

Synthesis of functional 1,4-diphosphaindenes and their related anions

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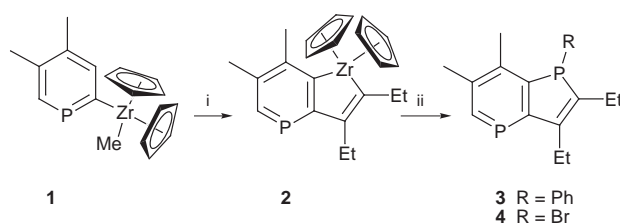
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Treatment of a 1-zircona-4-phosphaindene complex with PBr_3 affords a 1-bromo-1,4-diphosphaindene, which can be used as a convenient precursor for the preparation of the related 1,4-diphosphaindenyl mono- and tri-anions and (1R)-functional derivatives.

The search for new sophisticated ligands including sp^2 -hybridised phosphorus atoms as bonding sites is a current and topical field of investigation.¹ Among these ligands, phosphinines play a significant role and continuous efforts have been made to improve the synthesis of their functional derivatives.² Whereas several routes towards polyfunctional mono-, bis- and tris-phosphinine based ligands³ and macrocycles⁴ have been developed, fused aromatic and non-aromatic ring systems have received much less attention. Although some polyaromatic systems are known,⁵ only two examples of heterocyclic-fused ring systems incorporating the phosphinine nucleus have been described so far.⁶ In view of the importance of phospholes and their related phospholide anions in coordination chemistry,⁷ we decided to investigate the synthesis of 1,4-diphosphaindene species, a new type of ligand which could combine the chemistries of phosphinines and phospholes. Herein we report on these investigations.

Among the different synthetic approaches conventionally used for the synthesis of phospholes, metallacycle transfer reactions from zirconacyclopentadiene complexes appear very attractive.⁸ Indeed, this simple process was used for the preparation of 1-phosphaindene ligands from η^2 -benzyne zirconocene complexes, alkynes and PCl_3 .⁹ The recent discovery of η^2 -phosphabenzynes zirconocene complexes¹⁰ prompted us to investigate the corresponding transformation. All the experiments were conducted with the 1-zircona-4-phosphaindene complex **2** whose synthesis was previously reported from the reaction of the PMe_3 adduct of the η^2 -phosphabenzynes complex with hex-3-yne. As a prelude to this work we found that the use of the Zr–Me complex **1** as precursor provided a more straightforward access to **2**. This complex turns out to be less reactive than that of its corresponding carbon counterpart. It seems likely that the decrease of electron density at the β positions of the phosphinine is responsible for this situation.¹¹ Preliminary experiments with PCl_3 only led to the recovery of starting material after several hours of reaction in CH_2Cl_2 . Better results were obtained using $PhPCl_2$ as transfer reagent since the 1-phenyl-1,4-diphosphaindene **3** could be prepared after 5 to 10 days reaction, depending on the concentration used, in 15% yield. Finally, we found that the use of PBr_3 dramatically increased the rate of the reaction as well as the yield. After 1 h, the 1-bromo-1,4-diphosphaindene **4** was isolated in 80% yield as a slightly moisture- and oxygen-sensitive yellow oil after extraction with hexanes (Scheme 1).

The reaction of **4** with lithium is of particular interest. With a stoichiometric amount of lithium in THF at 25 °C, the monoanion **5a** is formed quantitatively according to ^{31}P NMR analysis. All available data (^{31}P , 1H , ^{13}C NMR) support the structure proposed for **5a**. Whereas the ^{31}P NMR chemical shift of **5a** is comparable to those recorded for other phosphaindenyl anions, that of the phosphinine subunit experiences a dramatic upfield shift (δ 146.6 in **5a** vs. 176 in **4**). This observation shows

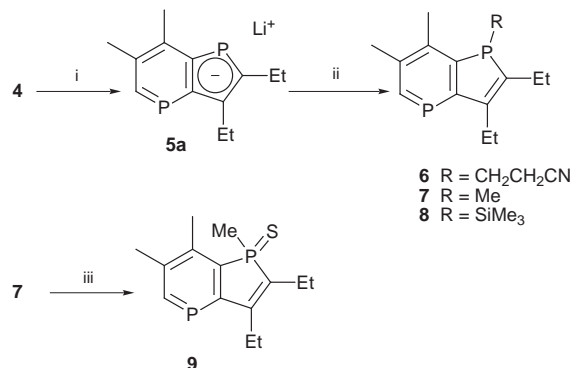


Scheme 1 Reagents and conditions: i, hex-3-yne, 80 °C, 3 h; ii, $PhPCl_2$, CH_2Cl_2 , 5–10 d, then PBr_3 , CH_2Cl_2 , 1 h.

that a substantial delocalization of the negative charge occurs in **5a**. As expected, anion **5a** can be used as a convenient source of functional derivatives *via* reaction of electrophiles at the nucleophilic P atom of the phospholide unit (Scheme 2). Reactions of **5a** with $Br(CH_2)_2CN$ and MeI afford compounds **6** and **7** which were isolated in modest yields (40 and 50% respectively).[†] The corresponding $PSiMe_3$ derivative **8** was too sensitive towards hydrolysis to be isolated. An X-ray crystal structure analysis (Fig. 1) was carried out on the sulfide **9**[‡] which was obtained by treating **7** with elemental sulfur in toluene. The structure of **9** deserves no special comment. Apparently, the phosphinine unit is not perturbed by the presence of the fused phosphole moiety as shown by the equivalency of the two C=P sp^2 bonds and by the value of the internal C–P–C angle, which is close to that recorded for other phosphinines.

Another interesting observation concerns the reduction of anion **5a**. We found that care must be taken to avoid over-reduction. Indeed, a prolonged contact with excess lithium or sodium cleanly affords a new species whose structure was ascribed to trianions **10a,b** on the basis of NMR data.¹² Evidence supporting the formulation proposed for **10** was given by oxidation with one equivalent of iodine, which leads back to the monoanions **5a,b** (Scheme 3). Further experiments aimed at developing the use in coordination chemistry of ligands such as monoanions **5**, whose synthesis was the real aim of this work, are currently under progress in our laboratories.

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Scheme 2 Reagents and conditions: i, Li, THF, 30 min; ii, $BrCH_2CH_2CN$ or MeI or Me_3SiCl , THF –80 to 25 °C; iii, 1/8 S_8 , toluene, 40 °C, 4 h.

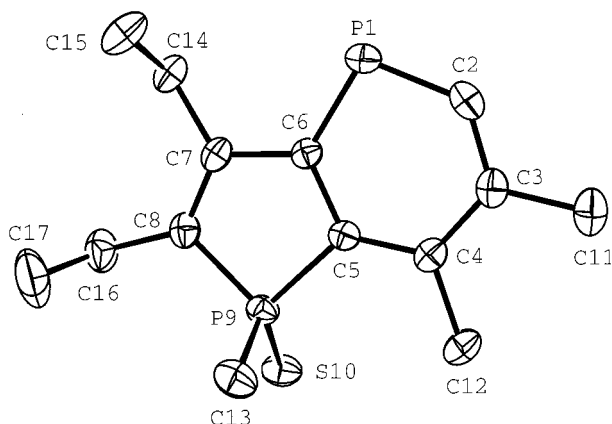
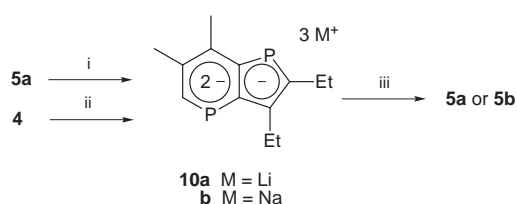


Fig. 1 Molecular structure of **9** showing the atomic number scheme. The numbering is arbitrary, not the systematic system used in the spectroscopic data. Selected interatomic distances (Å) and angles (°): P(1)–C(2) 1.734(2), C(2)–C(3) 1.377(3), C(3)–C(4) 1.419(2), C(4)–C(5) 1.388(3), C(5)–C(6) 1.417(3), C(6)–P(1) 1.730(2), C(6)–C(7) 1.480(2), C(7)–C(8) 1.349(2), C(8)–P(9) 1.797(2), P(9)–C(5) 1.813(2), C(6)–P(1)–C(2) 99.65(9), C(5)–P(9)–C(8) 93.40(8), P(9)–C(5)–C(6) 107.6(1), C(5)–C(6)–C(7) 113.9(1).



Scheme 3 Reagents and conditions: i, Li (excess), 1 h; ii, Na (excess), 20 min; iii, I₂ (1 equiv.), THF.

Notes and references

† All isolable compounds (**3**, **6** and **9**) gave analytical data consistent with the proposed structures. *Selected data for 3*: δ_{P} (81 MHz, CDCl₃ unless otherwise stated) 171.5 (P₄), 6.5 (P₁). For **4**: δ_{P} 176.5 (P₄), 59.6 (P₁); δ_{H} (200 MHz, CDCl₃) 8.42 (d, 1H, $^2J_{\text{H,P}}$ 39.75, H₅); δ_{C} (50 MHz, CDCl₃) 172.7 (d, $^1J_{\text{P,C}}$ 50.6, C₉), 155.10 (d, $^1J_{\text{P,C}}$ 48.8, C₅). For **5a**: δ_{P} (C₄D₈O) 146.6 (d, $^3J_{\text{P,P}}$ 10.5, P₄), 63.7 (P₁); δ_{H} (C₄D₈O) 7.66 (d, 1H, $^2J_{\text{H,P}}$ 38.05, H₅); δ_{C} (C₄D₈O) 157.1 (dd, $^1J_{\text{P,C}}$ 36.2, $^2J_{\text{P,C}}$ 14, C₈), 156.5 (dd, $^1J_{\text{P,C}}$ 38.6, $^3J_{\text{P,C}}$ 6.8, C₂), 153.8 (dd, $^1J_{\text{P,C}}$ 42.4, $^2J_{\text{P,C}}$ 2.1, C₉); 143.9 (d, $^1J_{\text{P,C}}$ 36.9, C₅), 135.7 (dd, $J_{\text{P,C}}$ 16.5, $J_{\text{P,C}}$ 17.2, C₆ or C₇), 132.6 (dd, $^2J_{\text{P,C}}$ 23, $^2J_{\text{P,C}}$ 3.6, C₃), 122.6 (dd, $J_{\text{P,C}}$ 10.5, $J_{\text{P,C}}$ 17, C₇ or C₆). For **5b**: δ_{P} 153.6 (d, $^3J_{\text{P,P}}$ 10.3, P₄), 53.7 (P₁). For **6**: δ_{P} 174 (P₄), –1.8 (P₁). For **7**: δ_{P} 171.3 (P₄), –10.8 (P₁). For **8**: δ_{P} 170 (P₄), –43.6 (P₁). For **9**: δ_{P} 174 (P₄), 50.8 (P₁). For **10a**: δ_{P} (C₄D₈O) 34.7 (d, $^3J_{\text{P,P}}$ 13.8, P₁), 24 (P₄); δ_{H} (C₄D₈O) 7.20 (d, 1H, $^2J_{\text{H,P}}$ 40.1, H₅); δ_{C} (C₄D₈O) 150.6 (dd, $^2J_{\text{P,C}}$ 17.6, $^3J_{\text{P,C}}$ 3.9, C₆), 150 (dd, $^1J_{\text{P,C}}$ 37.1, $^2J_{\text{P,C}}$ 6.8, C₂), 146

(dd, $^1J_{\text{P,C}}$ 43.3, $^3J_{\text{P,C}}$ 4.2, C₉), 144.9 (d, $^1J_{\text{P,C}}$ 41.6, C₅), 139 (dd, $^1J_{\text{P,C}}$ 40, $^2J_{\text{P,C}}$ 10.4, C₈), 114.7 (dd, $^2J_{\text{P,C}}$ 12, $^2J_{\text{P,C}}$ 7.5, C₃), 61.1 (dd, $^3J_{\text{P,C}}$ 24.2, $^2J_{\text{P,C}}$ 8.4, C₇). For **10b**: δ_{P} (C₄D₈O) 39.3 (d, $^3J_{\text{P,P}}$ 12.2, P₁), 20.4 (P₄).

‡ *Crystal data for 9*: Crystals of **9** (C₁₄H₂₀P₂S) were grown from MeOH. Data were collected at 123 ± 0.5 K on an Enraf-Nonius CAD4 diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf-Nonius MOLEN package. The compound crystallises in space group *P2₁/n* (14), *a* = 9.861(1), *b* = 15.219(2), *c* = 10.715(1) Å, $\beta = 110.95(1)^\circ$, *V* = 1501.89(59) Å³, *Z* = 4, *D_c* = 1.249 g cm^{–3}, $\mu = 4.0$ cm^{–1}, *F*(000) = 600. A total of 4725 unique reflexions were recorded in the range $2 \leq 2\theta \leq 60.0$ of which 1153 were considered as unobserved [$F^2 < 2.0\sigma(F^2)$], leaving 3572 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were refined with isotropic temperature factors in the final stages of least-squares while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a *p* factor equal to 0.08. The final agreement factors were *R* = 0.033, *R_w* = 0.053, GOF = 1.10. CCDC 182/1177. Crystallographic data are available in CIF format from the RSC web site, see: <http://www.rsc.org/suppdata/1999/537/>

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