

A New Route to Chiral Bis-tertiary Phosphine Ligands: Synthesis, Resolution, and Crystal Structure of *trans*-Bis-1,2-(diphenylphosphino)-cyclopentane and the Nickel Adduct $\text{NiBr}_2[\textit{trans}\text{-}1,2\text{-(PPh}_2)_2\text{C}_5\text{H}_8]$

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Heating of white phosphorus, phosphorus trichloride, and cyclopentene at 220 °C gives *trans*-1,2-bis(dichlorophosphino)cyclopentane (**1**), which with phenylmagnesium bromide gives *trans*-1,2-bis(diphenylphosphino)-cyclopentane (dpcp) (**2**); compound (**2**) forms the adduct $\text{Ni}(\text{dpcp})\text{Br}_2 \cdot \text{CH}_2\text{Cl}_2$, which readily crystallises as a conglomerate and the pure enantiomers may be separated by hand allowing resolution of (**2**), and catalytic hydrogenation of methyl(*N*-benzoyl)dehydrophenylalanine using resolved (**2**) and a rhodium catalyst gave a hydrogenated product of 100% optical purity.

The useful precursor, $\text{Cl}_2\text{PCH}_2\text{CH}_2\text{PCl}_2$, for chelating bis-tertiary phosphines is readily prepared from ethylene, white phosphorus, and phosphorus trichloride.^{1,2} We were interested in preparing chiral tertiary phosphines of the class *trans*-1,2-(R_2P)₂cyclopentane in view of their potential application in asymmetric synthesis. Therefore, we treated cyclopentene with white phosphorus and phosphorus trichloride in a steel autoclave at 220 °C. Careful distillation of the reaction mixture gave a small yield of the more volatile $\text{PCl}_2(\text{C}_5\text{H}_9)$ and the major product was the desired *trans*-1,2-bis(dichlorophosphino)cyclopentane (**1**). In a typical reaction PCl_3 (340 cm³), P_4 (29 g), and cyclopentene (180 g) were heated in a steel autoclave at 215 °C for 40 h and distillation of the products gave 109.2 g of (**1**) (b.p. 103–105 °C at 0.1 mmHg) as a colourless liquid.[†]

The n.m.r. data unambiguously showed (**1**) to be the *trans*-isomer and there was only a trace (<5%) of bands assignable to the *cis*-isomer. Treatment of (**1**) with phenylmagnesium bromide in tetrahydrofuran gave the tetraphenyl derivative (\pm)-*trans*-1,2-bis(diphenylphosphino)cyclopentane (dpcp) (**2**) in 77% yield as white crystals. The crystal structure of (**2**) has been determined.

Crystal data for (2): $\text{C}_{20}\text{H}_{28}\text{P}_2$, $M = 438$, triclinic, space group $P\bar{1}$, $a = 10.325(3)$, $b = 14.368(5)$, $c = 17.817(4)$ Å, $\alpha = 110.465(2)^\circ$, $\beta = 92.983(3)^\circ$, $\gamma = 99.786(3)^\circ$, $U = 2422$ Å³, $Z = 4$, $D_c = 1.20$ g cm⁻³. Intensities of 10 162 reflections were measured ($2\theta_{\text{max}} = 56^\circ$) on a CAD-4 diffractometer using graphite-monochromated Mo- K_α radiation. 6355 Independent reflections [$I > 3\sigma(I)$], uncorrected for absorption [$\mu(\text{Mo-}K_\alpha) = 1.97$ cm⁻¹], were used in the refinement. The structure was solved using a combination of direct methods (MULTAN-80) and Fourier synthesis. It was refined using a cascade approach to the large-block approximation to the normal matrix. All

non-hydrogen atoms were refined anisotropically, and hydrogen atoms were then placed geometrically ($\text{C-H} = 1.0$ Å). The final R -value is 0.039 ($R_w = 0.044$).[‡]

Treatment of (**1**) with RMgBr ($\text{R} = \text{methyl or cyclohexyl}$) gives the corresponding derivatives *trans*-1,2-(R_2P)₂ C_5H_8 .

Treatment of (**2**) in ethanol–water (95:5) with nickel(II) bromide gave a red adduct which crystallised readily from dichloromethane with one molecule of solvent of crystallisation as the compound $\text{NiBr}_2(\text{dpcp}) \cdot \text{CH}_2\text{Cl}_2$ (**3**), whose crystal structure has been determined.

Crystal data for (3): $\text{C}_{20}\text{H}_{28}\text{Br}_2\text{NiP}_2 \cdot \text{CH}_2\text{Cl}_2$, $M = 741.9$, monoclinic, space group $P2_1$, $a = 8.612(2)$, $b = 14.996(4)$, $c = 11.819(2)$ Å, $\beta = 97.616(2)^\circ$, $U = 1513$ Å³, $Z = 2$, $D_c = 1.63$ g cm⁻³. Intensities of 7734 reflections were measured ($2\theta_{\text{max}} = 54^\circ$) on a CAD-4 diffractometer using graphite-monochromated Mo- K_α radiation. 4268 Independent reflections [$I > 3\sigma(I)$], corrected for absorption [$\mu(\text{Mo-}K_\alpha) = 37.4$ cm⁻¹], were used in the refinement. The structure was solved using a combination of direct methods (MULTAN-80) and Fourier synthesis. It was refined using the large-block approximation to the normal matrix. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were then placed geometrically ($\text{C-H} = 1.0$ Å). The polarity of the structure was determined by refining a 'Polarity Factor'.³ The

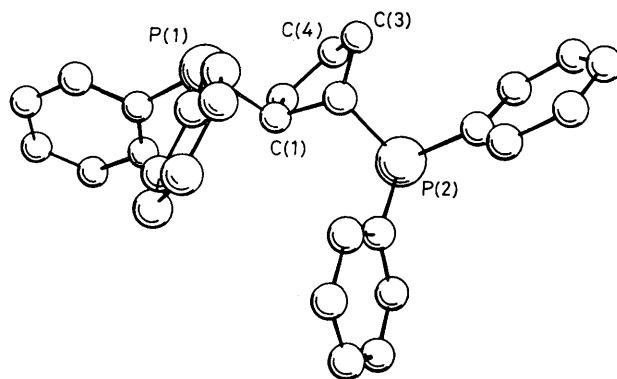
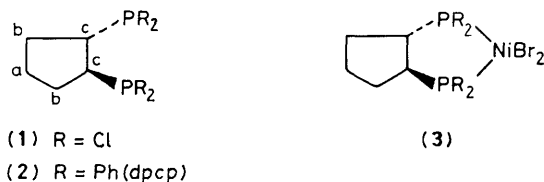


Figure 1. Crystal structure of (**2**) with the phenyl hydrogen atoms omitted for clarity. Selected distances and angles are: $\text{C}(1)\text{--P}(1)$ 1.858(2), $\text{C}(2)\text{--P}(2)$ 1.867(2), $\text{C}(1)\text{--C}(2)$ 1.544(3) Å; $\text{P}(1)\text{--C}(1)\text{--C}(2)$ 109.8(1), $\text{P}(2)\text{--C}(2)\text{--C}(1)$ 109.2(2), $\text{C}(3)\text{--C}(2)\text{--C}(1)$ 102.9(2), $\text{C}(2)\text{--C}(1)\text{--C}(5)$ 103.7(2)°. The configuration is (*S,S*).

[†] N.m.r. data for (**1**) in C_6D_6 with coupling constants in Hz: ^1H , δ 1.46 (2H, binomial quintet, $J_{\text{ca}} 7, 2 \times \text{H}^a$), 1.78 (4H, apparent 1:3:4:4:3:1 sextet, $J 7, J_{\text{PH}} 13, 4 \times \text{H}^b$), and 2.48 (2H, 22-line m, $J 6.2$ and $7.1, J_{\text{PH}} 20.0, 2 \times \text{H}^c$); ^{13}C , broad-band proton-decoupled [with proton-coupled multiplicity and coupling constants in square brackets], δ 26.94 (1C, s [t, $J_{\text{CH}} 97.3$], C^a), 29.54 (2C, d, $J_{\text{PC}} 13.5$ [d of t, $J_{\text{CH}} 104.2, J_{\text{PC}} 13.5$], $2 \times \text{C}^b$), and 50.54 p.p.m. (2C, dd, $J_{\text{PC}} 50.9$ and 12.4 [d of d of d, $J_{\text{CH}} 103.8, J_{\text{PC}} 50.9$ and 12.4], $2 \times \text{C}^c$).

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

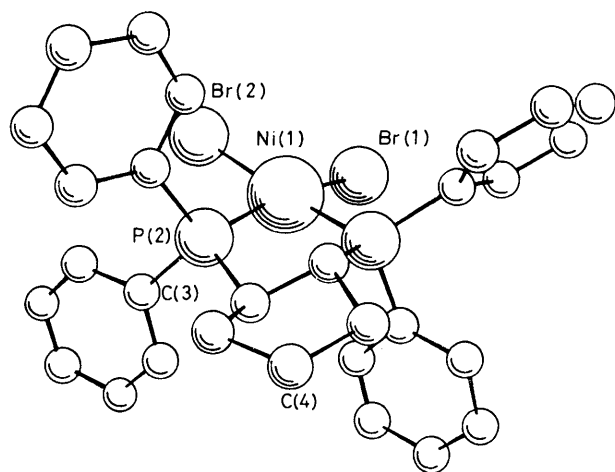


Figure 2. Crystal structure of (3) with the phenyl hydrogen atoms omitted for clarity. Selected distances and angles are: Ni–Br(1) 2.336(1), Ni–Br(2) 2.347(1), Ni–P(1) 2.178(1), Ni–P(2) 2.158(1), P(1)–C(1) 1.843(5), P(2)–C(2) 1.829, C(1)–C(2) 1.535(7) Å; Br–Ni–Br 94.91(3), Br(1)–Ni–P(1) 92.10(4), Br(2)–Ni–P(2) 86.84(4), P(1)–Ni–P(2) 88.33, P(1)–C(1)–C(2) 105.7(4), C(1)–C(2)–P(2) 107.0(4)°. The configuration is (*R,R*).

origin was defined by constraining the sum of the y shifts to be zero. The final refinement of 335 parameters led to $R = 0.036$ ($R_w = 0.048$) and a polarity of 1.02(2). \ddagger

The crystal structure shows the crystal to contain only one enantiomer of (3). The dihedral angle P–C–C–P in (2) is 161.8° and the P–P distance is 4.450 Å so that at first it appears that (2) is not suitably disposed to act as a chelate ligand. However, in (3) the P–C–C–P angle has closed dramatically to 53.7° and the P–P distance is 3.021 Å; thus the familiar five-membered ring chelate system is formed. The sign of the optical rotation of the crystal (in CH_2Cl_2) used for the structural determination was negative (–)(*R,R*).

Large prismatic single crystals of (3) were readily obtained (50–250 mg each from dichloromethane) and upon inspection

they could be seen to form two distinctive shapes which were essentially mirror images. Determination of the optical rotation of hand-separated crystals showed them to be resolved enantiomers, $[\alpha]_{589}^{20} 319 \pm 13$ or $-325 \pm 8^\circ$. Thus compound (3) undergoes spontaneous resolution upon crystallisation to give a conglomerate of large well formed crystals.³

Treatment of the (+)-(*S,S*)-enantiomer of (3) with sodium cyanide led to the recovery of the (–)-(*S,S*)-dpcp (2), $[\alpha]_{589}^{20} -179 \pm 4^\circ$.

The effectiveness of (2) as a catalyst for asymmetric hydrogenation was tested by standard procedures⁴ using $[\text{Rh}(\text{cyclo-octa-1,4-diene})\text{Cl}]_2$ with resolved (*S,S*)-dpcp (2) in methanol and the prochiral substrates methyl(*N*-benzoyl)dehydrophenylalanine and (*N*-benzoyl)dehydrophenylalanine. The optical purity of the hydrogenated products, determined by optical rotation and use of a chiral shift reagent in n.m.r. experiments, was found to be $100 \pm 2\%$. There was no evidence for more than one diastereoisomer in the hydrogenated products.

In conclusion, the tetrachloro compound (1) is readily prepared and can be envisaged to be a useful precursor for chelate tertiary phosphine ligands. The tetraphenyl compound (2) may be very readily resolved and is a highly effective ligand for applications in asymmetric hydrogenation.

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