Chiral Bisphosphanes, VII[◇]

(1*S*,2*S*)-Cyclopentane-1,2-diyl-bis(phosphonous dichloride), (1*S*,2*S*)-$C_5H_8(PCl_2)_2$ − A Versatile Optically Active Reagent

Lutz Dahlenburg* and Anja Kaunert

Institut für Anorganische Chemie der Universität Erlangen-Nürnberg,
Egerlandstrasse 1, D-91058 Erlangen, Germany
Fax: (internat.) +49 (0)9131/85-7387
E-mail: dahlbg@anorganik.chemie.uni-erlangen.de

Received March 12, 1998

Keywords: Chirality / P ligands / Synthetic methods / Triphosgene

Treatment of (1*S*,2*S*)-$C_5H_8(PH_2)_2$ (**1**) with $OC(OCCl_3)_2$ gave (1*S*,2*S*)$C_5H_8(PCl_2)_2$ (**2**) as the first example of an optically active bis(phosphonous dichloride). **2** was converted to (1*S*,2*S*)-$C_5H_8(PX_2)_2$ [PX_2 = $P(OMe)_2$ (**3**), $P(OPh)_2$ (**4**), P[OCH(Me)Et-(*S*)]$_2$ (**5**), P[2-$OC_{10}H_6C_{10}H_6O$-2′-(*R*)] (**6**), $P(NC_4H_8O$-*cyclo*$)_2$ (**7**), $P(C_6H_{11}$-*cyclo*$)_2$ (**8**)] by reactions with oxygen, nitrogen, and carbon nucleophiles.

The design of new chiral phosphanes for use in transition metal-based asymmetric catalysis continues to play an important role in synthetic organic and organometallic chemistry[2]. Our current research in this field has been focused on the development of variable methods of synthesis for chiral bidentate phosphorus ligands with electron-rich and/or electron-poor donor atoms, starting from the resolved enantiomers of chiral bis(primary phosphanes)[3][4]. We herein report the details of a synthetic procedure that allows the facile transformation of (1*S*,2*S*)-cyclopentane-1,2-diyl-bisphosphane, (1*S*,2*S*)-$C_5H_8(PH_2)_2$[3] (**1**), into its PCl_2 homologue (1*S*,2*S*)-$C_5H_8(PCl_2)_2$ (**2**) and present selected examples of how the optically pure multi-purpose P−Cl reagent **2** is easily converted to the 1*S*,2*S* enantiomers of various $C_5H_8(PX_2)_2$ ligands containing sterically and electronically different P−C-, P−N-, or P−O-bonded substituents X on phosphorus.

Results

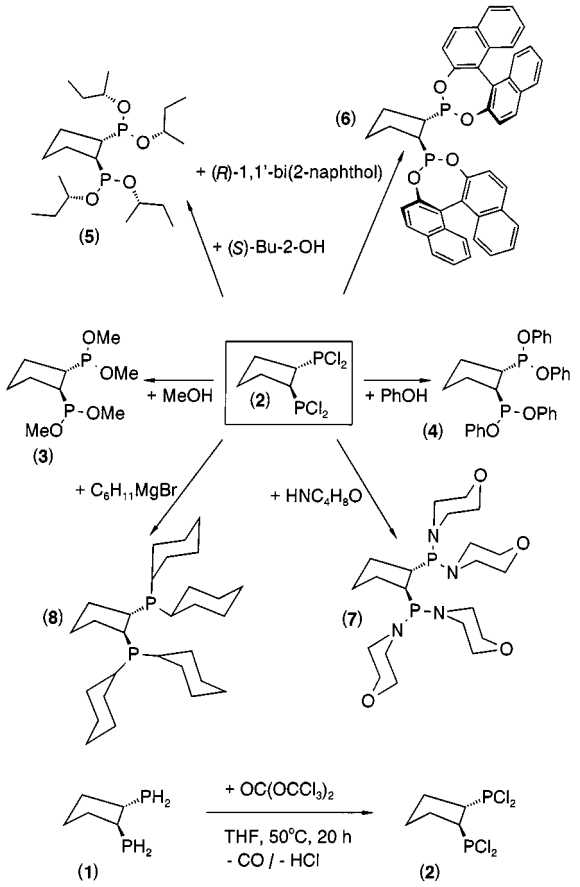
Formerly, primary phosphanes RPH_2 were reported to produce bis(phosphonous dichlorides) $RPCl_2$ on treatment with chlorine in inert halogenated solvents[5]. These results could not be reproduced, however, in later work where it was shown that both phosphonous and phosphinous chlorides are more readily prepared from a primary or secondary phosphane by oxidizing the P−H bond with $COCl_2$ ("phosgene") rather than with Cl_2[6][7]. Bis(trichloromethyl) carbonate, $OC(OCCl_3)_2$ ("triphosgene"), has served as a convenient crystalline alternative to the highly toxic phosgene in miscellaneous laboratory reactions and its use as an electrophile, dehydrating agent, or specific oxidant in the preparation of many classes of organic compounds has been studied thoroughly during the past decade[8]. We reasoned that triphosgene would also turn out useful as a synthetic auxiliary in the conversion of the easily accessible (1*S*,2*S*)-$C_5H_8(PH_2)_2$[3] (**1**) to the more reactive and, hence, more versatile (1*S*,2*S*)-$C_5H_8(PCl_2)_2$ (**2**). Actually, bis(phosphonous dichloride) **2** formed smoothly when bis(primary phosphane) **1** and $OC(OCCl_3)_2$ where combined in THF at 50°C in 3:4 stoichiometry, as required for the quantitative transformation of the two $-PH_2$ groups into $-PCl_2$ functions. This procedure provided solutions of **2** exhibiting no extraneous signals in their ^{31}P-NMR spectra, from which the pure product was isolated in 66% yield by vacuum distillation.

Compound **2** represents the hitherto only example of an optically active P_2 ligand possessing reactive P−Cl bonds, opening up variable synthetic routes to a wide range of enantiomerically pure electron-rich and electron-poor P−C-, P−N-, and P−O-bonded derivatives (1*S*,2*S*)-$C_5H_8(PX_2)_2$, potentially useful as supporting ligands in asymmetric catalysis. So far, we have prepared bidentates of the former type with PX_2 = $P(OMe)_2$ (**3**), $P(OPh)_2$ (**4**), P[OCH(Me)Et-(*S*)]$_2$ (**5**), P[2-$OC_{10}H_6C_{10}H_6O$-2′-(*R*)] (**6**), $P(NC_4H_8O$-*cyclo*$)_2$ (**7**), and $P(C_6H_{11}$-*cyclo*$)_2$ (**8**) by conventional reactions of **2** with mono- and difunctional alcohols, secondary amines, and Grignard reagents (Scheme 1). The ease of synthesis of ligands **3**−**8**, starting from enantiopure **2**, may be contrasted with, e. g., the previously described tedious preparation of **8**, which involved oxidation of *rac*-$C_5H_8[P(C_6H_{11}$-*cyclo*$)_2]_2$ to *rac*-$C_5H_8[P(O)(C_6H_{11}$-*cyclo*$)_2]_2$, followed by optical resolution of the *P*,*P*′-dioxide with (+)-di-*O*-benzoyl tartaric acid and reduction of the resolved P=O enantiomers in neat diphenylsilane at 150°C[9].

[◇] Part VI: Ref.[1]

  1434−1948/98/0707−0885 $ 17.50+.50/0

Scheme 1



Discussion

The usefulness of the above procedures for the synthesis of optically active P_2 ligands rests on the following features[10]: First, the formation of bis(phosphonous dichlorides) or bis(phosphinous chlorides) by chlorination with triphosgene of bis(primary phosphanes) or bis(secondary phosphanes) can conceivably be performed with any other suitable chiral $H_2P{\cap}PH_2$ or H(R)P∩P(R)H precursor, as will be examplified elsewhere for the correspondent transformations of systems as different as $C_5H_8[P(H)R]_2$[11] and $Fe(C_5H_4PH_2)_2$[12]. Second, substitution reactions undergone by P−Cl functional phosphorus(III) compounds upon treatment with carbon, nitrogen or oxygen nucleophiles are among the most general and most easily accomplished coupling methods in organic chemistry. Finally, the fact that it is possible to incorporate virtually any other P−O-, P−N-, or P−C-bonded residue R into chiral $Cl_2P{\cap}PCl_2$ or Cl(R)P∩P(R)Cl frameworks makes it possible to utilize the method for the preparation of a wide range of optically active P_2 ligands having fine-tunable and, perhaps, rationally designed steric and electronic requirements.

Financial support from the *Deutsche Forschungsgemeinschaft* (Bonn) and the *Fonds der Chemischen Industrie* (Frankfurt/Main) is gratefully acknowledged. We are also indebted to *Hoechst AG* (plant Vlissingen/NL) for a generous gift of P_4.

Experimental Section

All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. − NMR: Bruker DPX 300 (300.1 MHz for ^1H, 75.5 MHz for ^{13}C, 121.5 MHz for ^{31}P) at ambient temperature with TMS as internal or H_3PO_4 as external standard (downfield positive). − Mass spectra: Jeol MS 700. − Optical rotation: Schmidt & Haensch POLARTRONIC E.

CAUTION: Although at the time of writing this article no conclusive data on the toxicity of triphosgene were available to the authors, the reagent should be handled using similar precautions as for the more dangerous phosgene, even if $OC(OCCl_3)_2$ is safer because of its lower vapor pressure and higher stability[8][13].

(1S,2S)-$C_5H_8(PCl_2)_2$ (**2**): A solution of 23.7 g (80 mmol) of $OC(OCCl_3)_2$ (Aldrich) in 250 ml of THF was added dropwise within 2 h to a stirred solution of 8.1 g (60 mmol) of (1*S*,2*S*)-$C_5H_8(PH_2)_2$[3] in 400 ml of THF, heated to 50°C. The mixture was stirred overnight at 50°C, solvent was then evaporated, and the residue was distilled in the vacuum of an oil pump at 80 to 110°C (pot temperature) to give 10.8 g (66%) of **2** as a colorless liquid. − ^1H NMR (C_6D_6): δ = 1.25 [qui, ^3J(H,H) = 7.1 Hz; 2 H, CH_2-4], 1.60 (m; 4 H, CH_2-3,5), 2.36 (m; 2 H, CH-1,2). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 26.9 [t, ^3J(P,C) = 3.1 Hz; C-4], 29.6 [*A*XX′-d, ^2J(P,C) + ^3J(P′,C) = 14.5 Hz; C-3,5], 50.5 [dd, ^1J(P,C) = 51.8, ^2J(P,C) = 13.6 Hz; C-1,2]. − $^{31}P\{^{13}C\}$ NMR (C_6D_6): δ = 188.6 (s). − $[\alpha]_D^{25}$ = −19.8 (neat).

(1S,2S)-$C_5H_8\{P[OCH(Me)Et\text{-}(S)]_2\}_2$ (**5**): At dry-ice temperature, a quantity of 1.95 g (7.1 mmol) of **2**, dissolved in 20 ml of diethyl ether, was added dropwise, within 30 min, to a stirred solution containing 2.65 ml (28.7 mmol) of (*S*)-(+)-butan-2-ol (Aldrich) and 4.0 ml (28.7 mmol) of triethylamine in 200 ml of diethyl ether. Precipitation of $[Et_3NH]Cl$ occurred immediately to give a pasty suspension which was diluted by adding additional quantities of solvent in order to maintain stirring. After warming to room temperature overnight, the mixture was filtered and evaporated to leave bis(phosphinite) **5** as an opaque oil. Occasionally, this material contained impurities which in view of their $^{31}P\{^1H\}$ NMR signals (δ ca. 40−45) were strongly suspected to be onium salts, e. g., $[(1S,2S)\text{-}C_5H_8\{P[OCHC(Me)Et\text{-}(S)]_2\}_2H_n]Cl_n$ (*n* = 1, 2). These could be removed quantitatively by stirring the crudes with excess sodium amide in toluene. Subsequent filtration and evaporation of solvent afforded diastereomerically pure **5** as a colorless liquid (1.37 g; 45%), spectroscopically free from contaminating admixtures. − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 9.9, 10.1 (both s; both $CH_2\mathit{C}H_3$, pairwise diastereotopic), 22.0, 22.1 (both s; both $CH\mathit{C}H_3$, pairwise diastereotopic), 27.5 [m; $(CH_2)_3$], 31.6, 31.7 (both s; both $\mathit{C}H_2CH_3$, pairwise diastereotopic), 43.5 [dd, *J*(P,C) = 10.8 and 18.0 Hz; PCH], 75.5, 76.6 [both *A*XX′-t, Σ*J*(P,C) = 16.5 Hz; both POCH, pairwise diastereotopic]. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 179.6 (s). − MS (FD; toluene, 35 mA, 10 kV): *m*/*z* = 423 [M^+].

(1S,2S)-$C_5H_8\{P[2\text{-}OC_{10}H_6C_{10}H_6O\text{-}2'\text{-}(R)]\}_2$ (**6**) was obtained analogously from 1.78 g (6.5 mmol) of **2** and 3.75 g (13.1 mmol) of (*R*)-(+)-1,1′-bi(2-naphthol) (Aldrich) in 200 ml of diethyl ether containing 3.68 ml (26.4 mmol) of added triethylamine; yield: 3.69 g (81%) of a yellow waxy solid. − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 21.5 (s; $CH_2\mathit{C}H_2CH_2$), 27.0 [*A*XX′-t, ^2J(P,C) + ^3J(P′,C) = 20.3 Hz; $\mathit{C}H_2CH_2\mathit{C}H_2$], 41.9 [dd, ^1J(P,C) = 38.6, ^2J(P,C) = 17.9 Hz; PCH], 121.4, 122.2, 123.6, 124.7, 125.2, 125.6, 126.5, 126.9, 127.1, 128.5, 128.7, 129.3, 130.1, 130.8, 131.4, 131.7, 133.0, 133.2 (all s; 18 anisochronous aromatic C), 149.5, 150.7 th d, ^2J(P,C) = 6.9 Hz; both POC]. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 203.5 (s). − MS (FD; toluene, 35 mA, 10 kV): *m*/*z* = 698 [M^+].

Compounds **3**, **4**, **7**, and **8** were prepared as described previously for the associated racemats[1][9]. As expected, the products exhibited NMR and MS data corresponding in all respects to those reported for the racemic mixtures.

[1] L. Dahlenburg, C. Becker, J. Höck, S. Mertel, *J. Organomet. Chem.*, in press.
[2] W. A. Herrmann, B. Cornils in *Apllied Homogeneous Catalysis with Organometallic Componds* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**, Vol. 2, chapter 4.1.
[3] C. Eckert, L. Dahlenburg, A. Wolski, *Z. Naturforsch*. **1995**, *50b*, 1004−1008.
[4] L. Dahlenburg, V. Kurth, *Eur. J. Inorg. Chem*. **1998**, 597−603.
[5] C. Walling (E. I. Du Pont de Nemours & Co.), U. S. 2437798, **1948** [*Chem. Abstr.* **1948**, *42*, P4199c].
[6] W. A. Henderson, Jr., S. A. Buckler, N. E. Day, M. Grayson, *J. Org. Chem.* **1961**, *26*, 4470−4471.
[7] E. Steininger, *Chem. Ber.* **1963**, *96*, 3184−3194.
[8] L. Cotarca, P. Delogu, A. Nardelli, V. Sunjic, Synthesis **1995**, 553−576.
[9] A. Saare, L. Dahlenburg, *Z. Naturforsch*. **1995**, *50b*, 1009−1017.
[10] L. Dahlenburg, Ger. Pat. Appl. 197 32 805.9, **1997**.
[11] V. Kurth, Dissertation, Universität Erlangen-Nürnberg, in progress.
[12] S. Nückel, Diploma Thesis, Universität Erlangen-Nürnberg, **1998**.
[13] S. B. Damle, Chem. Eng. News **1993**, *71 (6)*, 4.

[98058]