Zirconaindane phospholanes: key reagents for the synthesis of mono- or tri-cyclic phosphanes and related species

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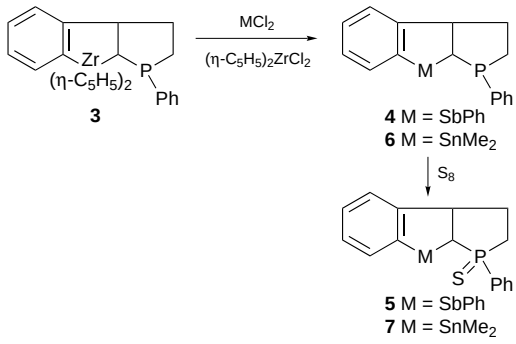
The zirconaindane phospholane 3 reacts either with $PhSbCl_2$ or Me_2SnCl_2 to give tricyclic systems incorporating phosphorus, antimony or tin; the same reaction involving 3 and R_2PCl (R = Ph, Et) leads to acyclic–cyclic diphosphanes.

There is an extensive literature on the topic of cyclic phosphanes such as phospholanes, phospholenes or phospholes.[1] In contrast only a limited number of fused bicyclic and tricyclic phosphanes have been prepared and only very recently a few tricyclic 1,1-diphosphanes were described.[2] As far as we are aware, fused tricyclic systems incorporating phosphorus and other heavier main group elements, are not known. With this in mind we became interested in developing synthetic routes to these species because of the intrinsic interest in phosphane and polyphosphane derivatives as reagents for mediating organic transformations or as ligands for complex formation and use in catalysis.

This prompted us to initiate the chemistry of the zirconaindane phospholane **3** which was regioselectively prepared *via* the treatment of 1-phenyl-2-phospholene PhP–CH=CHCH$_2$CH$_2$ **1** with the transient (benzyne)zirconocene [(η-C_5H_5)$_2$Zr(η^2-C_6H_4)] **2**. [2] Here we will detail the formation, from **3**, of unusual phosphorus and antimony (or tin) tricyclic systems as well as that of new acyclic–cyclic diphosphanes.

Reactions of **3** with $PhSbCl_2$ in benzene at 5 °C for 1 h led to the stibaphospholane **4** [δ(^{31}P) 5.9] which was isolated in 80% yield as its sulfide adduct **5** [δ(^{31}P) 61.9] (Scheme 1). The formulation of **5** was confirmed by NMR spectroscopy,[3] mass spectrometry (FAB [M + 1]$^+$ 470) and by elemental analysis.

An analogous exchange reaction performed with **3** and Me_2SnCl_2 at 0 °C for 3 h gave the tin–phosphorus containing tricyclic species **6** [δ(^{31}P) 5.6] which was also fully characterized as its sulfide adduct **7** obtained in 75% yield [δ(^{31}P) 64.1)] (Scheme 1). NMR data corroborated such an assignment.† Compounds **4**–**7** are the first examples of fused tricyclic systems incorporating phosphorus and antimony or phosphorus and tin in the cyclic skeleton.



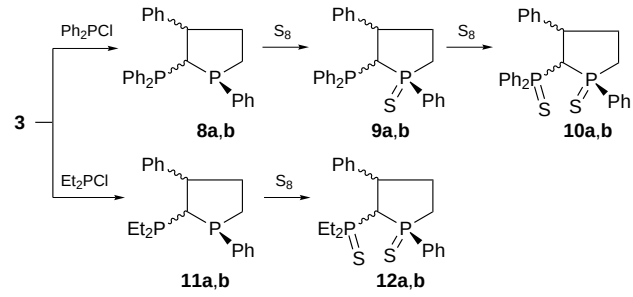
Scheme 1

All these reactions proceeded with ring retention. In contrast an exchange reaction with concomitant ring opening was observed when **3** was reacted with a chlorophosphane such as Ph_2PCl at −40 °C for 1 h (Scheme 2). The 1,1-diphosphane **8** was obtained as two isomers **8a**,**b** in a 4 : 1 ratio as shown by ^{31}P NMR spectroscopy: two doublets at δ 5.1 (PPh) and −12.0 (PPh_2) ($^2J_{PP}$ 7.8 Hz) for the major compound and δ 3.9 (PPh) and −16.3 (PPh_2) ($^2J_{PP}$ 19.5 Hz) for the minor one. Monosulfurization occurred regioselectively on the intracyclic phosphorus atom by adding 1 equiv. of elemental sulfur to **8a**,**b** and led to the adducts **9a**,**b** {two isomers in a 4 : 1 ratio. δ(^{31}P): 65.5 [P(S)Ph] and −9.6 (PPh_2), $^2J_{PP}$ 31.5 Hz (major); δ 64.1 [P(S)Ph] and −11.8 (PPh_2), $^2J_{PP}$ = 31.5 Hz (minor)}. Further addition of a second equivalent of sulfur led predominantly to the formation of the disulfide **10a** {δ(^{31}P) 65.2 [P(S)Ph] and 43.3 [P(S)Ph_2], $^2J_{PP}$ 0 Hz} isolated by silica gel column chromatography.‡ ^{13}C and ^{1}H NMR spectra coupled with mass spectrometry and microanalytical data showed clearly that cleavage of the two zirconium–carbon bonds occurred with grafting of the diphenylphosphino group in α position to the intracyclic P–Ph moiety.

A similar ring opening process initiated also by an exchange reaction between **3** and a chlorophosphane was detected when **3** was reacted with Et_2PCl. Addition of sulfur to the resulting 1,1-diphosphanes **11a**,**b** (two isomers) led to the 1,1-dithiodiphosphanes **12a**,**b** (two isomers in 9 : 1 ratio). The major isomer **12a** was isolated by chromatography and fully characterized by NMR,† mass spectrometry and elemental analysis.

X-Ray structures have been obtained for **10a**[3] and for **12a** (Fig. 1):§ they showed similar features for the two derivatives. Indeed substituents on the intracyclic carbon atoms C(1) [P(S)Ph_2] and C(2) (Ph) of the phospholane ring are *cis* in both cases [P(1)–C(1)–C(2)–C(21) torsion angle: 85.7° for **10a**, 73.2° for **12a**] while the substituent on C(1) and the phenyl group on the phosphorus atom P(2) are *trans* [P(1)–C(1)–P(2)–C(221) torsion angle: 3.2° for **10a**, 14.0° for **12a**].

Remarkably the regioselectivity of the reaction of phospholene **1** with a more hindered benzyne zirconocene precursor such as (η^5-Bu^tC_5H_4)$_2$ZrPh_2 was found to be the same: the zirconaindane phospholane **3″** was formed nearly quantitatively



Scheme 2

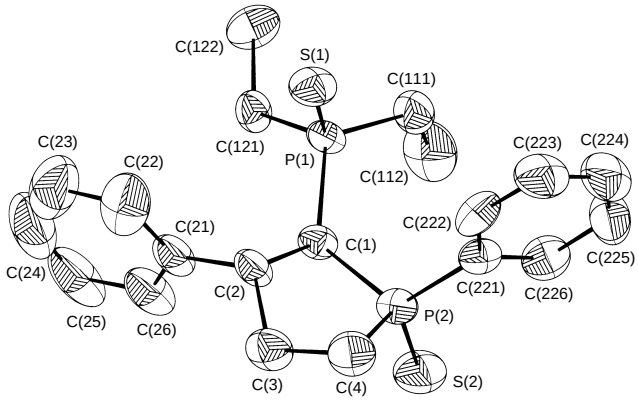
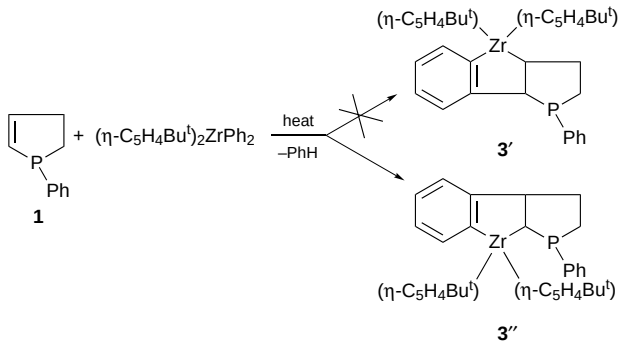


Fig. 1 Molecular structure (CAMERON[6]) of **12a** with crystallographic numbering scheme. Selected bond lengths (Å) and angles (°): P(2)–C(1) 1.84 (1), P(2)–C(4) 1.80 (1), C(1)–C(2) 1.56 (1), C(2)–C(3) 1.53 (1), C(3)–C(4) 1.50 (2), P(2)–C(221) 1.82 (1); C(1)–P(2)–C(221) 112.8 (5), P(2)–C(1)–C(2) 105.7 (6), P(2)–C(1)–P(1) 124.0 (5).



Scheme 3

and no trace of **3′** was detected (Scheme 3). These results can be explained by considering that, whatever the steric hindrance encountered on zirconium, the regioselectivity of the reaction of zirconocene–benzyne complexes with phospholene **1** is governed by the transient formation of a zirconocene stabilized phosphorus benzyne complex leading in the final products **3** and **3″** to a P–Zr dative bond. Moreover, treatment of **3″** with $PhSbCl_2$ also led to the formation of the stibaphospholane **4**.

In conclusion, zirconaindane phospholanes **3** and **3″** appeared to be versatile reagents, leading to new mono- and tricyclic heavier main group element compounds *via* disubstitution reactions with ring retention (formation of **4**–**7**) or monosubstitution reactions with ring opening (formation of **10**, **12**).

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Footnotes

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† **5** $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.9. ^1H NMR (C_6D_6) (*J*/Hz): δ 1.69–2.20 (m, 4 H, CH_2), 3.26 [dd, ^2J(HP) 8.0, ^3J(HH) 6.1, 1 H, PCHSb], 3.97 (m, 1 H, CH), 6.89–7.35, 7.75–7.87 (m, 9 H, H_{aryl}). ^{13}C NMR ($CDCl_3$): δ 34.8 [d, ^2J(CP) 6.6, PCH_2CH_2], 36.6 [d, ^1J(CP) 51.8, PCH_2], 51.6 [d, ^1J(CP) 46.6, PCHSb], 58.1 [d, ^2J(CP) 8.1, PCHCH], 126.1, 128.2, 128.9, 129.4 (s, Ph), 129.3 [d, *J*(CP) 10.3, Ph], 131.4 [d, *J*(CP) 9.5, Ph], 131.6 [d, *J*(CP) 3.0, Ph], 135.8, 136.1 (s, C_6H_4), 136.2 [d, ^1J(CP) 68.2, *ipso*-PPh], 140.9 [d, ^1J(CP) 8.9, SbPh), 144.5 [d, ^3J(CP) 2.1, *ipso*-C_6H_4], 156.7 [d, ^3J(CP) 4.5, C_6H_4]. FABMS (MNBA–DMF): *m*/*z* 391 (100, $[M - S]^+$). **7** $^{31}P\{^1H\}$ NMR (C_6D_6): δ 64.1. ^1H NMR (C_6D_6): δ 0.73 (s, 6 H, CH_3), 1.77–2.16 (m, 4 H, CH_2), 3.42 [dd, ^2J(HP) 9.6, ^3J(HH) 9.6, 1 H, PCHSn], 4.24 (m, 1 H, PCHC*H*), 7.02–7.41, 7.65–7.96 (m, 9 H, H_{aryl}). ^{13}C NMR (C_6D_6): δ 4.9 (s, CH_3), 33.4 [d, ^2J(CP) 6.3, PCH_2CH_2], 35.2 [d, ^1J(CP) 49.8, PCH_2], 51.7 (s, PCH*C*H), 52.1 [d, ^1J(CP) 33.7, PCHSn], 127.0 (s, *p*-Ph), 128.7 [d, *J*(CP) 11.9, Ph], 130.6 [d, *J*(CP) 11.4, Ph], 127.0. 127.6, 131.8, 136.0 (s, C_6H_4), 142.8 (s, *ipso*-C_6H_4), 148.1 [d, ^3J(CP) 4.5, C_6H_4]. **10a** $^{31}P\{^1H\}$ NMR (thf): δ 64.2, 43.3. ^{13}C NMR ($CDCl_3$): δ 34.2 [dd, ^2J(CP) 10.2, ^3J(CP) 3.4, PCH_2CH_2], 34.7 [d, ^1J(CP) 55.1, PCH_2], 49.1 [d, ^2J(CP) 7.8, PCHPh], 56.2 [dd, ^1J(CP) 38.1, ^1J(CP) 42.9, PCHP], 127.1, 128.9, 128.6, 128.4, 131.4, 131.3 (s, Ph), 127.5 [d, *J*(CP) 13.3, Ph], 128.2 [d, *J*(CP) 12.5, Ph], 130.8 [d, *J*(CP) 2.5, Ph], 131.8 [d, *J*(CP) 9.4, Ph], 132.7 (s, *ipso*-Ph), 133.8 [d, *J*(CP) 9.8, *ipso*-Ph], 134.7 [d, *J*(CP) 11.6, Ph], 142.9 [d, *J*(CP) 8.5, *ipso*-Ph]. **12a** $^{31}P\{^1H\}$ NMR (thf): δ 62.8, 55.1 (5.1). ^{13}C NMR ($CDCl_3$): δ 6.8 [d, ^2J(CP) 4.0, PCH_2CH_3], 7.1 [d, ^2J(CP) 3.8, PCH_2CH_3], 23.0 [d, ^1J(CP) 52.4, P*C*H$_2$CH$_3$], 25.9 [dd, ^1J(CP) 49.7, ^3J(CP) 4.8, P*C*H$_2$CH$_3$], 34.4 [d, ^2J(CP) 11.3, PCH_2CH_2], 36.8 [d, ^1J(CP) 54.1, PCH_2], 50.0 [d, ^2J(CP) 8.0, PCHPh], 55.1 [dd, ^1J(CP) 36.4, ^1J(CP) 36.4, PCHP], 128.1, 128.6, 129.4 (s, Ph), 130.3 [d, *J*(CP) 69.3, *ipso*-PPh_2], 133.0 [d, *J*(CP) 2.8, Ph], 134.9 [d, *J*(CP) 11.4, Ph], 142.7 [d, *J*(CP) 11.6 *ipso*-PPh].

‡ The second disulfide adduct **10b** arising from sulfurisation of **9b** was not isolated.

§ *Crystal data* for $C_{20}H_{26}P_2S_2$ **12a**: M = 392.49, monoclinic, space group $P2_1/n$, a = 10.944 (1), b = 12.033 (2), c = 16.654 (1) Å, β = 107.114 (8)°, U = 2096.3 Å^3, Z = 4, D_c = 1.24 g cm^{-3}, μ = 3.94 cm^{-1}. Crystal size: 0.35 × 0.15 × 0.35 mm, 1308 measured reflections (2740 independent), R_{av} = 0.047, R = 0.0540, R_w = 0.070 from 1344 reflections with $I > 1.5\sigma(I)$. The data collection was performed at 293 K on a I.P.D.S. STOE diffractometer using graphite-monochromated Mo-Kα radiation for the two compounds. The structures were solved by direct methods using the program SIR92[4] and subsequent Fourier maps. The refinement of models were performed by using full-matrix least-squares techniques with the aid of the package CRYSTALS.[5] All hydrogen atoms were found on difference Fourier maps but they were introduced as fixed contributors with C–H = 0.96 Å and isotropic thermal parameters fixed 20% higher than those of the carbon atoms to which they were attached their positions were recalculated after each cyclic of refinement. For the two structures all non-hydrogen atoms were anisotropically refined. 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 182/506.

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