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Selective P–N bond cleavage in chiral triquinphosphoranes promoted by zirconocene complexes

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Abstract

Chiral bicyclic phosphanes incorporating a five- and an eight-membered ring were prepared via selective P–N bond cleavage of chiral triquinphosphoranes induced by dimethylzirconocene Cp_2ZrMe_2 or diphenylzirconocene Cp_2ZrPh_2. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Zirconium derivatives were found to be useful tools in the preparation of linear or cyclic phosphorus compounds [1]. We have very recently developed a large variety of new zirconium-promoted ring-opening reactions [2]. This new method was applied to triquinphosphoranes derivatives as rare examples of their open tautomers were observed [3].

We have previously shown [4] that the NMR spectroscopic data of the triquinphosphoranes are consistent with either a time-averaged spectrum characteristic of a low-energy Berry pseudo-rotation process [5] with the hydrogen atom as the pivot between the two possible diastereomeric trigonal pyramid structures (TBP (R_P), TBP (S_P)) [6], with epimerization at the phosphorus atom and interchange of the anisochronous atoms of the tricyclic structure or the chiral square pyramidal structure (SP) (Scheme 1). In the TBP structure the five-membered rings are in apical–equatorial positions with one nitrogen atom in the uncustomary apical position [7]; in the SP structure the five-membered rings occupy basal positions.

We describe here the preparation of chiral phosphane compounds **2a**–**c** and **3** from triquinphosphoranes via zirconocene complexes.

2. Results and discussion

An equimolar amount of triquinphosphoranes **1a**–**c** and $[Cp_2ZrMe_2]$ were treated in refluxing toluene. ^{31}P-NMR showed the formation of **2a**–**c** with the presence of some remaining hydridophosphorane starting compounds **1a**–**c**. Addition of half an equivalent of $[Cp_2ZrMe_2]$ helps the reaction to go to completion. Then the $^{31}P\{^1H\}$-NMR spectra of the reactions exhibit only one single low-field signal ($\delta = 130$) for the compounds **2a**–**c**, characteristic of tri-coordinated phosphorus compounds; no $^1J_{PH}$ coupling constant was observed. ^1H- and ^{13}C-NMR data of the Cp groups showed that two different zirconocene fragments $[Cp_2Zr]$ are present in the isolated compounds **2a**–**c**. ^1H-NMR integration of the Cp and ZrMe groups is in agreement with the stoichiometry used for the reaction. Then the proposed structure for **2a**–**c** is the following (Scheme 2). One of the two metal centers is connected on a nitrogen atom of the phosphorus derivative skeleton resulting from the loss of methane during the reaction sequence; the other one, corresponding to a Cp_2ZrMe_2 moiety, is most likely coordinated to two bicyclic oxazaphospholidine zirconium complexes by the basic oxygen sites. The formation of such dimer complexes is due to the oxophilicity of the zirconium. Unfortunately no suitable crystals for X-ray analysis were obtained to confirm this assumption. An identical reaction under the same experimental conditions described for the preparation of **2a**–**c** was performed with

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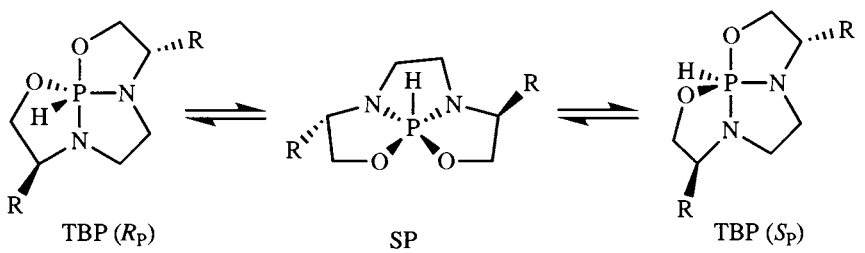
$[Cp_2ZrPh_2]$ and **1a**. The phosphane–zirconocene complex **3** was obtained in 85% isolated yield. Note that non-substituted triquinphosphorane (R = H) gave a multitude of products when reacted with $[Cp_2ZrR'_2]$ (R′ = Me, Ph). In marked contrast **1d** does not react with the same zirconocene complexes $[Cp_2ZrR'_2]$ (R′ = Me, Ph).

As for the borane addition on the triquinphosphoranes, **1** [3,8], Cp_2ZrMe_2 reacted on the apical nitrogen atom of the TBP in the *anti* position with respect to the pseudoapical substituent R bonded to the oxazaphospholidine ring. As for the addition of isocyanate compounds [8], this reaction led to tricoordinated phosphorus bicyclic compounds **2a–c**, **3** including an oxazaphospholidine ring and a eight-membered ring. The ring opening occurred with a total diastereoselectivity with a R_P absolute configuration at the phosphorus atom. In the same way, **1d** showed no reactivity toward electrophiles. This lack of reactivity may be due to the extreme steric hindrance exhibited by this compound.

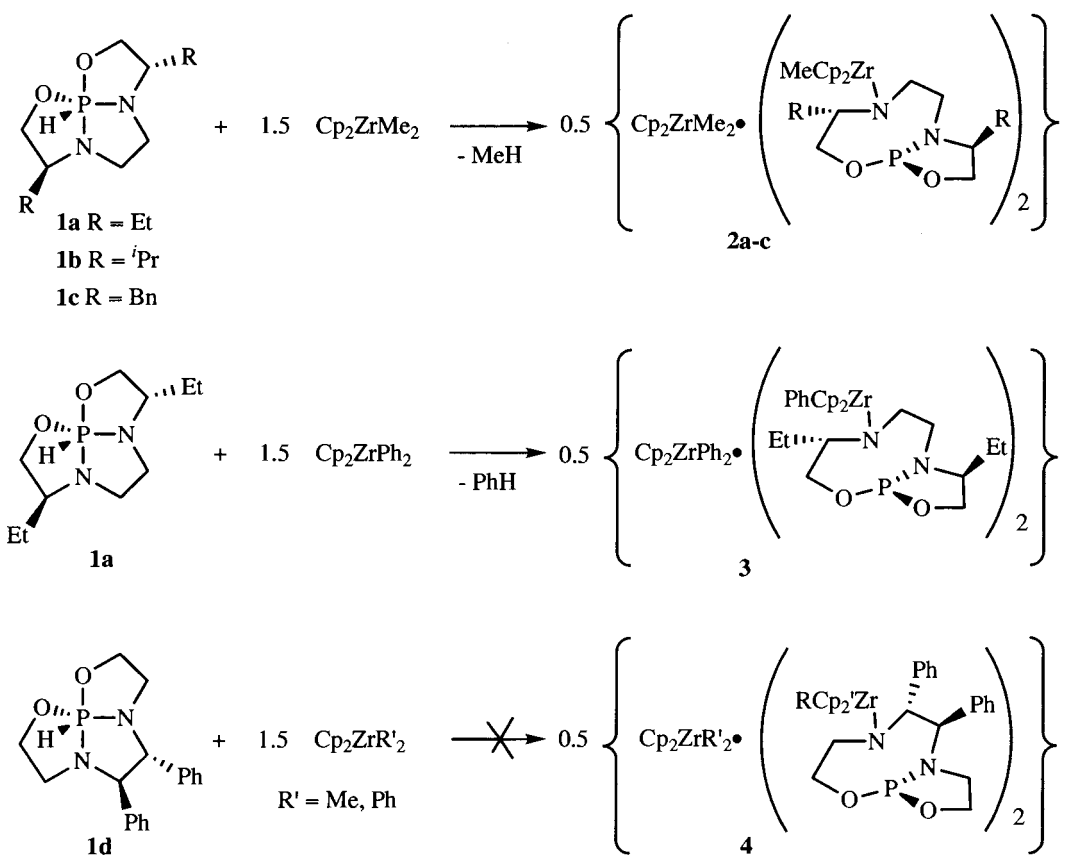
Cleavage with H^+ of the zirconium–nitrogen bond in **2a** gave back the corresponding starting compound **1a** in quantitative yield (Scheme 2).

In order to keep the open structure, addition of $W(CO)_5THF$ to **2a** was performed and **6** was identified by $^{31}P\{^1H\}$-NMR (δ 143.6) and isolated after treatment with methanol as the final product **7** (Scheme 3).

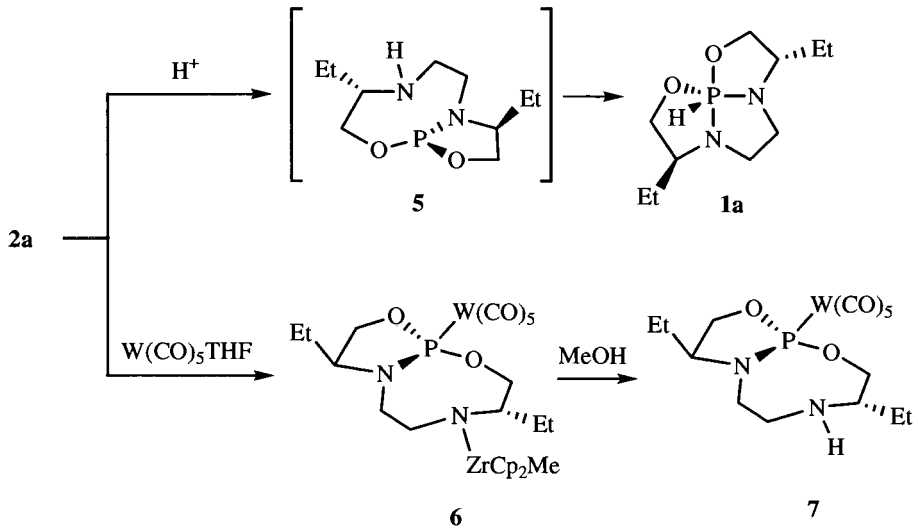
Studies of the properties of the chiral cyclic phosphanes reported here and further work on ring-opening reactions induced by zirconocene complexes are in progress.



Scheme 1.



Scheme 2.



Scheme 3.

3. Experimental

3.1. General

All manipulations were carried out under an argon atmosphere, either on a high-vacuum line using standard Schlenk techniques or in a Braun MB 200-G drybox. Solvents were freshly distilled from sodium (toluene, MeOH) and lithium aluminum hydride (pentane). MeOH was used as received. C_6D_6 and $CDCl_3$ were treated, respectively, with $LiAlH_4$ and CaH_2, distilled, and stored under argon. Cp_2ZrMe_2 [9] and Cp_2ZrPh_2 [10] were prepared as described in the literature. NMR spectra were recorded at 25°C on Bruker AMX 400, WM-250, AC-200, and AC-80 Fourier transform spectrometers. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants (J) are given in Hertz. The ^{13}C-NMR assignments were confirmed by proton-decoupled and/or selective heteronuclear-decoupled spectra.

3.2. Compounds (2a–c)

3.2.1. General procedure

As an example, a Schlenk flask was charged with **1a** (88 mg, 0.38 mmol), toluene (10 ml), and a stir bar. Then a solution of Cp_2ZrMe_2 (137 mg, 0.57 mmol, 1.5 equiv.) in toluene (5 ml) was added. The mixture was stirred under reflux for 4 h. Removal of the solvent in vacuo gave a yellow oil, which was extracted with pentane (2 × 10 ml) to afford **2a** in 95% isolated yield. **2a**: $^{31}P\{^1H\}$-NMR (C_6D_6): δ 130.1. ^1H-NMR (C_6D_6): δ 0.23 (s, 6H, NZrMe), 0.25, 0.28 (s, 3H, ZrMe), 0.84 (t, J(HP) = 7.4 Hz, 6H, Me), 0.93 (t, J(HP) = 7.3 Hz, 6H, Me), 1.20–1.52 (m, 8H, CH_2), 2.30–2.38 (m, 2H, NCH), 2.51–2.64 (m, 4H, NCH_2), 2.67–2.79 (m, 2H, NCH), 3.11–3.22 (m, 4H, NCH_2), 3.36–3.52 (m, 4H, $POCH_2$), 3.81–3.98 (m, 4H, $POCH_2$), 5.75 (s, 10H, OZrCp), 5.81, 5.83 (s, 10H, NZrCp). ^{13}C-NMR ($CDCl_3$): δ 11.6, 11.8 (s, Me), 19.9 (s, $OZrMe_2$), 23.4 (d, J(CP) = 6.2 Hz, CH_2), 29.7 (s, CH_2), 30.8 (s, NZrMe), 44.9 (d, J(CP) = 5.0 Hz, NCH_2), 56.7 (d, J(CP) = 9.0 Hz, NCH_2), 60.7 (d, J(CP) = 21.7 Hz, CH), 67.8 (d, J(CP) = 5.1 Hz, CH), 70.0 (d, J(CP) = 8.4 Hz, $POCH_2$), 78.4 (d, J(CP) = 3.1 Hz, $POCH_2$), 110.0, 110.3, 111.0, 111.2 (ZrCp). **2b**: 95%, $^{31}P\{^1H\}$-NMR (C_6D_6): δ 129.7. ^1H-NMR (C_6D_6): δ 0.25 (s, 6H, NZrMe), 0.33, 0.38 (s, 3H, ZrMe), 0.84–0.90 (m, 24H, Me), 0.99–1.10 (m, 4H, C*H*Me), 2.30–2.50 (m, 4H, NCH_2), 2.70–2.90 (m, 4H, NCH_2), 3.43–3.52 (m, 2H, NCH), 3.62–3.78 (m, 2H, NCH), 3.95–4.20 (m, 4H, $POCH_2$), 3.95–4.20 (m, 4H, $POCH_2$), 5.73 (s, 10H, $OZrCp_2$), 5.82, 5.89 (s, 10H, NZrCp). ^{13}C-NMR ($CDCl_3$): δ 19.4, 19.9, 20.1, 20.3 (s, Me), 20.2, 20.5 (s, $OZrMe_2$), 28.0 (d, J(CP) = 5.5 Hz, $CHCH_3$), 29.7 (s, $NCHCH_2$), 33.7 (s, NZrMe), 44.9 (d, J(CP) = 5.0 Hz, NCH_2), 56.7 (d, J(CP) = 9.0 Hz, NCH_2), 60.7 (d, J(CP) = 21.7 Hz, CH), 67.8 (d, J(CP) = 5.1 Hz, CH), 70.0 (d, J(CP) = 8.4 Hz, $POCH_2$), 78.4 (d, J(CP) = 3.1 Hz, $POCH_2$), 110.2, 110.3, 110.7, 111.1 (ZrCp). **2c**: 95%, $^{31}P\{^1H\}$-NMR (C_6D_6): δ 130.6. ^1H-NMR (C_6D_6): δ 0.25 (s, 6H, NZrMe), 0.37, 0.38 (s, 3H, ZrMe), 1.20–1.38 (m, 8H, $NCHCH_2$), 2.38–2.61 (m, 4H, NCH_2), 2.79–2.97 (m, 6H, NCH_2 and NCH), 3.24–3.32 (m, 2H, NCH), 3.49–3.63 (m, 4H, $POCH_2$), 3.95–4.18 (m, 4H, $POCH_2$), 5.75 (s, 10H, $OZrCp_2$), 5.82, 5.83 (s, 10H, NZrCp), 7.02–7.21 (m, 20H, Ph). ^{13}C-NMR

($CDCl_3$): δ 19.2, 19.7 (s, OZrMe), 30.7 (s, NZrMe), 38.2 (d, $J(CP) = 5.5$ Hz, NCH), 42.8 (s, PhCH_2), 46.5 (d, $J(CP) = 3.9$ Hz, NCH_2), 56.1 (d, $J(CP) = 8.2$ Hz, NCH_2), 61.3 (d, $J(CP) = 21.5$ Hz, CH), 67.6 (d, $J(CP) = 5.6$ Hz, CH), 69.0 (d, $J(CP) = 8.0$ Hz, $POCH_2$), 77.5 (s, $J(CP) = 4.1$ Hz, $POCH_2$), 110.8, 111.0, 111.1, 111.7 (ZrCp), 129.7, 129.9, 130.1, 131.2, 131.3, 141.2, 141.5 (s, Ph).

3.3. Compound (3)

A Schlenk flask was charged with **1** (116 mg, 0.50 mmol), toluene (10 ml), Cp_2ZrPh_2 (282 mg, 0.75 mmol, 1.5 equiv.), and a stir bar. The reaction mixture was stirred at 80°C for 3.5 h. Volatiles were removed in vacuo. The residue was washed with pentane (2×20 ml) to give **3** as a clear brown solid in 85% isolated yield. $^{31}P\{^1H\}$-NMR (C_6D_6): δ 130.6. ^1H-NMR (C_6D_6): δ 0.82–0.97 (m, 12H, Me) 1.18–1.55 (m, 8H, NCHCH_2), 2.25–2.78 (m, 8H, NCH_2), 3.12–3.58 (m, 6H, POCHH′ and CH), 3.97–4.07 (m, 4H, $POCH_2$), 4.29–4.33 (m, 2H, POCHH'), 5.86 (s, 10H, OZrCp), 5.95, 5.96 (s, 10H, NZrCp), 7.14–7.24 and 7.28–7.48 (m, 20H, Ph). ^{13}C-NMR ($CDCl_3$): δ 11.5, 11.7 (s, Me), 23.7, 24.5 (s, NCHCH_2), 44.9 (d, $J(CP) = 4.8$ Hz, NCH_2), 56.5 (d, $J(CP) = 7.9$ Hz, NCH_2), 61.0 (d, $J(CP) = 21.6$ Hz, CH), 67.7 (d, $J(CP) = 4.0$ Hz, CH), 69.8 (d, $J(CP) = 8.7$ Hz, $POCH_2$), 77.9 (s, $POCH_2$), 112.1, 112.4 (NZrCp), 125.1, 127.5, 128.0, 133.7, 139.1, 139.4 (s, Ph).

3.4. Compound (7)

A 7×10^{-3} solution of $W(CO)_5THF$ (83 ml, 0.6 mmol) was transferred to **2a** (116 mg, 0.5 mmol) and stirred for 3 h at room temperature. $^{31}P\{^1H\}$-NMR showed the formation of the expected compound **6** (δ ^{31}P 143.6). The reaction mixture was then concentrated to 5 ml and **6** was treated with an excess of methanol (10 equiv.) to give **7**. Removal of the solvents led to an air stable solid, which was purificated through column chromatography on silica gel (eluent: CH_2Cl_2). **7** was obtained in 80% isolated yield as a pale yellow solid. $^{31}P\{^1H\}$-NMR (C_6D_6): δ 129.5 (d, $^1J(PW) = 227$ Hz). ^1H-NMR (C_6D_6): δ 0.89 (t, $J(HP) = 7.4$ Hz, 3H, Me), 0.94 (t, $J(HP) = 7.3$ Hz, 3H, Me), 1.20–1.58 (m, 4H, NCHCH_2), 2.81–3.40 (m, 5H, NCH and NCH_2), 3.67–4.36 (m, 5H, $POCH_2$ and NCH). ^{13}C-NMR ($CDCl_3$): δ 9.8, 10.7 (s, Me), 25.3, 25.4 (s, NCHCH_2), 46.3 (d, $J(CP) = 7.3$ Hz, NCH_2), 48.8 (s, NCH_2), 61.5, 61.9 (s, CH), 70.1 (d, $J(CP) = 9.2$ Hz, $POCH_2$), 70.8 (d, $J(CP) = 8.9$ Hz, $POCH_2$), 196.7 (d, $J(CP) = 11.4$ Hz, CO).

Acknowledgements

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