Unusual addition reactions of lithium alkoxides to 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene†

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2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene (1) reacts selectively with a mixture of the primary lithium alkoxides 2a,b and the corresponding alcohols 3a,b to afford the novel 2,4,6-tri-*tert*-butyl-1,3,5-alkoxy-1,3,5-triphosphacyclohexane derivatives 4a,b; treatment of 4a with sulfur results in oxidation of all phosphorus atoms to furnish the triphosphane sulfide 5.

The polarity of the P/C double bond resulting from the electronegativity difference between phosphorus and carbon generally favours the addition of H-acidic compounds.[1] In this process, the proton is added to the carbon atom of the phosphaalkene unit while the nucleophilic part is attached to the positively polarised phosphorus atom.[2,3] It has recently been shown that the addition of alcohols to isolated P/C double bonds is particularly successful when a mixture of a lithium alkoxide with at least an equimolar amount of the corresponding alcohol in THF as solvent is used.[4] In the course of these studies we posed the question of whether this reagent system would be able to undergo addition to phosphaalkene units incorporated in a delocalised, heteroaromatic[5] bonding system. For this purpose, we have chosen 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene[6] (1) as a reaction partner. To date, only the unusual addition of water to a η¹-bonded 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene platinum(II) complex has been reported.[7]

When the triphosphabenzene 1 was allowed to react with three equivalents of the lithium alkoxides 3a,b and an excess of the respective alcohol 2a,b, a highly regio- and stereoselective, three-fold addition of alcohol to all three P/C double bonds of 1 was indeed observed. The products are the 1,3,5-trialkoxy-1,3,5-triphosphabenzenes 4a‡ (84%, mp 51 °C) and 4b (72%, 74 °C) obtained as microcrystalline solids (Scheme 1). For the reaction of 1 + 2a/3a we found that the use of merely 10% of the stoichiometric amount of lithium ethoxide can also result in the

same product yield when a longer reaction time is allowed. The rate-determining step is most certainly the 1,2- or 1,4-addition of the first equivalent of the alcohol which destroys the aromaticity of 1.[5] The thus-formed 1,3,5-triphosphacyclohexa-1,3(or 1,4)-diene then reacts much more rapidly so that intermediates cannot be detected by ³¹P NMR spectroscopic monitoring of the reaction.

The ³¹P and ¹³C NMR spectra of 4a and 4b are in accord with the assumed saturation of the double bonds of the heteroarene 1 (³¹P: δ = 232.6 , ¹³C: δ = 211.8). The ³¹P NMR signals of 4a are shifted to higher field in comparison to those of 1 and appear at δ = 162.8 (d, P-1/P-5) and δ = 162.4 (t, P-3) with $^2J_{P,P}$ coupling constants of 3.1 Hz. The corresponding signals for 4b show the same splitting pattern but are slightly diagmagnetically shifted (δ = 156.3 and δ = 155.5, respectively). Also noteworthy are the high-field shifts of the signals of the ring carbon atoms of 4a and 4b appearing at δ = 57.2 and 56.9 (C-2/C-4) and δ = 60.7 and 59.9 (C-6), respectively.

For the structural elucidation of the 1,3,5-triphosphacyclohexanes 4a,b it is justifiable to assume that the framework prefers the chair form in analogy to the cyclohexane system. The sterically demanding *tert*-butyl substituents should adopt an equatorial arrangement for energetic reasons. However, a conclusive assignment of the configurations of the three phosphorus atoms is not possible at this stage.

The final structure elucidation was established by an X-ray crystallographic analysis of 4a (Fig. 1).§ The highly distorted, chair conformation of the ring skeleton with equatorial linked *tert*-butyl substituents is clearly apparent.

In the crystal the two methoxy substituents at P-1 and P-5 occupy approximately equatorial positions while that at P-3 is in an axial position. The P/C bond lengths measured in the ring range from 1.824(3) Å to 1.874(3) Å and thus exhibit only minor deviations from the average literature value.[8] Other characteristic features in the crystal structure of compound 4a
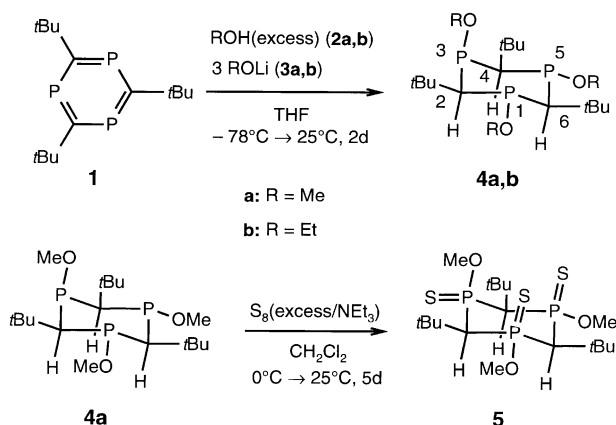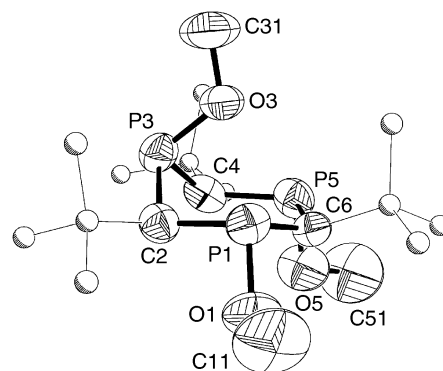

Scheme 1

Fig. 1 Crystal structure of **4a**. Selected bond lengths (Å) and angles (°): P(1)–C(2) 1.843(3), P(1)–C(6) 1.870(3), P(3)–C(2) 1.840(3), P(3)–C(4) 1.824(3), P(5)–C(4) 1.834(3), P(5)–C(6) 1.874(3), P(1)–O(1) 1.660(2), P(3)–O(3) 1.653(2), P(5)–O(5) 1.656(2); C(2)–P(1)–C(6) 104.34(11), C(4)–P(3)–C(2) 99.10(12), C(4)–P(5)–C(6) 107.51(12), P(1)–C(2)–P(3) 109.93(14), P(3)–C(4)–P(5) 112.33(14), P(1)–C(6)–P(5) 126.15(14).

are the widely differing folding angles between the planes defined by the atoms P-1/C-6/P-5 and C-2/P-3/C-4 to that defined by the atoms C-2/P-1/P-5/C-4 (23.9 and 112.8°, respectively). The widely opened endocyclic bonding angle at C-6 [126.15(14)°] is comparable to that of a 1,3-diphosphor-inane described in the literature.[9]

Since the novel products **4a,b** represent the first members of a new class of compounds we have also investigated their functionalisation reactions with chalcogens. The reaction of **4a** with an excess of sulfur in the presence of triethylamine proceeded with coordination increases at all phosphorus atoms to furnish the triphosphane trisulfide **5** (74%, colourless solid, mp 84 °C).¶ The ^{13}C NMR data for compound **5** confirm the retention of the cyclic structure while the absorption at $v = 1261$ cm^{-1} in the IR spectrum is characteristic for the newly introduced P/S double bonds. We also assume that the configurations at the phosphorus atoms remain unchanged by this reaction. The oxidation of **4a** with bis(trimethylsilyl) peroxide proceeded analogously to furnish **5** (O in place of S) but this product still contains traces of impurities (^{31}P NMR).

Notes and references

‡ *Selected data* for **4a**: δ_P (81 MHz, C$_6$D$_6$) 162.8 (d, $^2J_{P,P}$ 3.1, P-1, P-5), 162.4 (d, $^2J_{P,P}$ 3.1, P-3); δ_H (400 MHz, C$_6$D$_6$) 1.34 [s, 18 H, C(CH$_3$)$_3$], 1.49 [s, 9 H, C(CH$_3$)$_3$], 2.12 (d, 2H, $^2J_{H,P}$ 1.7, H-2, H-4), 2.20 (t, 1H, $^2J_{H,P}$ 3.8, H-6), 3.19 (d, 3H, $^3J_{H,P}$ 12.1, OCH$_3$), 3.40 (m, 6H, OCH$_3$); δ_C (100.6 MHz, C$_6$D$_6$) 30.4 [m, C(CH$_3$)$_3$], 30.9 [t, $^3J_{C,P}$ 11.8, C(CH$_3$)$_3$], 34.3 [m, C(CH$_3$)$_3$], 35.6 [t, $^2J_{C,P}$ 24.3, C(CH$_3$)$_3$], 55.3 (m, OCH$_3$), 57.2 (m, C-2, C-4), 60.7 (t, $^1J_{C,P}$ 49.3, C-6); IR (CCl$_4$) $v = 2958$ (vs), 2827 (m), 1464 (m), 1398 (m), 1362 (w), 1219 (s), 1047 (m), 796 (s), 772 (s), 748 (m), 727 (s); *m/z* (EI, 70 eV): 396 (93) [M]$^+$, 381 (100) [M − CH$_3$]$^+$, 365 (13) [M − OMe]$^+$, 339 (18) [M − ^{t}Bu]$^+$, 57 (14) [^{t}Bu]$^+$. (Calc. for C$_{18}$H$_{39}$O$_3$P$_3$: C, 54.40; H, 9.90. Found C, 54.35; H, 10.09%).

§ *Crystal data* for **4a**: C$_{18}$H$_{39}$O$_3$P$_3$, $M = 396.43$ g mol^{-1}, monoclinic, space group $P2_1/n$, $a = 9.384(2)$, $b = 24.807(5)$, $c = 10.901(2)$ Å, $\beta = 111.90(3)°$, $V = 2354.8$ Å^3, $Z = 4$, $D_c = 1.118$ Mg m^{-3}, $\mu = 0.265$ mm^{-1}, $F(000) = 864$. Crystal dimensions $0.80 \times 0.50 \times 0.30$ mm^3, 15039 reflections collected, 3641 independent reflections ($R_{int} = 0.0579$), 2731 reflections with $I > 2\sigma(I)$, goodness-of-fit on F^2: 1.279, $R[I > 2\sigma(I)] =$ 0.0478, $wR_2 = 0.1223$; R (all data) = 0.0618, $wR_2 = 0.1315$; maximum and minimum residual density 0.543 and 0.223 e Å^{-3}. Data were collected on a STOE Imaging Plate Diffraction System at room temperature with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved with SHELXS-86 [ref. 10(*a*)] and refined with SHELXL-93 [ref. 10(*b*)]. CCDC 182/1755. See http://www.rsc.org/suppdata/cc/b0/b006795o/ for crystallographic files in .cif format.

¶ *Selected data* for **5**: δ_P (81 MHz, C$_6$D$_6$) 99.5 (s, P-1, P-5), 123.5 (s, P-3); δ_H (400 MHz, C$_6$D$_6$) 1.29 [s, 18 H, C(CH$_3$)$_3$], 1.75 [s, 9 H, C(CH$_3$)$_3$], 2.74 (pseudo t, 2 H, $^2J_{H,P}$ 19.2, H-2, H-4), 3.11 (m, 1 H, H-6), 3.47 (d, 6 H, $^2J_{H,P}$ 14.1, OCH$_3$), 3.52 (d, 3 H, $^2J_{H,P}$ 12.1, OCH$_3$); δ_C (100.6 MHz, C$_6$D$_6$) 30.2 [m, C(CH$_3$)$_3$], 31.7 [t, $^3J_{C,P}$ 6.0, C(CH$_3$)$_3$], 36.2 [dd, $^2J_{P,C}$ 19.9, 1.8, C(CH$_3$)$_3$], 39.2 [m, C(CH$_3$)$_3$], 49.5 (m, OCH$_3$), 57.2 (d, $^2J_{C,P}$ 22.6, OCH$_3$), 60.4 (dd, $^1J_{C,P}$ 49.9, 27.3, C-2, C-4), 66.0 (t, $^1J_{C,P}$ 51.8 Hz, C-6); IR (CCl$_4$) $v = 2956$ (vs), 1466 (m), 1393 (m), 1261 (m), 1364 (m), 1047 (vs), 825 (s), 790 (s), 783 (vs), 763 (s), 745 (s); *m/z* (EI, 70 eV): 492 (6) [M]$^+$, 461 (16) [M − OMe]$^+$, 460 (62) [M − S]$^+$, 403 (26) [M − ^{t}BuS]$^+$, 57 (70) [^{t}Bu]$^+$. C$_{18}$H$_{39}$O$_3$P$_3$S$_3$.

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