T. 0200, Australia*

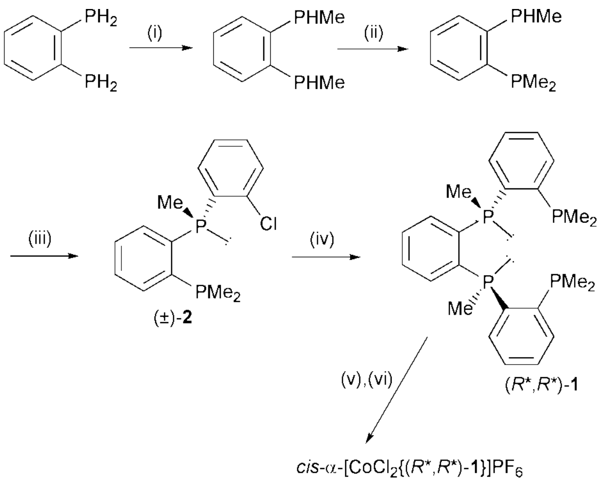
Received 4th March 2000, Accepted 11th May 2000
Published on the Web 26th May 2000

Reaction of (±)-(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine with sodium (2-dimethylphosphinophenyl)methylphosphide is completely stereoselective giving (*R,*R**)-1,2-bis[(2-dimethylphosphinophenyl)methylphosphino]benzene, (*R**,*R**)-1; as confirmed by a crystal structure determination of *cis*-α-[CoCl$_2${(*R**,*R**)-1}]PF$_6$.**

Following the reported preparation of tris(2-diphenylphosphinophenyl)phosphine in 1963,[1] a variety of tetra(tertiary phosphines) have been synthesised and utilised as ligands in coordination chemistry.[2] Of particular relevance to the current work are the linear tetradentate phosphines, of which 1,2-bis{(diphenylphosphinoethyl)phenylphosphino}ethane, tetraphos,[3] is arguably the best known example. Several examples of ligands of this type have been reported in the literature in which the four phosphorus centres are linked by one or more methylene groups.[2] Furthermore, they typically contain two stereogenic donor atoms (the terminal phosphorus donor atoms are non-stereogenic) and hence exist in racemic and *meso* diastereomeric forms. The two diastereomers have been separated for certain of these linear tetradentate phosphines, including tetraphos. In addition, the (*R**,*R**) form of tetraphos has been successfully resolved by the method of metal complexation.[4] To date, however, there has been no report of a stereoselective synthesis of a linear tetra(tertiary phosphine). This is an important consideration if ligands of this type are to be investigated as potential chiral auxiliaries in asymmetric synthesis.

In this communication, we report on the completely stereoselective synthesis of the dissymmetric tetra(tertiary phosphine) (*R**,*R**)-1,2-bis[(2-dimethylphosphinophenyl)methylphosphino]benzene, (*R**,*R**)-**1**. An essential feature of the ligand is the presence of three 1,2-phenylene linkages. Their presence is not only responsible for the high stereoselectivity observed in the synthesis of (*R**,*R**)-**1** but also for the exclusive formation of the *cis*-α diastereomer on complexation of the tetra(tertiary phosphine) to cobalt(III).

The basic strategy behind the synthesis of (*R**,*R**)-**1** involved the coupling of two suitably designed bidentate ligands, (±)-(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine, (±)-**2**, and sodium (2-dimethylphosphinophenyl)methylphosphide (Scheme 1). This approach was taken for two reasons: firstly, the coupling of appropriately designed optically active bidentate ligands could provide a general synthetic route to optically active quadridentate ligands; and secondly, the resolution of chiral bidentate ligands *via* the method of metal complexation is particularly well established.[5] We have previously demonstrated the appropriateness of this approach in the stereoselective synthesis of a related chiral quadridentate ligand with As$_2$NP donor atoms, *viz.* (*R**,*S**)-(±)-1-[(2-dimethylarsinophenyl)methylarsino]-2-[(2-aminophenyl)methylphosphino]benzene.[6,7]



Scheme 1 Only one of the enantiomers of (*R**,*R**)-**1** and (±)-**2** is depicted. *Reagents and conditions*: (i) 2 Bu^{n}Li, THF; 2 MeI, THF; (ii) K, NH$_{3(l)}$; MeI, THF; (iii), Na, THF; 1,2-dichlorobenzene, THF; (iv), sodium (2-dimethylphosphinophenyl)methylphosphide, THF; (v), [Co(H$_2$O)$_6$]Cl$_2$, MeOH, air; (vi), MeOH, NH$_4$PF$_6$ in water.

Compound (±)-**2** was prepared *via* stepwise alkylation of 1,2-phenylenebis(phosphine)[8] (Scheme 1). Deprotonation of the bis(primary phosphine) by reaction with two equivalents of *n*-butyllithium in THF followed by the addition of a solution of methyl iodide in the same solvent gave (*R**,*R**)- and (*R**,*S**)-1,2-phenylenebis(methylphosphine) in high yield.[8] Monodeprotonation of the bis(secondary phosphine) was achieved using potassium in liquid ammonia and gave a *ca.* 4:1 mixture of (±)-(2-dimethylphosphinophenyl)methylphosphine and 1,2-phenylenebis(dimethylphosphine), **3**, upon the addition of methyl iodide. Subsequent reaction of the *ca.* 4:1 mixture with sodium in THF followed by the addition of 1,2-dichloro-

---

† Electronic supplementary information (ESI) available: experimental and spectroscopic data for (±)-(2-dimethylphosphinophenyl)methylphosphine, (±)-**2**, **3**, *cis*-(±)-[CoCl$_2${(*R**,*R**)-**1**}]PF$_6$ and *trans*-[CoCl$_2$(**3**)$_2$]Cl. See http://www.rsc.org/suppdata/dt/b0/b002662j/

DOI: 10.1039/b002662j

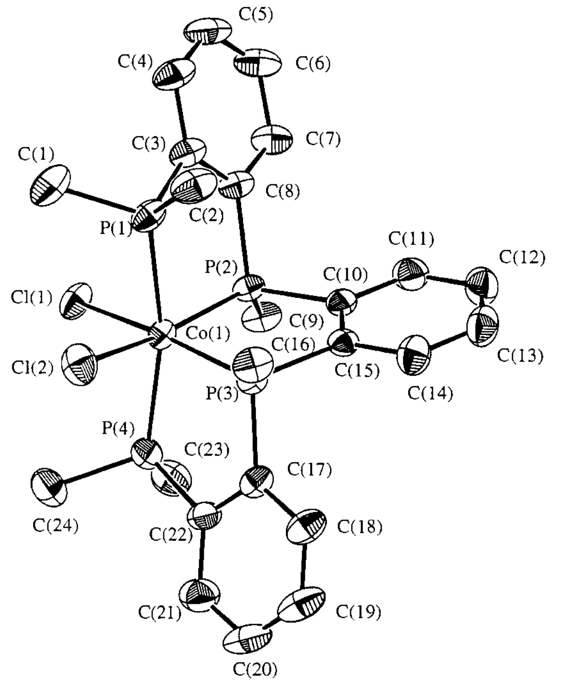


Fig. 1 Molecular structure of the cation *cis*-α-$[CoCl_2\{(R^*,R^*)\text{-}\mathbf{1}\}]^+$. Selected bond distances and angles are as follows: Co–P(1) 2.243(2), Co–P(2) 2.176(2), Co–P(3) 2.173(2), Co–P(4) 2.248(2), Co–Cl(1) 2.314(2), Co–Cl(2) 2.270(2) Å; P(1)–Co–P(2) 85.73(6), P(1)–Co–Cl(2) 84.46(7), P(2)–Co–Cl(2) 168.18(7), P(2)–Co–P(4) 104.00(6), Cl(1)–Co–P(3) 168.88(6), P(3)–Co–P(4) 86.95(6), P(1)–Co–Cl(1) 86.88(6), P(1)–Co–P(3) 102.34(7), P(2)–Co–P(3) 88.12(6), Cl(1)–Co–Cl(2) 99.65(7), Cl(1)–Co–P(4) 85.03(6) and Cl(2)–Co–P(4) 86.74(7)°.

benzene gave (±)-**2** and unreacted **3**, which were separated by fractional distillation.

The product, (R^*,R^*)-**1**, from the reaction of (±)-**2** with sodium (2-dimethylphosphinophenyl)methylphosphide (containing **3**) in THF was separated from **3** by complexation to cobalt(III). Two complexes were isolated containing these tertiary phosphines, *viz*. *cis*-α-$[CoCl_2\{(R^*,R^*)\text{-}\mathbf{1}\}]Cl$ and *trans*-$[CoCl_2(\mathbf{3})_2]Cl$. The former was converted to the corresponding hexafluorophosphate salt by metathesis with an aqueous solution of NH_4PF_6 and its structure has been confirmed by an X-ray crystallographic analysis (Fig. 1).‡ The complex is a racemic compound with the Δ-(S,S) and Λ-(R,R) forms of the cation being present in the unit cell (only the former is shown in Fig. 1). It is clear from the structural data that the *cis*-α diastereomer is formed exclusively and that both stereogenic atoms of the quadridentate ligand have the same relative configurations.

Resolution of (±)-**2** *via* the metal complexation method is currently in progress. The optically active bidentate (R)-**2** [or (S)-**2**] should again react with sodium (2-dimethylphosphino phenyl)methylphosphide in a completely stereoselective manner to give (R,R)-**1** [or (S,S)-**1**]. A stereoselective route to chiral tetra(tertiary phosphines) which form *cis*-α complexes exclusively on coordination to a transition metal ion has important implications in asymmetric synthesis.

Acknowledgements

The authors gratefully acknowledge the financial support of this project by the Australian Research Council.

Notes and references

‡ Crystal data for *cis*-α-$[CoCl_2\{(R^*,R^*)\text{-}\mathbf{1}\}]PF_6$: $C_{24}H_{30}F_6Cl_2CoP_5$, $M = 717.20$, monoclinic, space group $P2_1/a$ (no. 14), $a = 12.630(4)$, $b = 19.034(4)$, $c = 12.745(4)$ Å, $\beta = 95.75(2)°$, $U = 3048(1)$ Å^3, $T = 23$ °C, $D_c = 1.563$ g cm^{-3} for $Z = 4$, $F(000) = 1456$, μ(Mo-Kα) = 10.47 cm^{-1}. Of 5846 measured intensities, 5582 were considered observed [$I > 3\sigma(I)$]. After correction for Lorentz and polarisation effects, the structure was solved by direct methods and expanded using Fourier techniques. Subsequent refinement (full-matrix least squares) afforded R and Rw values of 0.045 and 0.046, respectively. CCDC reference number 186/1979. See http://www.rsc.org/suppdata/dt/b0/b002662j/ for crystallographic files in .cif format.

1 J. G. Hartley, L. M. Venanzi and D. C. Goodall, *J. Chem. Soc.*, 1963, 3930.

2 F. A. Cotton and B. Hong, *Prog. Inorg. Chem.*, 1992, **40**, 179, and references therein. For more recent examples see: H. Schmidbaur, S. Manhart and A. Schier, *Chem. Ber.*, 1993, **126**, 2389; N. Bampos, L. D. Field, B. A. Messerle and R. J. Smernik, *Inorg. Chem.*, 1993, **32**, 4084; A. A. Barney, P. E. Fanwick and C. P. Kubiak, *Organometallics*, 1997, **16**, 1793.

3 R. B. King and P. N. Kapoor, *J. Am. Chem. Soc.*, 1971, **93**, 4158.

4 A. L. Airey, G. F. Swiegers, A. C. Willis and S. B. Wild, *J. Chem. Soc., Chem. Commun.*, 1995, 693; A. L. Airey, G. F. Swiegers, A. C. Willis and S. B. Wild, *Inorg. Chem.*, 1997, **36**, 1588.

5 R. J. Doyle, G. Salem and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1995, 1867; J. Leitch, G. Salem and D. C. R. Hockless, *J. Chem. Soc., Dalton Trans.*, 1995, 649; C. E. Barclay, G. Deeble, R. J. Doyle, S. A. Elix, G. Salem, T. L. Jones, S. B. Wild and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1995, 57; S. B. Wild, *Coord. Chem. Rev.*, 1997, **166**, 291.

6 R. J. Doyle, G. Salem and A. C. Willis, *J. Chem. Soc., Chem. Commun.*, 1994, 1587.

7 R. J. Doyle, G. Salem and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1997, 2713.

8 E. P. Kyba, M. C. Kerby and S. P. Rines, *Organometallics*, 1983, **2**, 1877.