Inorg. Chem. **2004**, *43*, 6543–6545

Inorganic Chemistry
Communication

(R/S)$_{A2}$- or (R,S/S,R)$_{p,p'}$-[Pd(κ^2-P,P-{P(OC$_6$H$_3$Bu$^t_2$-2,4)$_2$N(Me)C(O)N(Me)PPh$_2$}Cl$_2$]: Chirality Created by Ring Tilting

Olaf Kühl*,[†,‡] **and Steffen Blaurock**[§]

Institut für Chemie und Biochemie, EMAU Greifswald, Soldmannstrasse 16,
D-17487 Greifswald, Germany, and Institut für Anorganische Chemie,
Universität Leipzig, Johannesallee 29, D-04103 Leipzig, Germany

Received June 15, 2004

The reaction of the unsymmetric bisphosphanyl urea ligand P(OC$_6$H$_3$Bu$^t_2$-2,4)$_2$N(Me)C(O)N(Me)PPh$_2$ with [Pd(cod)Cl$_2$] (cod = 1,5-cyclooctadiene) results in the chiral palladacycle (R,S)$_{A2}$-[Pd-(κ^2-P,P-{P(OC$_6$H$_3$Bu$^t_2$-2,4)$_2$N(Me)C(O)N(Me)PPh$_2$}Cl$_2$]. The chirality of the title compound is caused by the tilting of the central, six-membered PdP$_2$N$_2$C ring along one of the two P–N vectors and comprises two chiral planes and one chiral axis.

Chirality is a very important concept in chemistry and has major implications in catalysis, biochemistry, and pharmacology to name but a few.[1] Chirality is described as central, axial, and planar chirality depending on the dimension of the chiral element.[2] Prominent examples include asymmetric carbon and metal atoms,[3] a form of atropisomerism known as "axial chirality",[4] and substituted arene transition metal carbonyl complexes.[5] Axial chirality is defined by any one-dimensional chiral element known as an axis. This chirality often, but not always, originates from a hindered rotation along the phenyl−phenyl C−C bond and is therefore a form of atropisomerism.[4] Other examples of axially chiral compounds include allenes, alkylidene cycloalkanes, and spiranes.[6] Chirality caused by a tilted ring system is comparatively rare[7a] whereas distorted chiral metalated macrocycles play an important role in biochemistry.[7b,c]

In the present contribution, we will describe a palladium complex containing a bidentate phosphoramidate ligand where the complex displays planar and axial chiral elements.

Title complex **1** can be synthesized by mixing THF solutions of the ligand and [Pd(cod)Cl$_2$] (cod = 1,5-cyclooctadiene) followed by precipitation with hexane.[8] No attempt was made to separate the pair of enantiomers.

Crystals of **1**·THF suitable for an X-ray diffraction study were obtained from THF/hexane solution (Figure 1).[9−12] The palladium atom has the usual square planar coordination of Pd(II) with a P1−Pd1−P2 angle of 93.20(3)°. The central Pd1−P1−N1−C1−N2−P2 ring is tilted by 58° along the N1−P2 vector effectively creating two chiral planes (Figure 2). The two Pd−Cl bond lengths are essentially equal (233.1(1) and 233.60(9) pm) whereas the two Pd−P bond lengths (217.77(9) and 221.78(9) pm) are not. A similar

---

[†] EMAU Greifswald.

[‡] Current address: Institut für Angewandte Photophysik, TU Dresden, George-Bähr-Strasse 1, D-01069 Dresden, Germany. E-mail: kuhl@iapp.de.

[§] Universität Leipzig.

(1) *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999.

(2) (a) Cahn, R. S.; Ingold, C. K. *J. Chem. Soc.* **1951**, 612. (b) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Experienta* **1956**, *12*, 81. (c) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem.* **1966**, *78*, 413. (d) Prelog, V.; Helmchen, G. *Angew. Chem.* **1982**, *94*, 614.

(3) (a) Paiaro, G.; Panunzi, A. *J. Am. Chem. Soc.* **1964**, *86*, 5148. (b) Flood, T. C.; Campbell, K. D.; Downs, H. H.; Nakanishi, S. *Organometallics* **1983**, *2*, 1590.

(4) Bringmann, G.; Menche, D. *Acc. Chem. Res.* **2001**, *34*, 615.

(5) Salzer, A. *Coord. Chem. Rev.* **2003**, *242*, 59.

(6) Hauptmann, S. *Organische Chemie*; Deutscher Verlag für Grundstoffindustrie: Leipzig, 1985.

(7) (a) Sumby, C. J.; Steel, P. J. *Organometallics* **2003**, *22*, 2358. (b) Fekner, T.; Gallucci, J.; Chan, M. K. *J. Am. Chem. Soc.* **2004**, *126*, 223. (c) Fekner, T.; Gallucci, J.; Chan, M. K. *Org. Lett.* **2004**, *6*, 989.

(8) Complex **1** was prepared by adding 285 mg (1 mmol) of [Pd(COD)-Cl$_2$] to a solution of 713 mg (1 mmol) of P(OC$_6$H$_3$Bu$^t_2$-2,4)$_2$N(Me)-C(O)N(Me)PPh$_2$ in 20 mL of THF. After stirring for 2 h, the solution was concentrated under reduced pressure and layered with 20 mL of hexane. The pale yellow product was filtered off and dried in vacuo. Crystals suitable for single crystal X-ray structure determination were grown from the mother liquor at −20 °C. Yield 632 mg (73%); mp 178−80 °C (dec). NMR (CDCl$_3$, 213 and 300 K): ^{1}H δ 7.91 (m, 4H, *o*-Ph), 7.68 (m, 2H, *p*-Ph), 7.57 (m, 4H, *m*-Ph), 7.42 (s, 2H, 3-C$_6$H$_3$Bu$^t_2$), 7.24 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 5-C$_6$H$_3$Bu$^t_2$), 6.76 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 6-C$_6$H$_3$Bu$^t_2$), 3.18 (d, $^3J_{PH}$ = 5.2 Hz, 3H, Me), 3.01 (d, $^3J_{PH}$ = 5.6 Hz, 3H, Me), 1.49 (s, 9H, Bu^t), 1.29 (s, 9H, Bu^t). ^{13}C{^{1}H}: δ 157.24 (s, CO), 148.04 (s, C^1), 147.88 (s, C^6), 139.51 (d, J_{PC} = 7.55 Hz, *i*-Ph), 133.99 (s, C^2), 133.87 (s, C^4), 133.61 (d, J_{PC} = 2.31 Hz, *o*-Ph), 130.17 (s, *m*-Ph), 130.04 (s, *p*-Ph), 117.90 (s, C^5), 117.79 (s, C^3), 38.27 (s, NMe), 35.89 (s, *C*Me), 35.18 (s,*C*Me), 32.46 (s, NMe), 32.05 (s, C*Me*), 31.01 (s, C*Me*). ^{31}P{^{1}H}: δ 86.99 (s, PO$_2$N), 72.49 (s, PNPh$_2$). IR (KBr, cm^{-1}): 1680 (s, CO). Anal. Calcd for C$_{47}$H$_{66}$Cl$_2$N$_2$O$_4$P$_2$Pd (962.44): C 58.65, H 6.91, N 2.92. Found: C 58.23, H 7.12, N 2.76.

(9) Crystallographic study (215 K): a = 1100.4(2) pm, b = 1232.3(2) pm, c = 1909.2(3) pm, α = 104.548(3)°, β = 99.170(3)°, γ = 91.801(3)°, with Z = 2 in the triclinic space group $P\bar{1}$. R(int) = 0.0214, R1 = 0.0595, wR2 = 0.1253 for 14310 unique reflections. All hydrogen atoms were found and refined. Absorption correction was performed with SADABS.

(10) Sheldrick, G. M. *SADABS, A Program for Empirical Absorption Correction*; University of Göttingen: Göttingen, Germany, 1998.

(11) *SHELXTL PLUS, XS, Program for Crystal Structure Solution, XL, Program for Crystal Structure Determination, XP, Interactive Molecular Graphics*; Siemens Analytical X-ray Institute Inc.: Madison, WI, 1990.

(12) Farugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

10.1021/ic049222e CCC: $27.50

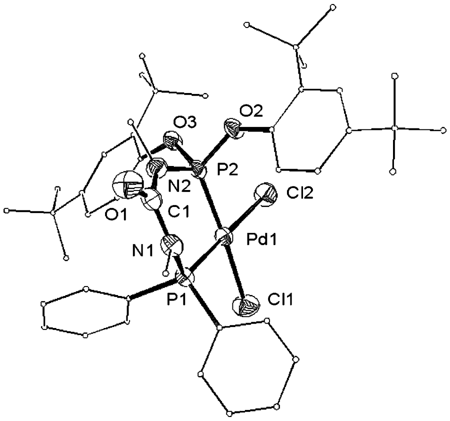


Figure 1. ORTEP plot of **1** showing 50% probability levels. Hydrogen atoms have been omitted, and atoms of peripheric substituents were reduced in size for clarity.

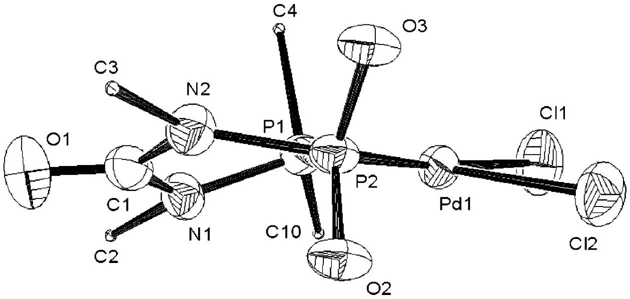


Figure 2. Central metallacycle in **1** and adjacent atoms.

inequality is observed for the two P−N bonds (168.9(3) and 171.4(3) pm). The two longer bonds both contain the P1 atom of the tilt vector P1−N2. No inequivalencies in M−P and P−N bond lengths were reported in similar Pd, Pt, and Mo complexes of $CO(PPh_2NR)_2$ (R = Me, Et).[13] Thus, the electronic influence of the aryloxy substituents on P2 is the likely cause for this observed bond shortening. Whereas most Pd−phosphoramidate bond lengths are longer than 220 pm,[13] bond lengths between 217.5(5) and 218.2(2) pm have been reported for Pd(II) complexes of *N*,*N′*-bisphosphityl-*N*,*N′*-dialkylhydrazines (alkyl = methyl,[14a] ethyl[14b]). All other bond lengths and angles are unremarkable. The unit cell has a center of inversion converting the one enantiomer into the other.

The two chiral planes are linked by two common atoms, the P1−N2 tilt vector. This vector effectively forms a chiral axis that is not independent of the two chiral planes. The chiral information provided by this chiral axis is sufficient to fully describe the chirality of the molecule, but the information is equally well provided by the two chiral planes.

It is worth mentioning that the tilted metallacycle in **1** is not merely another puckered ring system. A puckered six-membered metallacycle can be described as consisting of two groups of three adjacent atoms that form two planes without any atoms common to both. In contrast, the tilted ring in **1** is best described as consisting of two groups of four adjacent atoms that form two planes having two atoms in common that form a chiral axis. In addition, both of the two planes are chiral.

The tilt vector P1−N2 not only creates the chirality of the molecule, but also is responsible for a general inequivalence of the two phosphorus positions. As the ligand is unsymmetrical with two different phosphorus atoms, the plane (P1, Pd1, P2, N2) becomes chiral in its own right. Of the two diastereomers possible, only the one where the phosphino phosphorus is on the tilt vector (P1) is observed for **1**.

In a related molybdenum complex, both diastereomers are obtained in a ratio of 85:15.[15] As the present Pd(II) complex is structurally closely related to the Mo(0) complex previously reported, the occurrence of a major and a minor diastereomer was expected.

The absence of the minor diastereomer is confirmed by multinuclear NMR studies (^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$) of a bulk sample. The phosphorus NMR spectrum displays no coupling between the two different phosphorus centers. As dynamic behavior is known in tetrahedral nickel(0) complexes of similar ligands,[16] low-temperature NMR (^1H and $^{31}P\{^1H\}$) was performed to find out whether the absence of P−P coupling in the NMR spectrum of **1** is due to the palladium or dynamic behavior of the P−Pd bonds. As expected, the spectra at 213 and 300 K were identical except for a small temperature-dependent shift. Thus, the complex can be considered to be temperature stable up to 300 K with no racemization due to a fast dissociation−association mechanism occurring. Racemization by ring inversion can be ruled out by the findings of Suarez et al.[17] on a related rhodium complex. The authors show that four aryl substituents on the two phosphorus atoms are quite sufficient to prevent any racemization without bond fission.

The reason for the absence of the other pair of enantiomers remains unclear. Since there is more space available on the square planar palladium as compared to the octahedral molybdenum complex, steric considerations in the resulting complex do not seem to play a major role. However, steric reasons cannot be ruled out for indermediates or transition states during the displacement of the cod ligand.

The chirality of **1** can be determined applying the well-known rules developed by Cahn, Ingold, and Prelog.[2] Complex **1** posseses two chiral planes (P1, Pd1, P2, N2 and P1, N1, C1, N2). The pilot atoms for the chiral planes are Pd1 (P1, N1, C1, N2) denoted p and O2/O3 (P1, Pd1, P2, N2) denoted p′ in Chart 1. As palladium has a higher priority than oxygen, the chiral plane p takes priority over p′. Within p, the order of priority as shown in Chart 1 is P1, N2, and

---

(13) Slawin, A. M. Z.; Wainwright, M.; Woollins, J. D. *Dalton Trans*. **2001**, 2724 and references therein.

(14) (a) Reddy, V. S.; Katti, K. V.; Barnes, C. L. *Inorg. Chem*. **1995**, *34*, 5483. (b) Slawin, A. M. Z.; Wainwright, M.; Woollins, J. D. *Dalton Trans*. **2002**, 513. (c) Korostylev, A. V.; Bondarev, O. G.; Lyubimov, S. Y.; Kovalevski, A. Y.; Petrovskii, P. V.; Davankov, A. V.; Gavrilov, K. N. *Inorg. Chim. Acta* **2000**, *303*, 1. (d) Wong, E. H.; Sun, X.; Gabe, E. J.; Lee, F. L.; Charland, J.-P. *Organometallics* **1991**, *10*, 3010. (e) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C. *Phosphorus, Sulfur Silicon Relat. Elem*. **1994**, *87*, 1.

(15) Kühl, O. *Dalton Trans*. **2003**, 949.

(16) (a) Kühl, O.; Junk, P. C.; Hey-Hawkins, E. *Z. Anorg. Allg. Chem*. **2000**, *626*, 1591. (b) Kühl, O.; Langel, W. *Inorg. Chem. Commun*. **2003**, *6*, 74.

(17) Suarez, A.; Mendez-Rojas, M. A.; Pizzano, A. *Organometallics* **2002**, *21*, 4611.

Chart 1. Chirality of **1** as Described by the Chiral Planes (Tilt Angle Emphasized)

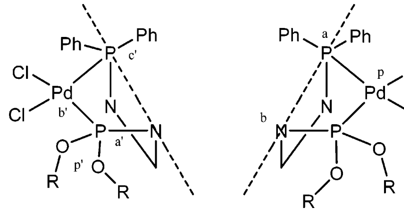
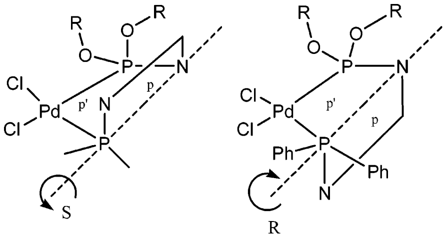


Chart 2. Chirality of **1** as Described by A2 (Dotted Line)



thus, the plane is *S* for the left-hand molecule. In the other molecule, created by the center of inversion within the crystal, this plane becomes *R*. The other chiral plane p′ is assigned the priorities P2, Pd1, P1 with the symbol *R* and is changed to *S* by the center of inversion.[18] Therefore, the molecule is obtained as the racemate $(S/R;\ R/S)_{\mathrm{p,p'}}$.

If the chiral axis is utilized to describe the chirality of the compound, the situation simplifies. There are two chiral axis (tilt vectors) possible, denoted P1−N2 and P2−N1, respectively. Complex **1** contains the axis P1−N2 with the lower priority P atom. It should thus be labeled A2 (A1 would be the axis P2−N1), Chart 2. If one now views the molecule along A2 from the near end (P1), the left-hand molecule in Chart 1 becomes *S* and the other *R*. *S* and *R* name the sense of direction along the shortest angle between the two chiral planes going from the higher priority plane to the lower one. The racemate would therefore be described as $(R/S)_{\mathrm{A2}}$.

Although chirality in closely related transition metal complexes has only been reported for unsymmetrically substituted bisphosphino urea ligands,[15] symmetrically substituted ones such as $(\mathrm{PPh_2NR})_2\mathrm{CX}$ (R = Me, Et; X = O, S)[13] also lead to chiral complexes as evidenced by their reported crystal structures. Only one pair of enantiomers is possible in such complexes, and the chirality can be described using either one of the chiral planes or the chiral axis. However, the two phosphorus atoms remain formally inequivalent, and it remains to be seen if dynamic NMR would be able to resolve the small difference of the two chemically equivalent P atoms seen in the solid state. The chirality of **1** can be accurately described in terms of axial as well as double planar chirality. As the description by axial chirality has the advantage of simplicity, it should be preferred.[2]

As geometrical constraints could be responsible for tilt vectors in otherwise planar rings, this type of chirality is likely to be more common than presently thought. Chirality caused by tilting requires a potentially planar metallacycle whose planarity is prevented by geometrical constraints. Geometrical constraints include large bond angle deviations from the mean value (e.g., 108° for a pentagon or 120° for a hexagon) or a broad spread of bond lengths (e.g., 139 pm for C−N, 170 pm for P−N, and 220 pm for Pd−P in **1**). For a potentially planar metallacycle, a degree of rigidity is required that is not provided by pure single bonds. Some double bond character will be needed, probably on all bonds. In the metallacycle formed in **1**, that is obviously the case for the Pd−P bonds (σ-donor and π-acceptor properties), the C−N bonds (amide character), and also the P−N bonds for which a varying degree of double bond character is discussed in the literature.[19]

In summary, we have described a metallacycle with a novel type of chirality displaying two chiral planes and one chiral axis. We have shown that for simplicity and consistency it is preferable to describe the chirality of these complexes in terms of axial rather than double planar chirality. It is likely that tilting is a general pathway to induce chirality into an otherwise planar ring system.

Acknowledgment. O.K. thanks J. Heinicke for his ongoing support and Dr. C. Drost and Ms. R. Zäbe for low temperature NMR measurements.

Supporting Information Available: Crystallographic details in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049222E

---

(18) Following the CIP rules strictly, Cl would take priority over P, and in the present case p′ would be R. As both Cl atoms have identical priority, p′ could not be determined unambiguously if one of the P−Pd−Cl angles exceeds 180°. Therefore, endocyclic ordering was preferred.

(19) Zubiri, M. R. I.; Woollins, J. D. *Comments Inorg. Chem.* **2003**, *24*, 189.