

Stereoselective synthesis of 2-phosphino-1-zirconaindenes and related 2-phosphinophospholes and stiboles

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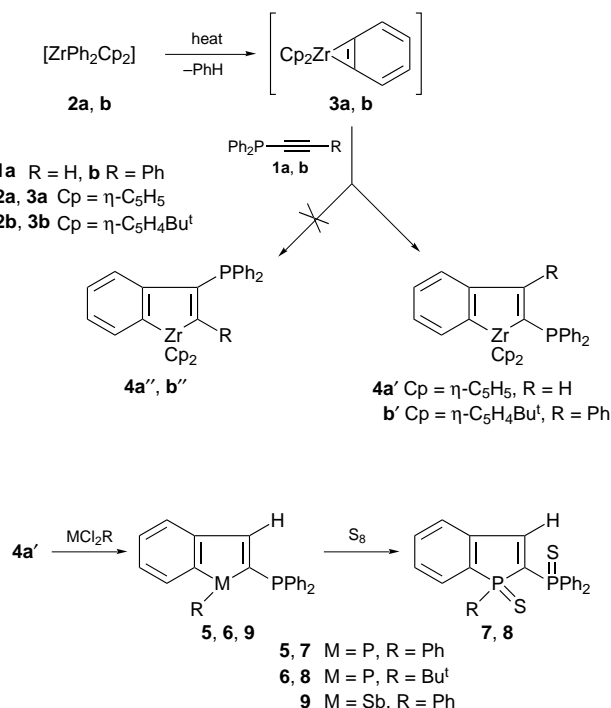
2-Phosphinophospholes and stiboles are prepared from the reaction of benzynezirconocene with alkynylphosphines followed by addition either of dichlorophosphines or a dichlorostibene.

The development of new and practical methods of stereoselective synthesis of main-group element derivatives is currently among the major objectives of a number of research groups throughout the world. Our ongoing investigations concern the study of interactions between group IV element and main-group element species¹ and are focused on the discovery of new methodologies of ring formation, opening or expansion but also on the preparation of ligands which have been regarded as laborious to prepare by conventional means.

The present report deals with an efficient synthesis of substituted zirconaindene compounds and their use as starting reagents for the formation of a variety of 2-phosphinophospholes and of a 2-phosphinostibole. Indeed phospholes² continue to attract considerable attention because of their use in different fields (*e.g.* catalysis, coordination chemistry) and therefore there is a need to diversify ways of preparation of these useful phosphorus heterocycles as well as the nature of these derivatives. To the best of our knowledge only one report described the preparation of a 2-thiophosphinophosphole which was obtained *via* a sequence of reactions involving metallation

of the 1-phenyl-3,4-dimethyl-2-thiophosphole followed by addition of diphenylchlorophosphane.³

Treatment of the alkynylphosphine **1a** with [ZrPh₂(η-C₅H₅)₂] **2a** in benzene at 80 °C for 6 h leads to the formation of a phosphinozirconaindene **4a** arising from insertion of the carbon–carbon triple bond of **1a** into a zirconium–carbon bond of the transient benzyne zirconocene **3a**. The reaction gave rise to only one phosphorus species as indicated by ³¹P NMR spectroscopy (**4a**, δ 6.9) (Scheme 1). **4a** was further characterized by ¹H and ¹³C NMR† but the spectroscopic data did not distinguish between the two possible structures for **4a**: the 2-phosphinozirconaindene form **4a'** or the 3-phosphinozirconaindene form **4a''**. In order to have a better knowledge of the structure of **4a**, exchange reactions with phenyl or *tert*-butyl dichlorophosphanes were attempted. Addition of these dichlorophosphanes RPhCl₂ to a solution of **4a** in thf afforded the phosphinophosphol derivatives **5** (R = Ph) or **6** (R = Bu^t) (Scheme 1). ³¹P NMR spectra exhibit as expected two doublets [**5**, δ –14 (PPh₂), 10.6 (PPh); **6**, δ –12 (PPh₂), 3.7 (PBu^t)] with a large ²J_{PP} of 50 Hz for **5** and 52 Hz for **6**. Compounds **5** and **6** were fully characterized as their disulfide adducts **7** and **8** {**7**, δ (³¹P) 39.2 [P(S)Ph₂], 51.4 [P(S)Ph], ²J_{PP} 24.7 Hz; **8**, δ (³¹P) 38.9 [P(S)Ph₂], † 78.6 [P(S)Bu^t], ²J_{PP} 24.9 Hz}. Confirmation of the identity of **8** was achieved by a single-crystal X-ray study‡ which shows that the 2- and not the 3-substituted thiophosphole



Scheme 1

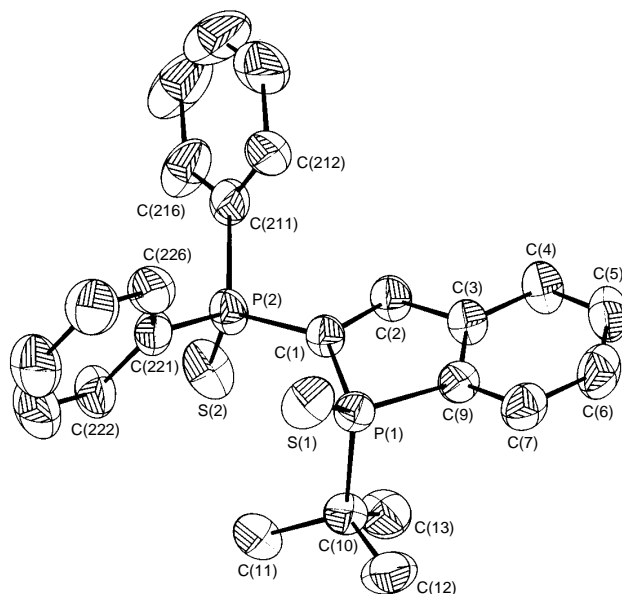


Fig. 1 Molecular structure of **8** with crystallographic numbering scheme. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.831(3), P(1)–C(9) 1.814(3), C(1)–C(2) 1.340(4), C(2)–C(3) 1.468(4), C(3)–C(9) 1.391(4), P(2)–C(1) 1.804(3); C(1)–P(1)–C(9) 91.4(1), P(1)–C(1)–C(2) 109.2(2), P(1)–C(1)–P(2) 130.7(2).

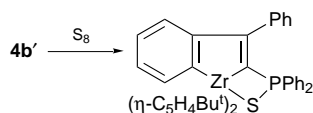
was formed. A molecule of **8** is shown in Fig. 1 and important bond lengths and angles are summarized.

Therefore these results clearly demonstrate that the 2-phosphinozirconaindene form **4a'** is selectively prepared when the acetylenic phosphane **1a** is treated with the benzynezirconocene **3a**.

A similar exchange reaction involving **4a'** and phenyl-dichlorostibene led to the formation of the corresponding 2-phosphinostibole **9** [$\delta(^{31}\text{P}) -2$] (Scheme 1).

Remarkably such a stereoselective synthesis of 2-phosphino-phospholes was also observed with more hindered acetylenic phosphanes such as **1b** and more hindered diphenylzirconocenes such as $[\text{ZrPh}_2(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2]$ **2b**.

Indeed treatment of **1b** with **2b** affords exclusively the complex **4b'** [$\delta(^{31}\text{P}) -27.1$]. Addition of S_8 to **4b'** led to the corresponding sulfide **10** [$\delta(^{31}\text{P}) 34.3$]† (Scheme 2). Successful X-ray diffraction analysis of a single crystal of **10**‡ shows several interesting features (Fig. 2). First, it corroborates that, here also, the insertion reaction of the benzynezirconocene **3b** into the carbon-carbon triple bond of **1b** is stereoselective and leads to an α -substituted zirconaindene. Secondly the structure reveals an interaction between zirconium and sulfur. The Zr-S distance is 2.797(1) Å, and compares well, for example, with the Zr-S bond lengths found in compounds with a chelating dithiocarbamate ligand such as $[\text{ZrCl}(\text{S}_2\text{CNEt}_2)(\eta\text{-C}_5\text{H}_5)_2]$ [Zr-S 2.635(2), 2.723(2) Å].^{4,5}



Scheme 2

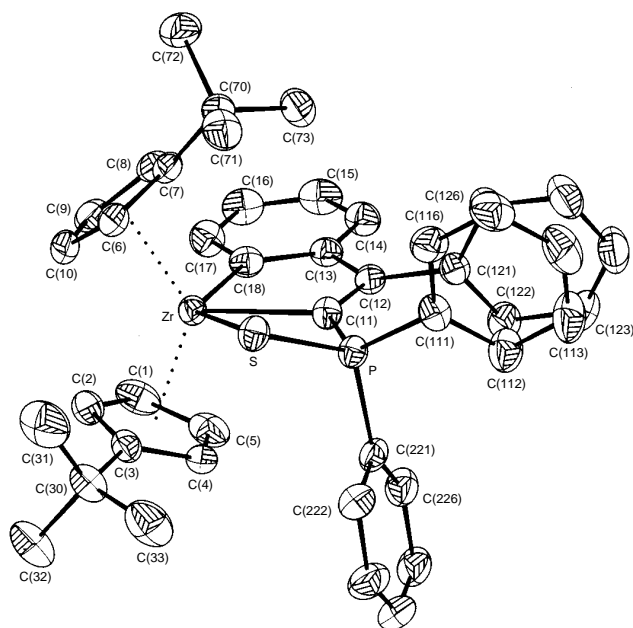


Fig. 2 Molecular structure of **10** with crystallographic numbering scheme. Selected bond lengths (Å) and angles ($^\circ$): P-S 2.005(1), P-C(1) 1.749(3), S-Zr 2.797(1), Zr-C(1) 2.490(4), Zr-C(8) 2.580(3), C(8)-C(3) 1.391(4), C(3)-C(2) 1.406(5), C(1)-C(2) 1.389(6), Zr-C(1)-P 106.4(2), Zr-S-P 85.4(4).

As a consequence the P-S bond length is found to be slightly larger [2.005(1) Å] than those generally observed for thio-phosphoryl groups (1.93–1.95 Å). Indeed, the P-S bond length lies in between those of a single and a double P-S bond.

In conclusion, we have discovered a new and easy approach to the synthesis of 2-phosphinophospholes and a related 2-phosphinostibole. The remarkable stereoselectivity in these reactions arises from the strong interaction between the phosphorus lone pair in **1a** or **1b** and zirconium in **3a** or **3b**. Such an interaction has been already demonstrated to be the driving force in many reactions involving phosphorus and zirconium.⁶

Footnotes

† Satisfactory analytical and/or spectral data were obtained for all new compounds. *Selected spectroscopic data* for compounds **8** and **10**. For **8**: DCIMS, m/z 439 ($[\text{M} + 1]^+$, 100%). NMR: δ_{H} (C_6D_6) 1.06 [d, $^3J(\text{HP})$ 18.2 Hz, 9 H, CH_3], 6.80–7.14 (m, 8 H, CH_{Ph}), 7.45 (m, 1 H, CH_{Ph}), 7.80 [dd, $^2J(\text{HP})$ 35.5, $^3J(\text{HP})$ 17.6 Hz, 1 H, CH], 8.18, 8.24, 8.50, 8.58 (m, 1 H, CH_{Ph}); δ_{C} 136.1 [dd, $^1J(\text{CP})$ 27.5, $^1J(\text{CP})$ 66.3 Hz, PCP], 138.1 [dd, $^1J(\text{CP})$ 78.9, $^3J(\text{CP})$ 3.2 Hz, CPBu^t], 140.9 [dd, $J(\text{CP})$ 17.2, $J(\text{CP})$ 22.0 Hz, CCPBu^t], 157.1 [dd, $^2J(\text{CP})$ 10.2, $^2J(\text{CP})$ 6.2 Hz, CH].

For **10**: DCIMS, m/z 727 ($[\text{M} + 1]^+$, 100%). NMR: δ_{H} (C_6D_6) 1.14 (s, 18 H, $\text{C}_5\text{H}_4\text{Bu}^t$), 5.75 (m, 4 H, $\text{C}_5\text{H}_4\text{Bu}^t$), 5.87, 6.16 (2 pseudo q, 4 H, $\text{C}_5\text{H}_4\text{Bu}^t$), 6.68 (m, 1 H, CH_{Ar}), 6.86–6.90 (m, 3 H, CH_{Ar}), 6.96–6.99 (m, 1 H, CH_{Ar}), 7.04–7.07 (m, 2 H, CH_{Ar}), 7.13–7.16 (m, 1 H, CH_{Ar}), 7.26–7.30 (m, 4 H, CH_{Ar}), 7.36–7.41 (m, 6 H, CH_{Ar}), 7.45–7.46 (m, 1 H, CH_{Ar}); δ_{C} 154.7 [d, $^2J(\text{CP})$ 6.3 Hz, $\text{ZrC}=\text{CPh}$], 154.8 [d, $^1J(\text{CP})$ 33.3 Hz, ZrCP], 170.5 [d, $^3J(\text{CP})$ 5.5 Hz, $\text{ZrC}=\text{C}$], 194.2 [d, $^3J(\text{CP})$ 6.5 Hz, ZrC].

‡ Crystal data recorded on an IPDS STOE diffractometer using a ϕ rotation scan, Mo-K α radiation was used ($\lambda = 0.71073$ Å). For **8**: $\text{C}_{24}\text{H}_{24}\text{P}_2\text{S}_2 \cdot 0.5\text{C}_6\text{H}_6$, crystal dimensions $0.50 \times 0.37 \times 0.25$ mm, monoclinic, space group $I2/a$, $a = 19.156(4)$, $b = 10.131(2)$, $c = 28.391(6)$ Å, $\beta = 109.50(2)^\circ$, $U = 5193.8$ Å³; $D_c = 1.22$ g cm⁻³, $\mu = 3.29$ cm⁻¹, number of reflections collected 16191, number of independent reflections 4100 ($R_m = 0.049$), $R = 0.0429$, $R_w = 0.0445$, GOF = 1.04.

For **10**: $\text{C}_{44}\text{H}_{35}\text{PSZr}$, crystal dimensions $0.60 \times 0.50 \times 0.50$ mm, monoclinic, space group $P2_1/c$, $a = 12.247(2)$, $b = 19.746(4)$, $c = 15.970(1)$ Å, $\beta = 106.41(1)^\circ$, $U = 3704.8$ Å³; $D_c = 1.31$ g cm⁻³, $\mu = 4.16$ cm⁻¹, number of reflections collected 23271, number of independent reflections 4163 ($R_m = 0.047$), $R = 0.0314$, $R_w = 0.0364$, GOF = 0.8.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/340.

References

- 1 See for example: J.-P. Majoral, M. Zablocka and A. Igau, *Chem. Ber.*, 1996, **129**, 879 and references therein; A. Mahieu, A. Igau, J. Jaud and J.-P. Majoral, *Organometallics*, 1995, **14**, 944.
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