The First Structural Characterization of a [2.2]PHANEPHOS−Transition-Metal Complex: Structure of *rac*-[Pd(4,12-bis(diphenylphosphino)[2.2]paracyclophane)Cl_2]

Philip W. Dyer,[†] Paul J. Dyson,*[,‡] Stuart L. James,[‡] Caroline M. Martin,[§] and Priya Suman[‡]

Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, U.K., Centre for Chemical Synthesis, Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, U.K., and Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.

Received May 22, 1998

Summary: The solid-state structure of the [2.2]PHANEPHOS−transition-metal complex rac-[Pd(4,12-bis(diphenylphosphino)[2.2]paracyclophane)Cl_2] has been established by single-crystal X-ray diffraction. The P−Pd−P bite angle is ideally suited to catalytic processes such as carbon−carbon cross-coupling reactions, which involve reductive elimination as the rate-determining step.

The synthesis of new phosphine ligands with interesting electronic or steric properties is an active area of research due to their widespread use in homogeneous catalysis.[1−4] Chelating phosphines are particularly important for conducting a wide range of organic transformations, and in particular diphosphine−palladium complexes catalyze many important reactions, including carbon−carbon bond formation.[4] Pye and Rossen recently reported the synthesis of the C_2-symmetric chiral diphosphine 4,12-bis(diphenylphosphino)[2.2]paracyclophane, which they named [2.2]-PHANEPHOS.[5] The backbone of this diphosphine comprises a [2.2]paracyclophane moiety, and the rhodium(I) triflate complex {[2.2]PHANEPHOS−Rh}$^+OTf^-$ is a highly efficient enantioselective hydrogenation catalyst. This is demonstrated by its ability to catalyze the hydrogenation of the HIV protease inhibitor Crixivan intermediate in 86% ee (100% conversion) under very mild conditions; a significant improvement over other catalysts (cf. BINAP, 56% ee; Et-DuPHOS, 50% ee).[6] A number of other applications involving a [2.2]PHANEPHOS/Pd_2dba_3 (dba = dibenzylideneacetone) system have also been described.[7]

We have been interested in the synthesis of [2.2]-paracyclophanyl-phosphines, including that of [2.2]-PHANEPHOS, and in this paper we report the single-crystal X-ray structure of the palladium(II) chloride complex of [2.2]PHANEPHOS, which indicates, together with preliminary reactivity studies, that it will be a useful diphosphine in catalytic processes which involve reductive elimination as the rate-determining step.

Our synthetic strategy differs slightly from that previously reported.[5] 4,12-Dibromo[2.2]paracyclophane was treated with *n*-BuLi at 0 °C, and after 30 min PPh_2-Cl was added. The reaction mixture was stirred for a further 3 h while it warmed to room temperature, affording *rac*-[2.2]PHANEPHOS in ca. 80% yield. Separation of the racemers may be achieved using the same method as that reported before, once the phosphine has been converted to the oxide by treatment with H_2O_2.[5] The reaction of *rac*-[2.2]PHANEPHOS with (cycloocta-1,5-diene)$PdCl_2$ in dichloromethane for 1 h at room temperature affords *rac*-[2.2]PHANEPHOS−$PdCl_2$ (**1**) in 90% yield.[8] The ^{31}P NMR spectrum of **1** reveals that the diphosphine exhibits a remarkably large coordination chemical shift (Δ) of 44.80 ppm. An important contribution to Δ for a diphosphine is the size of the chelate ring that it forms.[9] This ring contribution (Δ_r) can be evaluated by comparing the coordination chemical shift of a diphosphine with that of an appropriate monophosphine in an analogous complex. The most closely related monophosphine in this case is diphenylcyclophanylphosphine, but we have been unable to prepare the comparable *cis*-palladium complex (**A**) since the *trans* isomer (**B**) forms preferentially (Chart 1).[10] This is presumably due to the large steric bulk of the [2.2]paracyclophanyl substituent. Indeed, we are unaware of any studies in which Δ_r for a 10-membered ring has been evaluated, because most diphosphines will tend to bridge metals rather than chelate,[11] whereas

[†] University of Leicester.
[‡] Imperial College of Science, Technology and Medicine.
[§] University of Cambridge.

(1) Kagan, H. B.; Sasaki, M. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley: New York, 1990; Vol. 1.
(2) Gilheany, D. G.; Mitchel, C. M. In ref 1.
(3) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994.
(4) Ojima, I. *Catalytic Asymmetric Synthesis*; VCH: Weinheim, Germany, 1994.
(5) Pye, P. J.; Rossen, K.; Reamer, R. A.; Tsou, N. N.; Volante, R. P.; Reider, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 6207.
(6) Rossen, K.; Weissman, S. A.; Sager, J.; Reamer, R. A.; Askin, D.; Volante, R. P.; Reider, P. J. *Tetrahedron Lett.* **1995**, *36*, 6419.
(7) Rossen, K.; Pye, P. J.; Maliakal, A.; Volante, R. P. *J. Org. Chem.* **1997**, *62*, 6462.

(8) Synthesis and characterisation of [Pd(4, 12-bis(diphenylphosphino)-[2.2]paracyclophane)Cl_2] (**1**): The complex (cycloocta-1,5-diene)$PdCl_2$ (10 mg) and (4, 12-bis(diphenylphosphino)[2.2]paracyclophane) (20 mg) are dissolved in CH_2Cl_2 (5 mL) and stirred at room temperature. $^{31}P\{^1H\}$ NMR spectroscopy may be used to follow the reaction, which shows that the singlet resonance at δ 0.50 (due to the free ligand) decreases in intensity with the simultaneous growth of a singlet resonance at δ 44.30 (due to the complex), indicating complete conversion after 1 h. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 44.30 (s). Mass spectrum (FAB^+): *m/z* 768 ($M + H_2O^+$), 755 (M^+). 719 ($M - Cl^+$).

(9) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.
(10) Dyson, P. J.; Suman, P. Imperial College of Science, Technology and Medicine, unpublished results.

S0276-7333(98)00416-6 CCC: $15.00
Publication on Web 09/12/1998

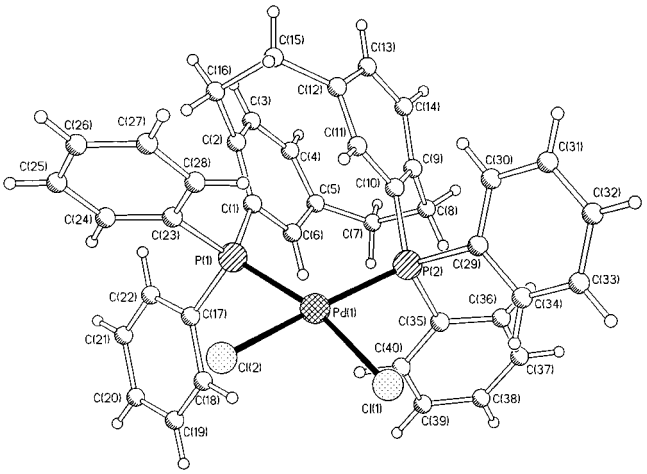
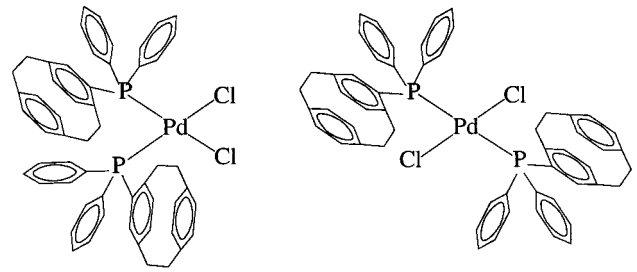


Figure 1. Molecular geometry of **1**.

Chart 1



A **B**

chelation in [2.2]PHANEPHOS is assured by the rigid backbone. In accord with the unusual value of Δ for [2.2]PHANEPHOS an X-ray crystal structure determination of **1** reveals an exceptionally large bite angle of 103.69(6)° (see below).

Single crystals of **1** suitable for X-ray analysis[12] were obtained from a solution of dichloromethane−diethyl ether after partial evaporation. The structure of **1** is shown in Figures 1 and 2, and some relevant bond parameters are listed in Table 1. In Figure 2 the phenyl rings and hydrogen atoms have been removed to reveal a clear view through the Pd square plane, showing the relationship with the diphosphine−[2.2]paracyclophane-

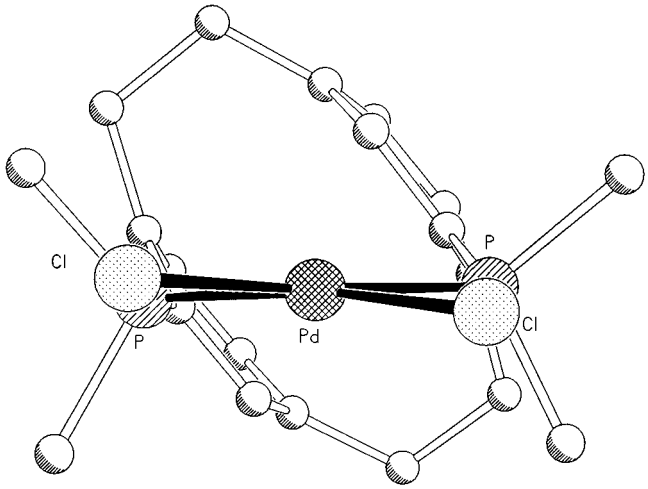


Figure 2. Molecular geometry of **1** viewed through the Pd square plane. Phenyl rings and H atoms have been removed for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

Pd(1)−P(1)	2.301(2)	C(9)−C(10)	1.405(7)
Pd(1)−P(2)	2.302(2)	C(10)−C(11)	1.393(7)
Pd(1)−Cl(1)	2.333(2)	C(11)−C(12)	1.384(7)
Pd(1)−Cl(2)	2.341(2)	C(12)−C(13)	1.392(8)
P(1)−C(1)	1.833(5)	C(13)−C(14)	1.365(8)
P(2)−C(10)	1.828(5)	C(2)−C(16)	1.512(7)
C(1)−C(6)	1.393(7)	C(12)−C(15)	1.505(8)
C(1)−C(2)	1.401(7)	C(15)−C(16)	1.577(8)
C(2)−C(3)	1.401(7)	C(5)−C(7)	1.504(8)
C(3)−C(4)	1.374(8)	C(7)−C(8)	1.559(9)
C(4)−C(5)	1.385(8)	C(8)−C(9)	1.507(8)
C(5)−C(6)	1.388(7)		
P(1)−Pd(1)−P(2)	103.69(6)	Cl(1)−Pd(1)−Cl(2)	86.38(6)

backbone. The distance between the two phosphorus atoms is 3.62 Å, which is considerably less than the related distance (4.8 Å) in the structure of 4,12-bis-(diphenylphosphino)-[2.2]paracyclophane oxide.[5] In this latter structure the two rings of the cyclophane are tilted at an angle of 5.7°; this is reduced to 4.8° in **1**, but in the other direction (Δ = 10.5°), such that the P atoms are drawn together. The most important feature of **1** is the large P−Pd−P bite angle of 103.69(6)°, one of the largest of any diphosphine complex in the Cambridge Structural Database,[13] although diphosphines with larger calculated bite angles have been reported.[14] Values for commonly encountered diphosphines on coordination to palladium(II) chloride are dppm (72.70°),[14] dppe (85.82°),[15] dppp (90.58°),[15] BINAP (92.70°),[16] dppf (98.00[17] and 99.10°[18]), and 1,8-bis(diphenylphosphino)-3,6-diazaoctane (105.31°).[19] However, with the last diphosphine both cis and trans isomers are obtained due to the flexible backbone and the trans species is dominant. It has been found that the bite angle of a

(11) Roundhill, R. M. In *Comprehensive Coordination Chemistry*; Wilkinson, G., McCleverty, J. M., Eds.; Pergamon: Oxford, U.K., 1987.

(12) Structural characterisation of [(4, 12-bis(diphenylphosphino)-[2.2]paracyclophane)]palladium(II) chloride (**1**): yellow crystal, $C_{41}H_{36}Cl_4P_2Pd$ (including CH_2Cl_2 solvent molecule), 0.22 × 0.20 × 0.20 mm^3, T = 173 K, M_r = 838.84, triclinic, space group $P\bar{1}$, a = 10.814(5) Å, b = 17.518(9) Å, c = 10.354(5) Å, α = 104.48(2)°, β = 108.66(2)°, γ = 83.38(2)°, U = 1798(2) Å^3, Z = 2, D_c = 1.549 Mg m^{-3}, λ(Mo Kα) = 0.710 69 Å, F(000) = 852, $R1$ = 0.0461 (5634 reflections with $I > 2\sigma(I)$), wR2 = 0.1145 for 5641 independent reflections corrected for absorption (μ(Mo Kα) = 0.933 mm^{-1}) and 430 parameters (all non-H atoms anisotropic except solvent molecule). The structure was solved by direct methods (Sheldrick, G. M. SHELXS 86, Program for Crystal Structure Solution *Acta Crystallogr., Sect. A* **1990**, 46, 467), and a series of difference Fourier maps were used to locate all light atoms except the H atoms. The H atoms were then added in calculated positions (C−H=0.96 Å) riding on the respective C atoms. All other calculations were performed using SHELXL 93 (Sheldrick, G. M. SHELXS 93, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993). Compound **1** crystallises with a dichloromethane solvent molecule in the asymmetric unit, which is disordered over two sites. Atomic coordinates, anisotropic thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

(13) Cambridge Crystallographic Data Centre.

(14) Kranenburg, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem*. **1998**, 155.

(15) Steffen, W. L.; Palenik, G. J. *Inorg. Chem*. **1976**, *15*, 2432.

(16) Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T.; Nishioka, E.; Yanagi, K.; Moriguchi, K. *Organometallics* **1993**, *12*, 4188.

(17) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc*. **1984**, *106*, 158.

(18) Butler, I. R.; Cullen, W. R.; Kim, T.-J.; Reltig, S. J.; Trotter, J. *Organometallics* **1985**, *4*, 972.

(19) Hill, W. E.; Taylor, J. G.; Falshaw, C. P.; King, T. J.; Beagley, B.; Tonge, D. M.; Pritchard, R. G.; McAuliffe, C. A. *J. Chem. Soc., Dalton Trans*. **1986**, 2289.

diphosphine in palladium complexes has a profound influence on the reactions which it catalyzes, most noteworthy being cross-coupling of carbon nucleophiles and electrophiles[20] and carbonylation reactions.[21] Reductive elimination is the rate-determining step in these processes, and Brown has observed that increasing the P−Pd−P angle results in a decreasing of the R−Pd−R′ angle, which is presumably responsible for accelerating reductive elimination.[20] Furthermore, Kamer suggests that as the P−Pd−P angle increases beyond a certain size the rate of the reductive elimination decreases, as the Pd(II) species no longer adopts a square-planar geometry.[14] It would appear that the optimum bite angle for reductive elimination is ca. 103°, which would suggest that [2.2]PHANEPHOS is ideally suited to these types of reactions.

(20) Brown, J. M.; Guiry, P. J. *Inorg. Chim. Acta* **1994**, *220*, 249.
(21) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1992**, *430*, 357.

Acknowledgment. We thank the Royal Society for a University Research Fellowship (P.J.D.) and the EPSRC (P.S.) for financial support.

Supporting Information Available: Tables giving crystal data and structure refinement details, atomic coordinates, thermal parameters, and bond distances and angles and a figure giving an additional view of **1** (8 pages). Ordering information is given on any current masthead page.

OM980416+