One pot synthesis of mono- or bi-cyclic phosphiranes and phosphirenes

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Treatment of phospholene oxide 1, vinylphosphine oxide 11 or alkynylphosphine oxide 14 with $[Cp_2Zr]$ 2 followed by addition of a chlorophosphine leads to various phosphiranes and phosphirenes.

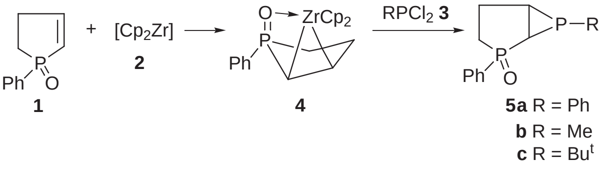
The heterocyclic chemistry of phosphorus is underdeveloped in comparison with its oxygen, nitrogen and sulfur counterparts in spite of the fact that a number of phosphorus rings appear to be useful reagents and ligands. Indeed, a recent review covers the rich and versatile chemistry of three-membered carbon–phosphorus heterocycles.[1] Several routes for the preparation of these derivatives, namely phosphiranes, phosphirenes, diphosphiranes, diphosphirenes and related species, have been reported. In contrast only a few syntheses of fused ring systems incorporating at least one phosphirane ring and another phosphorus containing heterocycle are known.

In the course of our studies devoted to the use of zirconium derivatives as tools in organic, organometallic and main group element chemistry,[2] we developed a new method for the preparation of fused ring systems involving phospholene oxide **1**, zirconocene $[Cp_2Zr]$ **2** and dichlorophosphines $RPCl_2$ **3**. Such a methodology can be extended to the synthesis of various substituted phosphiranes and phosphirenes. We report here the general one pot preparation of some of these new compounds.

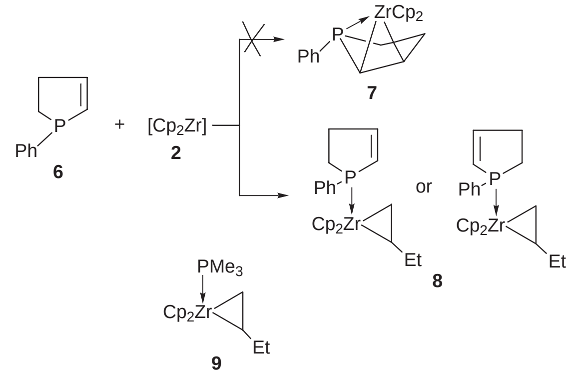
Treatment of phospholene oxide **1** with $[Cp_2Zr]$ **2**[3]—prepared *via* the reaction of Cp_2ZrCl_2 with 2 equiv. of Bu^nLi at −78 °C in THF—leads to the formation of the zirconacyclopropaphospholane oxide **4** (Scheme 1). The ^{31}P NMR spectrum of **4** exhibits a resonance at δ 81.5 (compared with **1**, δ = 62.0). Such a significant deshielding effect suggests the participation of the phosphoryl group to the stabilization of the resulting zirconium complex **4**.[4] This assumption is corroborated by IR spectroscopy: the ν(PO) band is shifted from 1193 (**1**) to 1162 cm^{-1} (**4**).[5] Compound **4** is further characterized by ^1H NMR as well as by ^{13}C NMR spectroscopy, which shows, for example, the expected deshielded signals for the carbon atoms directly linked to zirconium.[6] Addition of phenyl(dichloro)phosphine to **4** in THF at −78 °C proceeds with removal of Cp_2ZrCl_2 and formation of the phosphiranophospholane oxide **5a** [δ_P 60.6 and −177.4 (d, J_{PP} 8.3 Hz)]. The shielded signal at δ −177.4 is typical for a phosphirane structure,[1,7] while the resonance at δ 60.6 fits well with the phospholane part of **5a**. Such a bicyclic structure is corroborated by ^{13}C NMR analysis.[6]

A similar exchange reaction involving **4** and either methyl- or *tert*-butyl-(dichloro)phosphine affords the fused bicyclic systems **5b** or **5c**, respectively [**5b**: δ_P 63.6 and −191.1 (d, J_{PP} 7.1 Hz); **5c**: δ_P 55.0 and −174.8 (d, J_{PP} 30.1 Hz)] (Scheme 1).

It should be emphasized that, in marked contrast to the behaviour of **1** towards **2**, the phospholene **6** does not give the expected zirconacyclopropaphospholane derivative **7**, but instead the zirconocene complex **8** (Scheme 2) is characterized. The structure of **8** can be unambiguously established by NMR analysis.[6] Investigation of the $[Cp_2ZrCl_2 + 2Bu^nLi]$ reaction has been found to give $Cp_2Zr(nBu)_2$ at −78 °C, which then decomposes to give $Cp_2Zr(CH_2{=}CHEt)$ (the effective source of **2**) identified as its PMe_3 complex **9**.[8] Therefore compound **6** plays the role of PMe_3 and the olefinic part of **6** is not involved in the reaction. Addition of phenyl(dichloro)phosphine to **8** gives **6** and the products of the reaction of zirconocene **2** with phenyl(dichloro)phosphine, *i.e.* $(PhP)_4$ and $(PhP)_5$.



Scheme 1

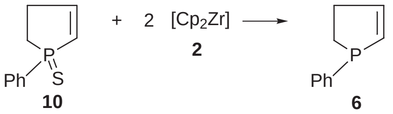


Scheme 2

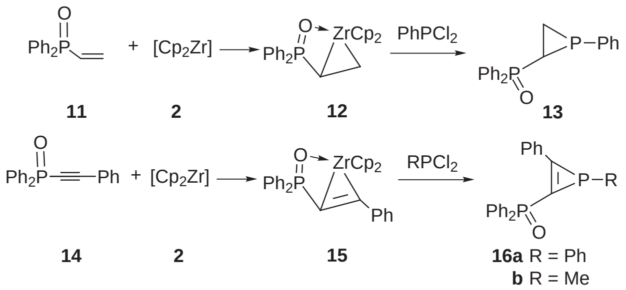
It should also be noted that the reaction of the phospholene sulfide **10** with **2** proceeds quite differently: only desulfurization occurs with the formation of **6**[9] (Scheme 3).

This demonstrates clearly, for the first time, the key role played by a phosphoryl group for the stabilization of intermediates and for the orientation of reactions involving phosphorus derivatives and zirconium species. Up to now only the dramatic influence of the phosphorus lone pair of phosphines has been pointed out.[10]

The same remarkable behaviour is found when the linear vinylphosphine oxide **11** is treated with **2** and then with phenyl(dichloro)phosphine. The reaction proceeds *via* the formation of the zirconium complex **12** (δ_P 47)[4] to give the phosphirane **13** [δ_P 31.3 and −178.3 (d, J_{PP} 30 Hz)][6] (Scheme 4). Such a reaction is not limited to olefinic systems. Indeed addition of the acetylenic phosphine oxide **14** to a THF solution of **2** at −78 °C leads to the fully characterized zirconacyclopropene species **15**.[4,6] Further addition of phenyl- or methyl-(dichloro)phosphine to **15** gives new phosphirene derivatives **16a** or **16b**, respectively (Scheme 4). No traces of phosphirane or phosphirene is detected when the same reactions are conducted with the corresponding linear vinyl or acetylenic phosphines instead of the phosphine oxides **11** or **14**.



Scheme 3



Scheme 4

Mechanistic studies and extension of these reactions to other substrates are underway.

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Notes and References

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3 For recent reviews on zirconocene, see for example: Y. Hanzawa, H. Ito and T. Taguchi, *Synlett*, 1995, 299; A. Ohff, S. Pulst, C. Lefeber, N. Peulecke, P. Arndt, V. V. Burkalov and U. Rosenthal, *Synlett*, 1996, 111 references cited therein.

4 A dimeric form cannot be totally ruled out for **4**, **12** and **15**.

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6 Selected data for **4**: δ_C(CDCl$_3$) 41.0 (d, J_{PC} 96.0, PCHZr), 58.1 (d, J_{PC} 13.5, CHZr), 33.2 (d, J_{PC} 19.2, CH$_2$), 29.0 (d, J_{PC} 73.6, PCH$_2$). For **5a**: δ_C 26.3 [dd, $J_{P(O)C}$ 16.5, J_{PC} 38.0, P(O)CHP], 24.7 (d, J_{PC} 51.0, CHP), 24.3 [d, J_{PC} 71.8, P(O)CH$_2$], 22.5 (d, J_{PC} 7.5, CH$_2$). For **8**: δ_C 21.6 (s, CH$_3$), 22.4 (d, J_{PC} 12.2, ZrCH$_2$), 35.6 (s, ZrCH*C*H$_2$), 39.4 (d, J_{PC} 18.2, PCH$_2$*C*H$_2$), 40.0 (d, J_{PC} 18.7, PCH$_2$), 41.8 (d, J_{PC} 3.3, ZrCH). For **13**: δ_C 28.2 (dd, J_{PC} 29.0, J_{PC} = 13.0, CH), 25.5 (dd, J_{PC} 13.5, J_{PC} 2.9, CH$_2$). For **15**: δ_C 153.5 [d, $^1J_{PC}$ 59.7, P(O)CZr], 148.3 (d, J_{PC} 6.1, ZrCPh). For **16a**: δ_C 145.0 [dd, J_{PC} 53.2, $J_{P(O)C}$ 10.2, P(O)C=], 139.6 (dd, J_{PC} 62.6, $J_{P(O)C}$ 2.7, PCPh).

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8 Compound **9** was isolated as two isomers (PMe$_3$/Et *cis* or *trans*) (refs. 11, 12). According to NMR spectroscopy only the *trans* isomer for **8** was formed. However, these data do not allow the determination of the position of the C=C π-system in the phospholane ring with respect to the zirconacyclopropane fragment.

9 Full desulfurisation occurs when 1 equiv. of **1b** is treated with 2 equiv. of **2**.

10 See for example: M. Zablocka, F. Boutonnet, A. Igau, F. Dahan, J.-P. Majoral and K. M. Pietrusiewicz, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1735; M. Zablocka, A. Igau, N. Cénac, B. Donnadieu, F. Dahan, J.-P. Majoral and K. M. Pietrusiewicz, *J. Am. Chem. Soc.*, 1995, **117**, 8083.

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