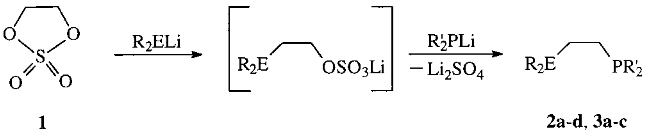
A New Synthetic Route to Unsymmetrical 1,2-Bis(phosphanyl)ethanes and 1,2-Arsanyl(phosphanyl)ethanes with and without a Stereogenic Center[**]

Guido Fries, Justin Wolf, Matthias Pfeiffer, Dietmar Stalke, and Helmut Werner*

Dedicated to Professor Egon Uhlig
on the occasion of his 70th birthday

Bistertiary phosphanes of the general composition 1,2-$C_2H_4(PR_2)_2$ are among the widest used chelating ligands in coordination chemistry.[1] The most well-known derivatives of this type, 1,2-bis(diphenylphosphanyl)ethane (dppe) and 1,2-bis(dimethylphosphanyl)ethane (dmpe), are commonly prepared either from 1,2-$C_2H_4Cl_2$ and $NaPPh_2$,[2] from 1,2-$C_2H_4Br_2$, $HPPh_2$, and NaOH,[3] or from 1,2-$C_2H_4(PCl_2)_2$ and excess CH_3MgI.[4] Corresponding 1,2-bis(phosphanyl)ethanes bearing *different* substituents at the phosphorus centers such as $Me_2PCH_2CH_2PPh_2$, $Me_2PCH_2CH_2P(CH_2CMe_3)_2$, or $Ph_2PCH_2CH_2P\textit{n}Bu_2$, are accessible upon stepwise addition of dimethylvinylthiophosphorane to HPR'_2 and $LiAlH_4$[5] or by reaction of $Ph_2P(CH{=}CH_2)$ with LiPRR′ and subsequent hydrolysis.[6] The yields are in most cases moderate (exception: $Me_2PCH_2CH_2PPh_2$), reaching rarely more than 50%.

In the search for reactive, coordinatively unsaturated rhodium and ruthenium complexes, which possibly could be used for metal-catalyzed C–C coupling reactions,[7] we recently became interested in the ligating properties of unsymmetrical 1,2-bis(phosphanyl)ethanes and report here a simple and fairly general one-pot synthesis for these compounds. The starting material for **2a–d** is the cyclic sulfate **1** (Scheme 1), which is obtained upon treatment of 1,2-ethanediol with $SOCl_2$ followed by catalytic oxidation with $NaIO_4$.[8, 9] The cleavage of one of the C–O bonds in **1** and the concomitant opening of the five-membered ring occurs rapidly and quantitatively by addition of the lithium phosphide $LiPR_2$ to a solution of **1** in THF at −70 °C. After warming the solution to room temperature and renewed cooling to −70 °C, the addition of the second P-nucleophile $LiPR'_2$ leads to the substitution of the sulfate group by the PR'_2 unit. Subsequent hydrolysis affords an oily residue, which can be eventually distilled by using a Kugelrohr at 2.5 mbar. Compounds **2a**, **2b**, and **2d** are isolated as highly viscous liquids, while **2c**, after crystallization from methanol, is obtained as a colorless crystalline solid. The yields range from 30% for **2d** to 65–75% for **2a–c**.



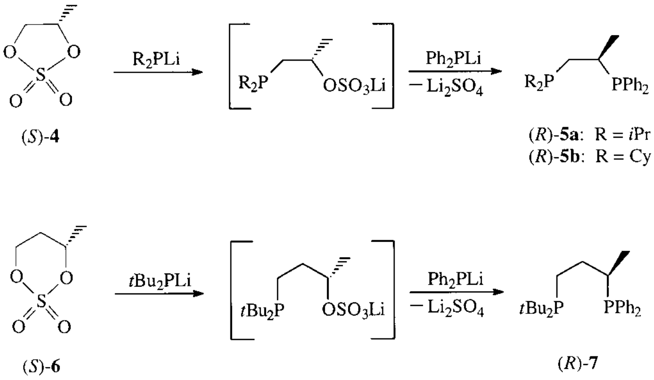
	E	R	R'
2a	P	*i*Pr	Ph
2b	P	*t*Bu	Ph
2c	P	Cy	Ph
2d	P	*i*Pr	*t*Bu

	E	R	R'
3a	As	*t*Bu	Ph
3b	As	*t*Bu	*i*Pr
3c	As	Cy	Ph

Scheme 1. Synthesis of **2a–d** and **3a–c**. Cy = cyclohexyl.

This one-pot procedure for the new unsymmetrical 1,2-bis(phosphanyl)ethanes **2a–d** is remarkable because of its easy synthetic approach, short reaction times, and high efficiency (except for **2d**). Moreover, the synthetic strategy can be extended to related 1,2-arsanyl(phosphanyl)ethanes (Scheme 1). Up to now, only two examples of compounds of the general composition $R_2AsCH_2CH_2PR'_2$, namely $Ph_2AsCH_2CH_2PPh_2$[10] and $Me_2AsCH_2CH_2PPh_2$,[11] were known; however, for the latter of those no detailed preparative procedure and analytical data were given. The new synthetic method described herein furnishes the chelating systems **3a–c** in good yields. For the preparation of **2a–c** as well as of **3a** and **3c** it is only important to note that the stronger nucleophile (for example, $LiP\textit{i}Pr_2$ for **2a** or $LiAs\textit{t}Bu_2$ for **3a**) is added first and the weaker nucleophile ($LiPPh_2$ for **2a** and **3a**) second. If this order is reversed, mixtures of products are obtained.

The results presently known led us to suggest that for the 1,2-bis(phosphanyl)ethanes as well as for the As,P-analogues a wide range of substituents R and R′ at the two donor atoms can be employed. With regard to possible applications in catalysis,[12] it is equally important that the new synthetic method is also suitable for the preparation of chiral unsymmetrical chelating ligands of the type $R_2PCH(R'')CH_2PR'_2$. In Scheme 2 two examples are shown. In a test experiment we initially treated the racemic mixture of the cyclic sulfate **4** stepwise with R_2PLi (R = *i*Pr, Cy)and Ph_2PLi and isolated the corresponding product in an analogous way to that described for **2a–d**. By using the *S* enantiomer of **4**, the *R* enantiomers **5a** and **5b** are obtained in a completely regioselective fashion by inversion of configuration at the stereogenic center. Although the yields of **5a** and **5b** (about 40%) are moderate, they are similar to those reported for PROPHOS[13] and



Scheme 2. Synthesis of **5a**, **5b** and **7**.

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[*] Prof. Dr. H. Werner, Dipl.-Chem. G. Fries, Dr. J. Wolf, Dipl.-Chem. M. Pfeiffer, Prof. Dr. D. Stalke
Institut für Anorganische Chemie der Universität
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4605
E-mail: helmut.werner@mail.uni-wuerzburg.de

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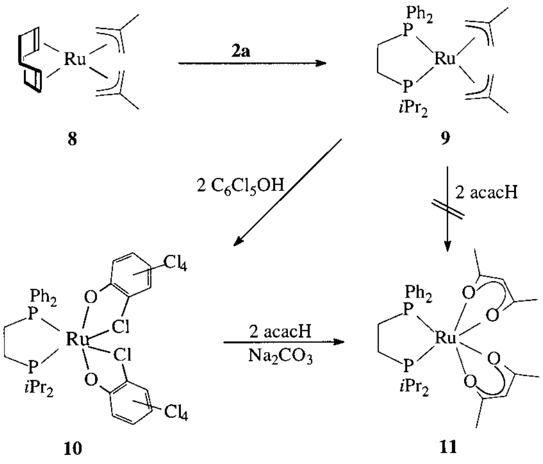
CYCPHOS[14] (these compounds were prepared from the corresponding chiral bis(tosylate) and two equivalents of $LiPPh_2$). The optical rotation $[\alpha]^{20}_{\mathrm{D}}$ of **5a** and **5b** (+201° and +167° in CH_2Cl_2, respectively) is comparable to that of PROPHOS ($[\alpha]^{20}_{\mathrm{D}} = +186°$).[13]

To explore the application of the new synthetic methodology further, we also prepared the chiral unsymmetrical 1,3-bis(phosphanyl)propane (*R*)-**7** (Scheme 2), which displayed an optical rotation of $[\alpha]^{20}_{\mathrm{D}} = +39°$ (in CH_2Cl_2). Recently, Huttner and co-workers reported the synthesis of related enantiopure 1,3-bis(phosphanyl)propanes of the general composition $R_2PCH_2CH(X)CH_2PR'_2$ (where X is an OH or OR functionality) from epichlorohydrins and attempted to use the corresponding cationic rhodium complexes $[C_8H_{12}Rh\{R_2PCH_2CH(X)CH_2PR'_2\}]^+$ as precatalysts for the enantioselective hydrogenation of (*Z*)-acetamidocinnamic acid.[15] Moreover, Gulyas, Arva, and Bakos prepared the chiral sulfate $Ph_2PCH(Me)CH_2CH(Me)OSO_3Li$, which is soluble in water and has been employed as cocatalyst in a biphasic reaction for the rhodium-catalyzed hydroformylation of 1-octene.[16] The composition of this chiral sulfate is related to that of the (not isolated) intermediate which is formed upon treatment of (*S*)-**6** with tBu_2PLi. The compound (*R*)-**7**, the bis(phosphanyl)ethanes **2a–d** and (*R*)-**5a**, **b**, and the arsanyl(phosphanyl)ethanes **3a–c** were characterized by elemental analysis, mass spectra (sometimes as the oxides), and NMR techniques.

In order to test the ligating properties of the unsymmetrical 1,2-bis(phosphanyl)ethanes, we treated, in analogy to work done by Jolly[17] and Leitner[18], the 1,5-cyclooctadieneruthenium complex **8**[19] with **2a** in hexane (4 h, reflux temperature). The substitution product **9** was isolated as a yellow, slightly air-sensitive solid in 72 % yield (Scheme 3).



Scheme 3. Synthesis of **9–11**. acacH = acetylacetone.

While even at elevated temperatures **9** is inert toward acetylacetone, it affords complex **10** almost quantitatively upon treatment with two equivalents of pentachlorophenol. The interesting feature is that the ^{13}C NMR spectrum of **10** (in $[D_8]$toluene) displays only one signal for the *ortho*- and *meta*-carbon atoms of the OC_6Cl_5 units both at 295 K and 188 K. This observation indicates that in solution a dynamic process takes place, which involves (on the NMR time scale) a rapid coordination/decoordination of the *ortho*-chlorine atoms of the six-membered ring to the metal center. The crystal structure of **10**[20] (Figure 1) confirms the existence of weak Ru–Cl interactions comparable to those between transition metals and other C–Cl bonds.[21] The Ru–Cl distances of 2.498(1) Å and 2.524(1) Å in **10** are significantly longer than in *trans*-$[RuCl_2(dppe)_2]$ (2.4325(12) Å)[22] and *trans*-$[RuCl_2(dppm)_2]$ (2.426(1) Å)[23], where "normal" covalent Ru–Cl bonds are present (dppm = bis(diphenylphosphanyl)methane).

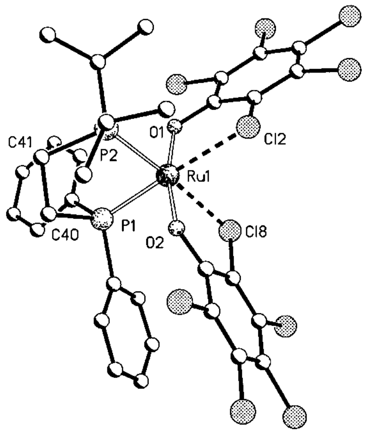


Figure 1. Molecular structure of **10** in the crystal. Selected bond lengths [Å] and bond angles [°]: Ru-P1 2.2341(13), Ru-P2 2.2578(13), Ru-O1 2.088(3), Ru-O2 2.078(3), Ru-Cl2 2.5240(13), Ru-Cl8 2.4978(13); P1-Ru-P2 84.32(5), P1-Ru-O1 99.45(9), P1-Ru-O2 89.24(9), P1-Ru-Cl2 176.70(4), P1-Ru-Cl8 94.03(5), P2-Ru-O1 94.51(9), P2-Ru-O2 93.00(8), P2-Ru-Cl2 98.90(5), P2-Ru-Cl8 174.32(4), O1-Ru-O2 169.03(11), O1-Ru-Cl2 79.60(9), O1-Ru-Cl8 91.12(9), O2-Ru-Cl2 91.34(9), O2-Ru-Cl8 81.53(8), Cl2-Ru-Cl8 82.85(4). The noncoordinated THF molecule is omitted for clarity.

In contrast to **9**, compound **10** reacts with acetylacetone and Na_2CO_3 to give the chelate complex **11** which was isolated as an air-stable yellow solid in 89 % yield. This result illustrates that **10** could be considered as a masked 14-electron species in which the additional interaction between the *ortho*-chlorine atoms of the C_6Cl_5 units and the metal prevents a subsequent oligomerization or decomposition process. Recent work by Baratta et al.[24] has demonstrated a second example of a ruthenium(II) complex with a formal 14-electron configuration; in this case two strong agostic Ru⋯CH interactions relieve part of the electronic unsaturation at the metal center.

Experimental Section

All reactions were carried out under an argon atmosphere. ^{31}P NMR: 81.0 MHz, $CDCl_3$; MS: CI, isobutane, 150 eV.

2a: A 1.76 M solution of *n*BuLi in hexane (8.1 mL, 14.24 mmol) was added to a solution of iPr_2PH (1.68 g, 14.24 mmol) in THF (25 mL) at −70 °C. The resulting reaction mixture was slowly allowed to warm to 25 °C and stirred for 30 min at this temperature. It was then again cooled to −70 °C and added dropwise to a solution of **1** (1.77 g, 14.24 mmol) in THF (45 mL) at −70 °C. After the reaction was complete, the colorless solution was allowed to thaw, stirred for 30 min at room temperature, and subsequently cooled to −70 °C. The solution was then treated with a solution of Ph_2PLi in THF (prepared from Ph_2PH (2.63 g, 14.11 mmol) in THF (20 mL) and a 1.76 M solution of *n*BuLi in hexane (8.0 mL, 14.11 mmol)). After the reaction mixture had been allowed to thaw, it was heated for 3 h at 60 °C. The volatiles were removed in vacuo, the residue was dissolved in diethyl ether (50 mL), and the solution was hydrolyzed with water (20 mL). The organic phase was separated, washed twice with water (10 mL), dried over Na_2SO_4, and filtered. After the solvent was removed, the remaining oily residue was distilled in a Kugelrohr at 200 °C/2.5 mbar. A colorless, highly viscous, air-sensitive liquid was obtained. Yield: 3.55 g (76 %); b.p. 200 °C (2.5 mbar); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.41$ (m, 10H; C_6H_5), 2.20 (m, 2H; PCH_2CH_2P), 1.73 (m, 2H; PC*H*CH_3), 1.48 (m, 2H; PCH_2CH_2P), 1.08 (dd, J(P,H) = 11.7, J(H,H) = 6.9 Hz, 6H; PCHCH_3), 1.02 (dd, J(P,H) = 9.0, J(H,H) = 7.1 Hz, 6H; PCHCH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 138.2$ (d, J(P,C) = 13.9 Hz; *ipso*-C of C_6H_5), 132.5 (d, J(P,C) = 18.5 Hz; *ortho*-C of C_6H_5), 128.1 (s; *para*-C of C_6H_5), 128.0 (d, J(P,C) = 12.0 Hz; *meta*-C of C_6H_5), 26.3 (dd, $J(P^1,C) = 20.4$, $J(P^2,C) = 12.9$ Hz; PCH_2CH_2P), 23.0 (d, J(P,C) = 12.9 Hz; PCHCH_3), 19.8 (d, J(P,C) = 14.8 Hz; PCHCH_3), 18.7 (d, J(P,C) = 10.2 Hz; PCHCH_3), 17.2 (dd, $J(P^1,C) = 19.4$, $J(P^2,C) = 15.7$ Hz; PCH_2CH_2P); ^{31}P NMR: $\delta = 10.3$ (d, J(P,P) = 33.0 Hz; $i$$Pr_2P$), -11.9 (d, J(P,P) = 33.0 Hz; Ph_2P); MS: *m*/*z* (%): 331 (5.3) $[M+1]^+$, 187 (14.3) $[Ph_2P+1]^+$, 119 (9.0) $[iPr_2P+1]^+$. Compounds **2b–d** were prepared as described for **2a**; **2c** was obtained after recrystallization from methanol as a colorless, air-sensitive, crystalline solid; **2b** and **2d** are colorless, highly viscous, air-sensitive liquids; yield 70 % (**2b**), 65 % (**2c**), 30 % (**2d**). Characteristic data for **2b**: b.p. 190 °C (2.5 mbar) ^{31}P NMR: $\delta = 36.4$ (d, J(P,P) = 34.3 Hz; tBu_2P), -12.3 (d, J(P,P) = 34.3 Hz; Ph_2P); MS: *m*/*z* (%): 359 (22.9) $[M+1]^+$, 187 (4.4) $[Ph_2P+1]^+$, 147 (3.2) $[tBu_2P+1]^+$; **2c**: m.p. 54 °C; ^{31}P NMR: $\delta = 2.3$ (d, J(P,P) = 30.5 Hz; Cy_2P), -11.9 (d, J(P,P) = 30.5 Hz; Ph_2P); MS: *m*/*z* (%): 411 (4.5) $[M+1]^+$, 199 (19.7) $[Cy_2P+1]^+$, 187 (28.9) $[Ph_2P+1]^+$; **2d**: ^{31}P NMR: $\delta = 36.9$ (d, J(P,P) = 30.5 Hz; tBu_2P), 10.7 (d, J(P,P) = 30.5 Hz; iPr_2P); MS: *m*/*z* (%): 323 (13.8) $[iPr_2P(O)CH_2CH_2P(O)tBu_2+1]^+$.

3a: Preparation analogous to **2a**, from tBu_2AsH (2.70 g, 14.18 mmol), a 1.77 M solution of *n*BuLi (8.00 mL, 14.18 mmol), **1** (1.76 g, 14.18 mmol), and Ph_2PLi (prepared from Ph_2PH (2.61 g, 14.02 mmol) and a 1.77 M solution of *n*BuLi in hexane (7.92 mL, 14.02 mmol)). Compounds **3b** and **3c** were prepared similarly; like **3a** they are colorless, highly viscous, air-sensitive liquids; yield 54 % (**3a**), 62 % (**3b**), 56 % (**3c**). Characteristic data for **3a**: b.p. 210 °C (2.5 mbar); ^{31}P NMR: $\delta = -11.7$ (s); MS: *m*/*z* (%): 403 (26.9) $[M+1]^+$, 191 (10.9) $[tBu_2As+1]^+$, 187 (17.4) $[Ph_2P+1]^+$; **3b**: Sdp. 140 °C (2.5 mbar); MS: *m*/*z* (%): 351 (7.3) $[iPr_2P(O)CH_2CH_2AstBu_2+1]^+$; **3c**: b.p. 245 °C (2.5 mbar); ^{31}P NMR: $\delta = -11.6$ (s); MS: *m*/*z* (%): 455 (10.6) $[M+1]^+$, 243 (19.1) $[Cy_2As+1]^+$, 187 (30.5) $[Ph_2P+1]^+$.

(*R*)-**5a**: Preparation anologous to **2a**, from iPr_2PH (735 mg, 6.22 mmol), a 1.74 M solution of *n*BuLi (3.6 mL, 6.22 mmol), (*S*)-**4** (842 mg, 6.22 mmol), and Ph_2PLi (prepared from Ph_2PH (1.56 g, 6.22 mmol) and a 1.74 M solution of *n*BuLi in hexane (3.6 mL, 6.22 mmol)). Compound (*R*)-**5b** was obtained similarly; like (*R*)-**5a** it is a colorless, highly viscous, air-sensitive liquid; yield 37 % [(*R*)-**5a**], 36 % [(*R*)-**5b**]. Characteristic data for (*R*)-**5a**: b.p. 200 °C (2.5 mbar); optical rotation $[\alpha]_D^{20} = +201°$ (c 0.73, CH_2Cl_2); ^{31}P NMR: $\delta = 1.9$ (d, J(P,P) = 19.1 Hz; iPr_2P), 0.2 (d, J(P,P) = 19.1 Hz; Ph_2P); MS: *m*/*z* (%): 345 (28.8) $[M+1]^+$, 187 (9.7) $[Ph_2P+1]^+$, 119 (8.9) $[iPr_2P+1]^+$; (*R*)-**5b**: b.p. 235 °C (2.5 mbar); $[\alpha]_D^{20} = +167°$ ($c = 0.73$, CH_2Cl_2); ^{31}P NMR: $\delta = 1.2$ (d, J(P,P) = 19.1 Hz; Cy_2P), -8.2 (d, J(P,P) = 19.1 Hz; Ph_2P); MS: *m*/*z* (%): 426 (6.2) $[M+1]^+$, 199 (21.6) $[Cy_2P+1]^+$, 187 (27.6) $[Ph_2P+1]^+$.

(*R*)-**7**: Preparation anologous to **2a**, from tBu_2PH (2.19 g, 14.96 mmol), a 1.76 M solution of *n*BuLi (8.50 mL, 14.96 mmol), (*S*)-**6** (2.28 g, 14.96 mmol), and Ph_2PLi (prepared from Ph_2PH (2.79 g, 14.96 mmol) and a 1.76 M solution of *n*BuLi in hexane (8.50 mL, 14.96 mmol)). (*R*)-**7** was obtained as a colorless, highly viscous, air-sensitive liquid; yield 3.06 g (53 %); b.p. 200 °C (2.5 mbar); optical rotation $[\alpha]_D^{20} = +39°$ ($c = 0.86$, CH_2Cl_2); ^{31}P NMR: $\delta = 28.3$ (s; tBu_2P), -2.4 (s; Ph_2P); MS: *m*/*z* (%): 387 (100) $[M+1]^+$.

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[20] Crystal data of **10**$\cdot C_4H_8O$**:** $C_{36}H_{36}Cl_{10}O_3P_2Ru$, $M_r = 1034.16$, triclinic, space group $P\bar{1}$, $a = 12.381(4)$, $b = 13.088(2)$, $c = 14.374(4)$ Å, $\alpha = 66.69(2)$, $\beta = 80.19(2)$, $\gamma = 71.57(2)°$, $V = 2026.7(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.695$ Mg m^{-3}, $F(000) = 1040$, $\lambda = 0.71073$ Å, $T = 193(2)$ K, $\mu = 1.162$ mm^{-1}. The data were collected on an Enraf-Nonius-CAD4-diffractometer. The intenisty measurements were carried out on a shock-cooled crystal (0.5 × 0.4 × 0.2 mm) in an oil drop[25] according to the $2\theta/\omega$ scan method in the range $6° < 2\theta < 45°$. Of a total of 7185 reflections collected, 5269 were independent ($R_{int} = 0.0245$) and were used for the refinement of 481 parameters. Max./min residual electron density: 507/569 e nm^{-3}, $R1(F > 2\sigma(F)) = 0.035$ and $wR2 = 0.083$ (all data) with $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = (\Sigma w(F_o^2\text{-}F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. The structure was solved by Patterson methods (SHELXS-97)[26] and refined with full-matrix least-squares on F^2 (SHELXL-97).[27] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133284. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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