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Unexpected Regioselective Synthesis of 1,1-Diphosphinoethanes and Related Compounds via Hydrozirconation of Vinylphosphines

M. Zablocka,† A. Igau,† J.-P. Majoral,*,† and K. M. Pietrusiewicz*,‡

Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne,
31077 Toulouse Cédex, France, and Centre of Molecular and Macromolecular Studies,
The Polish Academy of Sciences, ul. Sienkiewicza 112, 90-363 Lodz, Poland

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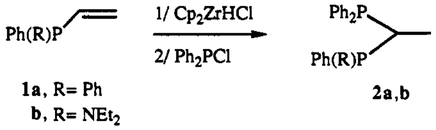
Summary: Hydrozirconation of vinylphosphines, $R_2PCH{=}CH_2$, and the corresponding phosphine oxides and sulfides, followed by addition of chlorodiphenylphosphine, led to the 1,1-diphosphinoethanes $R_2P(X)CH(CH_3)PPh_2$ (X = lone pair, O, S). Hydrozirconation of phospholene oxides 16 and 17 gave selectively the corresponding phospholene 18 and then the phospholane 19.

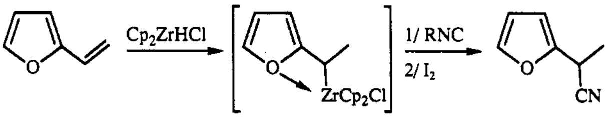
It is well-known that terminal alkylzirconation products are formed when Cp_2ZrHCl is reacted with alkenes even if the alkene is not terminal.[1] The regioselectivity for vinylarenes, 1,3-dienes, and vinyl ethers may be different, but these results are not unequivocal.[1] We thought that more information concerning the role of donor heteroatoms in α- or β-positions relative to the C=C unsaturation would be of interest in such reactions: do they significantly perturb the regiochemistry, and do the resulting heteroatom-containing alkylzirconium species behave similarly to those hydrozirconation products Cp_2ZrRCl in which no donor atoms are present?

We have shown in previous studies that hydro- or carbozirconation of low-coordinate phosphorus species leads to novel metallacycles as well as to new phosphorus, boron, or tin derivatives.[2] We describe here the unexpected, regioselective, one-pot synthesis of 1,1-diphosphinoethanes[3] and the reactivity of linear and cyclic vinyl- or allylphosphines and their corresponding oxides or sulfides toward Cp_2ZrHCl.

Treatment of a THF solution of phosphine **1a** or **1b** (1 equiv) with Cp_2ZrHCl (1 equiv) followed by addition of Ph_2PCl afforded the 1,1-diphosphinoethane **2a**[4,5] ($\delta(^{31}P)$ −6.5 ppm) or **2b** ($\delta(^{31}P)$ 71.1 (d), −31.9 (d), $^2J_{PP}$ = 170.2 Hz). No traces of 1,2-diphosphinoethane $Ph_2P(CH_2)_2PPh_2$ or $Ph[Et_2N]P(CH_2)_2PPh_2$ were detected by NMR (eq 1).



(1)



(2)

These results suggested at first sight that zirconation had taken place at the more hindered olefinic carbon atom, leading to the formation of alkylzirconium intermediates **3a,b**. Such an "abnormal" regioselectivity was already observed during the hydrocyanation of 2-vinylfuran[6] (eq 2). It was claimed that in the first step of the reaction, i.e., the hydrozirconation of 2-vinylfuran, the oxygen atom of the furan group acts as a donor site which forces the zirconium group $ZrCp_2Cl$ to add to the internal carbon of the vinyl system.

One could envisage a similar situation in our case with the phosphorus lone pair of **2a** or **2b** playing the same role as the oxygen of the furan group. However, on the basis of spectral evidence, the structure of the intermediates obtained by treatment of **1a,b** with Cp_2ZrHCl were

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† Laboratoire de Chimie de Coordination du CNRS.

‡ The Polish Academy of Sciences.

(1) Labinger, J.-A. *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, England, 1991; Vol. 8, p 667.

(2) (a) Majoral, J.-P.; Dufour, N.; Meyer, F.; Caminade, A.-M.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1990**, 507. (b) Dufour, N.; Majoral, J.-P.; Caminade, A.-M.; Choukroun, R.; Dromzee, Y. *Organometallics* **1991**, *10*, 45. (c) Boutonnet, F.; Dufour, N.; Straw, T.; Igau, A.; Majoral, J.-P. *Organometallics* **1991**, *10*, 3939. (d) Dufour, N.; Caminade, A.-M.; Basso-Bert, M.; Igau, A.; Majoral, J.-P. *Organometallics* **1992**, *11*, 1131.

(3) 1,1-Diphosphinoalkanes are excellent bridging ligands for the formation of homo- and heterobimetallic complexes as well as corresponding "A-frame" complexes: Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 94. Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191. For previous syntheses of 1,1-diphosphinoalkanes, see: Stelzer, O.; Langhans, K.-P. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed., Wiley: Chichester, England, 1990; Vol. 1, Chapter 8, pp 193–198.

(4) (a) Kraihanzel, C. S.; Maples, P. K. *J. Organomet. Chem.* **1976**, *117*, 159. (b) Van Der Ploeg, A. F. M. J.; Van Kloten, G. *Inorg. Chim. Acta* **1981**, *51*, 225.

(5) Preparation of **2a**: To a magnetically stirred solution of **1a** (190 mg, 0.9 mmol) in 5 mL of THF, prepared in a Schlenk flask under an inert atmosphere and cooled to −78 °C, was introduced slowly via cannula a suspension of Cp_2ZrHCl (255 mg, 0.99 mmol) in 10 mL of THF. The resulting pale yellow reaction mixture was kept at −78 °C for 0.5 h and then was warmed slowly to room temperature. During that time the mixture turned to orange-brown and became homogeneous. After it was stirred for an additional 2 h at ambient temperature, the mixture was cooled again to −78 °C. Diphenylchlorophosphine (198 mg, 0.90 mmol) was then added via syringe, and the reaction mixture was warmed slowly to room temperature. After ca. 2 h the resulting colorless solution was evaporated to dryness and the residue was extracted with pentane. Evaporation of pentane extracts gave crude **2a** (211 mg, 68%), of which the ^1H, ^{13}C and ^{31}P NMR spectra obtained matched exactly the pertinent literature data for **2a**.[4] The product can be further purified by recrystallization from EtOH: mp 113 °C (lit.[4] 113 °C). Preparation of **2b**: This compound was obtained by following exactly the above procedure: oil; yield 82%. Anal. Calcd for $C_{24}H_{29}NP_2$: C, 73.26; H, 7.43; N, 3.56; P, 15.74. Found: C, 73.11; H, 7.31; N, 3.49; P, 15.67. Selected NMR data: $^{13}C\{^1H\}$ NMR (δ, C_6D_6, TMS) 15.4 (d, J_{CP} = 6.2 Hz, $CHCH_3$), 47.9 (d d, J_{CP} = 15.4 Hz, J_{CP} = 14.8 Hz, CHP); ^{31}P NMR (δ, C_6D_6, H_3PO_4) 71.1 (d, J_{PP} = 170.2 Hz, Ph_2P), −31.9 (d, J_{PP} = 170.2 Hz, Ph_2P).

(6) Buchwald, S. L.; LaMaire, S. J. *Tetrahedron Lett.* **1987**, *28*, 295.

(7) **4a**, oil, selected NMR data: $^{13}C\{^1H\}$ (δ, C_6D_6) 33.3 (d, $^1J_{CP}$ = 19.2 Hz, PCH_2), 46.7 (s, CH_2Zr), 113.0 (s, Cp); ^{13}C (δ, C_6D_6) 33.3 (d, t, $^1J_{CP}$ = 19.2 Hz, $^1J_{CH}$ = 129.7 Hz, PCH_2), 46.7 (t, $^1J_{CH}$ = 121.0 Hz, CH_2Zr), 113.0 (d m, J_{CH} = 173.6 Hz, Cp); ^1H (δ, C_6D_6) 1.15 (m, CH_2), 2.46 (m, PCH_2). Anal. Calcd for $C_{24}H_{24}ClPZr$: C, 61.32; H, 5.14; P, 6.59. Found: C, 61.20; H, 5.03; P, 6.44. **4b**, oil, selected NMR data: $^{13}C\{^1H\}$ (δ, C_6D_6) 15.9 (d, $^3J_{CP}$ = 3.1 Hz, NCH_2CH_3) 33.5 (d, $^1J_{CP}$ = 21.2 Hz, PCH_2), 45.0 (d, $^2J_{CP}$ = 13.8 Hz, NCH_2CH_3), 47.2 (d, $^2J_{CP}$ = 4.1 Hz, CH_2Zr), 113.0 (s, CP); ^{13}C (δ, C_6D_6) 33.5 (d t, $^1J_{CP}$ = 21.2 Hz, $^1J_{CH}$ = 126.6 Hz, PCH_2), 47.2 (d, $^2J_{CP}$ = 4.1 Hz, $^1J_{CH}$ = 121.0 Hz, CH_2Zr), 113.0 (d m, J_{CH} = 171.0 Hz, Cp); ^1H (δ, C_6D_6) 1.25 (m, CH_2), 2.29 (m, PCH_2). Anal. Calcd for $C_{22}H_{29}ClPZr$: C, 58.57; H, 6.48; P, 6.86. Found: C, 58.39; H, 6.34; P, 6.77.

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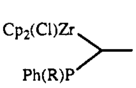
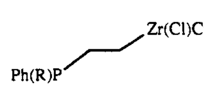
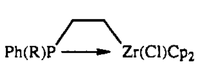
established to be **4a,b**.[7] Their ^1H and ^{13}C spectra were found to be fully consistent with the presence of $(CH_2)_2$ groups and not $CHCH_3$ groups in the two compounds. Also, the corresponding ^{31}P NMR spectra exhibited a singlet at δ −8.5 ppm for **4a** and at +62.4 ppm for **4b**, i.e., in the expected range for linear phosphines of type **4** and not for cyclic complexes of type **5**.[8] Moreover, formation of **5** can be excluded since coupling between protons of the Cp groups and the phosphorus atom should have been observed, as for example was found for compounds **6** and **7** (**6**, two doublets for the Cp groups, J_{HP} = 2.7, 1.9 Hz; **7**, two doublets for the Cp groups, J_{HP} = 2.4, 1.9 Hz).[2a,d]


3a,b


4a,b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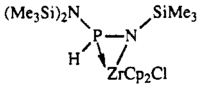
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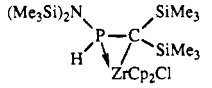
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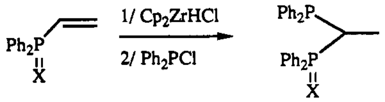
Migration of the metal group along the carbon chain by a sequence of reversible additions and eliminations involving β-hydrogen was reported to be facile[1] and could be invoked here in order to explain the eventual formation of compounds **2a,b** from **4a,b**. However, such a mechanistic proposal is at the moment debatable and requires additional experiments. Moreover, we have found that the closely related hydrozirconation of $Ph_2PCH_2CH{=}CH_2$, followed by addition of Ph_2PCl affords the expected terminal substitution product, $Ph_2P(CH_2)_3PPh_2$.

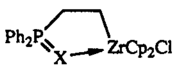
Reactions similar to those observed for **1a,b** occurred when the corresponding vinylphosphine oxide **8** or sulfide **9** was treated first with CP_2ZrHCl and then with Ph_2PCl: compound **10**[9] (δ(^{31}P) 31.4 (d), −10.1 (d), $^2J_{PP}$ = 64.4 Hz) or **11**[9] (δ(^{31}P) 50.9 (d), −12.5 (d), $^2J_{PP}$ = 95.0 Hz) was obtained in 85 or 65% yield, respectively (eq 3). Again, no traces of $Ph_2P(X)CH_2CH_2PPh_2$ (X = O, S) were detected by ^{31}P NMR. However, monitoring these reactions by ^{31}P NMR and IR spectroscopy revealed that, in marked contrast to the hydrozirconation of vinylphosphines **1a,b**, the hydrozirconation of the oxide **8** led to the cyclic product **12** and not to the linear compound **13**. In ^{31}P NMR, the resulting product exhibited a resonance at 51.2 ppm (to be compared with **8**, δ 18.7 ppm, and $Ph_2P(O)CH_2CH_3$, δ 28.3 ppm) while the ν_{PO} band in the IR spectrum (KBr pellet) was shifted from 1179 (**8**) to 1168 cm^{-1}.[10] Such significant deshielding in the ^{31}P NMR spectrum was not observed during the hydrozirconation of the sulfide **9**, suggesting that the formation of the linear derivative **15** rather than the cyclic **14** (**9**, δ 35.9; **15**, δ 44.9; $Ph_2P(S)CH_2CH_3$, δ 44.0 ppm) took place. It should also be noted that 1,1-diphosphinoethane **2a** was formed as a minor product (10%) in the reaction leading to sulfide **10**, while no reduction occurred during the formation of the corresponding oxide **11**.

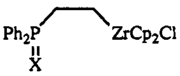


8, 9 **10, 11**

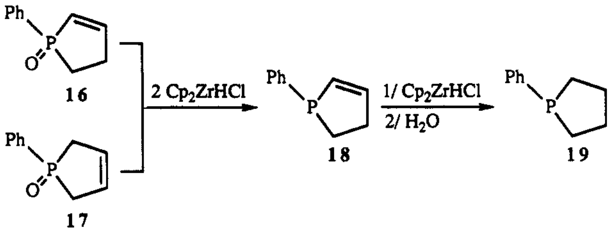
8, 10 X= O
9, 11 X= S

(3)


12 X= O
14 X= S


13 X= O
15 X= S

Due to the lower reactivity of cyclic alkenes toward Cp_2ZrHCl, it was possible to selectively reduce phospholene oxides **16** and **17** to phospholene **18**,[11] without concomitant reduction of the double bond by treatment of **16** and **17** (1 equiv) with 2 equiv of Cp_2ZrHCl (eq 4); this reduction was unexpectedly accompanied by the migration of the double bond in the case of **17**. On the other hand, addition of 3 equiv of Cp_2ZrHCl to **16** or **17** or addition of 1 equiv of Cp_2ZrHCl to **18**, followed in each case by careful hydrolysis of the resulting mixture, led to the phospholane **19**[12] isolated in 76% yield.



16 **17** **18** **19**

(4)

Mechanistic studies and extension to other substrates are underway.

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(8) A deshielding effect in ^{31}P NMR spectroscopy (Δδ 40 ppm) is generally observed when one moves from a linear phosphine to the corresponding P-metalated cyclic phosphine: $Me_2PCH_2ZrCp_2Cl$, δ −36.2; $Me_2PC(SiMe_3)_2ZrCp_2Cl$, δ 2.7;[13] $(Me_3Si)_2NPHCH_2SiMe_3$, δ 3.2; $(Me_3Si)_2NP(H)C(SiMe_3)_2ZrCp_2Cl$, δ 42.0. On the other hand, compound **4a** exhibits a ^{31}P NMR chemical shift close to those of the related acyclic phosphines $Ph_2PCH{=}CH_2$ (δ −11.5 ppm) and $Ph_2PC_2H_5$ (δ −12.0 ppm). The same situation occurs for **4b** and $Ph(NEt_2)PCH{=}CH_2$ (δ 58.0 ppm).

(9) Grim, S. O.; Satelc, L. C.; Mitchell, J. D. *Z. Naturforsch.* **1980**, *35B*, 832.

(10) In a series of $L_4M(ClO_4)_2$ complexes in which M = Mn, Fe, Co, Ni, Cu, Zn and L = $Ph_3P{=}O$, $(Me_2N)_3P{=}O$, the average Δν(P=O) values of −49 and −18 cm^{-1}, respectively, were observed upon complexation (Karayannis, N. N.; Mikulski, C. M.; Pytlewski, L. L. *Inorg. Chim. Acta Rev.* **1971**, *5*, 69. Hunter, S. H.; Nyholn, R. S.; Rodley, G. A. *Inorg. Chim. Acta* **1969**, *3*, 631). For a recent discussion on the use of Δν(P=O) as a probe for complexation, see: Goggin, P. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England 1987; Vol. 2, Chapter 15.8, pp 500–501.

(11) Compound **18** (δ(^{31}P) −2.0 ppm) was identified by internal spectral comparison with an authentic sample obtained by reduction of **16** with $PhSiH_3$ and was also reoxidized to give **16**.

(12) Preparation of **19**: Into a nitrogen-flushed Schlenk flask containing 337 mg (1.89 mmol) of **16** in 5 mL of THF cooled to −78 °C was cannulated a suspension of Cp_2ZrHCl (1.03 g, 3.94 mmol) in THF (10 mL). The reaction mixture was kept at −78 °C for 0.5 h and then at room temperature for ca. 3 h. To the resulting homogeneous orange-brown solution was cannulated the third equivalent of Cp_2ZrHCl (490 mg, 1.89 mmol, suspension in 5 mL of THF), and the reaction mixture was kept at room temperature for 20 h. After the reaction was quenched with wet THF, the volatiles were removed in vacuo and the dark brown residue was extracted with pentane (5 × 10 mL). Evaporation of pentane extracts followed by Kugelrohr distillation of the oily residue gave pure **19** (236 mg, 76%), bp 60 °C/0.05 Torr (oven temperature) (lit. 73 °C/0.5 Torr), the recorded ^1H, ^{13}C and ^{31}P NMR spectra of which were found in complete accord with the pertinent literature data for **19**:[14] ^1H NMR (δ, $CDCl_3$, TMS) 1.82 (m, 4H), 2.10 (m, 4H), 7.07 (m, 3H), 7.45 (m, 2H); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, TMS) 27.2 (d, J_{CP} = 14.0 Hz), 27.7 (d, J_{CP} = 14.0 Hz), 127.1, 128.2 (d, J_{CP} = 4.8 Hz), 130.3 (d, J_{CP} = 15.6 Hz), 142.6 (d, J_{CP} = 25.0 Hz); ^{31}P NMR (δ, $CDCl_3$, H_3PO_4) −16.3.

(13) Karsch, H. H.; Deubelly, B.; Hofmann, I.; Pieper, U.; Muller, G. *J. Am. Chem. Soc.* **1988**, *110*, 3654.

(14) (a) Sommer, K. *Z. Anorg. Allg. Chem.* **1970**, *579*, 56. (b) Gray, G. A.; Cremer, S. E.; Marsi, K. L. *J. Am. Chem. Soc.* **1976**, *98*, 2109.