From Unsymmetrical Diphosphene to New 1,3-Diphosphapropenes

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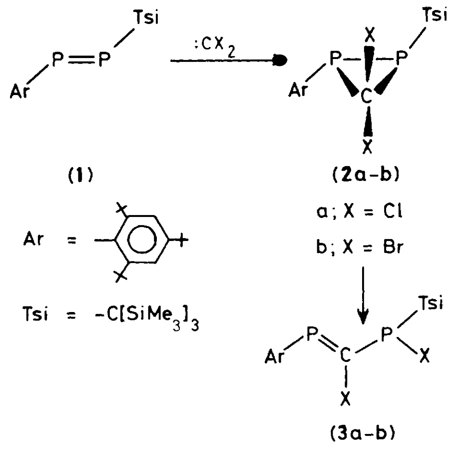
The (*Z*) 1,3-diphosphapropenes (**3**) obtained from dihalogenocarbenes and unsymmetrical diphosphene (**1**), *via* diphosphiranes (**2**), show, by *X*-ray structure analysis of (**3a**), a special conformation involving a coplanar P=C double bond and phosphorus lone pairs.

Diphosphenes are well known to undergo [2 + 1] cycloaddition reactions with carbenoids leading to three-membered heterocycles.[1—3] In this way some symmetrical[1,2] and very few unsymmetrical[3] diphosphiranes have been synthesised. Starting from the unsymmetrical diphosphene (**1**)[4] we have obtained the new diphosphiranes (**2**) differently substituted on phosphorus; the great interest of these highly strained heterocycles is their ability to undergo a selective opening reaction to the stable and functionalized 1,3-diphosphapropenes (**3**).

The addition of an excess of dihalogenocarbenes to (**1**) in pentane solution at low temperature leads to (**2a—b**) which can be unambiguously characterised.† These new heterocycles are stable, but less so than their symmetrical homologues[1,5] (**2a**) in an attempted purification on silica gel rearranges to 1,3-diphosphapropene (**3a**) by ring opening of the P–P bond and selective migration of chlorine to the phosphorus substituted by the tris(trimethylsilyl)methyl group (Scheme 1). After 10 h at room temperature in pentane solution, (**2b**) undergoes the same ring opening reaction with formation of (**3b**). As in the case of *gem* dihalogenocyclopropanes both



Scheme 1

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† Experimental procedure for (**2a**): To a stirred suspension of (**1**) (0.120 g, 0.223 mmol) and Bu^{t}OK (0.180 g; 1.60 mmol; 7 equiv.) in pentane maintained at 0 °C, is added chloroform (0.180 ml, 2.23 mmol, 10 equiv.) in pentane solution. The mixture is allowed to warm to room temperature. The solid residue is eliminated and pentane is evaporated to dryness *in vacuo*. Compound (**2a**) is obtained as a yellow oil. ^{31}P-{^{1}H} n.m.r. (C_6D_6) δ −29.4 [d, P(1)], −77.8 [d, P(2)] $^1J_{P(1)P(2)}$: 144 Hz. M.S. (70 ev), M^+: $m/z = 620$; (**2b**) Same procedure as above. ^{31}P-{^{1}H} N.m.r. (C_6D_6) $\delta = -17.3$ [d, P(1)], −77.0 [d, P(2)], $^1J_{P(1)P(2)}$: 151 Hz.

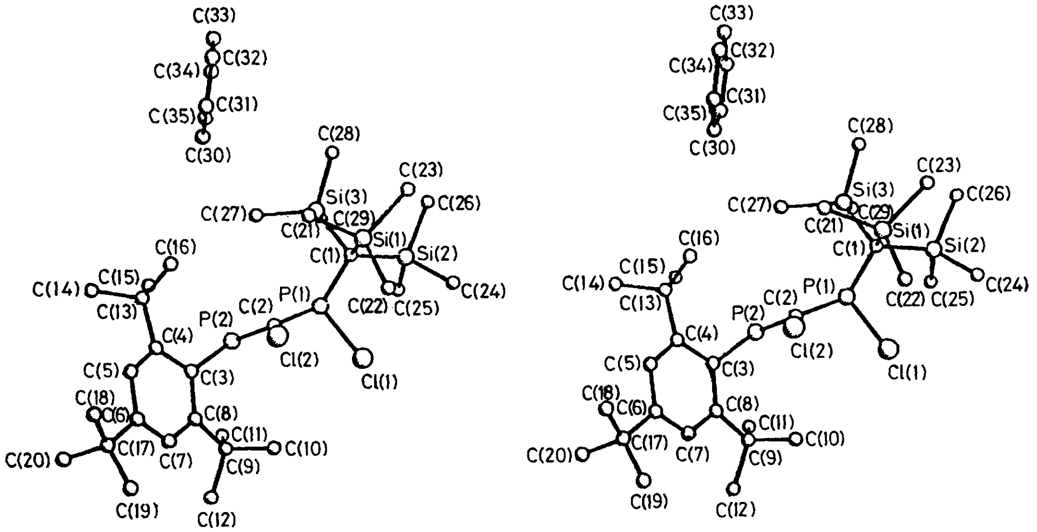

Figure 1. Stereoscopic view of (**3a**). Important bond lengths (Å) and angles (°): C(1)–P(1) 1.838(7); P(1)–C(2) 1.835(7), C(2)–P(2) 1.670(8), P(2)–C(3) 1.848(7), Cl(1)–P(1) 2.095(3), C(2)–Cl(2) 1.741(7); C(3)–P(2)–C(2) 104.7(3), P(2)–C(2)–P(1) 110.3(4), C(2)–P(1)–C(1) 117.0(3); torsional angles (°): Cl(2)–C(2)–P(1)–C(1) 54(2), Cl(2)–C(2)–P(1)–Cl(1) 54(2), C(3)–P(2)–C(2)–P(1) 168(2).

reactions are regioselective:[6] the formation of the P=C double bond occurs only on the phosphorus substituted by the aryl group.

Diphosphapropenes (**3a**—**b**) present unexpected n.m.r. data‡ in particular an extremely large ^{2}J(PP) coupling constant: respectively 457 and 484 Hz. Such values are close to the ^{1}J(PP) coupling constant between two unsaturated phosphorus atoms[7] and are much larger than the values found in the literature for diphosphapropenes[8,9] but similar high ^{2}J(PP) values have been observed in some diphosphinoamines.[10] The ^{13}C n.m.r. indicates that the ^{1}J(CP) coupling constant in the P(2)–C(2) double bond (74.0 Hz) is surprisingly less important than the ^{1}J(CP) coupling constant in the P(1)–C(2) single bond (108.5 Hz). No changes in n.m.r. data are observed between −80 °C and +80 °C.

The *X*-ray study confirms the structure of diphosphapropene (**3a**) in a *Z* configuration§ (Figure 1). Standard values are found for bond lengths, P(2)–C(2) : 1.670(8) Å and P(1)–C(2) : 1.835(7) Å. The P(2)–C(2)–P(1) angle [110.3(4)°] is smaller by about 17° than in other diphosphapropenes.[9] The aryl group is nearly perpendicular (89°) to the P(2)–C(2)–P(1) plane containing the double bond.

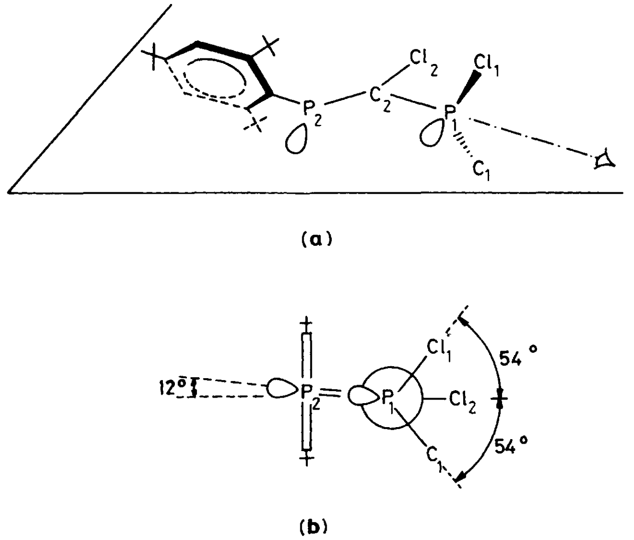

Figure 2. (a) Phosphorus lone pair position related to the P(2)–C(2)–P(1) plane. (b) Newman representation [P(1)–C(2) axis].

Torsional angles Cl(2)–C(2)–P(1)–C(1) and Cl(2)–C(2)–P(1)–Cl(1) are both 54(2)°, so the P(1)–C(1) and P(1)–Cl(1) bonds are symmetrical in relation to the P(1)–C(2)–Cl(2) plane (Figure 2). The two phosphorus lone pairs and the P(2)–C(2) double bond are nearly in the same plane. The dihedral angle between the two planes [P(2)–C(2)–Cl(2)] and [Cl(2)–C(2)–P(1) is 12°, so the P(1) phosphorus lone pair nearly eclipses the C=P double bond.

This special conformation probably stabilized by the bulky groups, was predicted by theoretical calculations in the case of vinylphosphanes[11] to be the most stable. Furthermore, the *syn* position of the two phosphorus lone pairs can explain the ^{2}J(PP) coupling constant enhancement.

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‡ *Selected spectroscopic data for* (**3a**): yellow crystals, m.p. 132 °C, yield ^{31}P n.m.r. spectroscopically quantitative. ^{31}P {^{1}H} n.m.r. (C_6D_6) δ = 328.5 (d, P2), 144 (d, P1) ^{2}J(P1P2) = 457 Hz; ^{1}H n.m.r. (C_6D_6): δ 0.48 [d, ^{4}J(HP1) = 0.88 Hz, 27H, SiMe$_3$], 1.34 (s, 9H, *p*-t-Bu), 1.55 (s, 9H, *o*-t-Bu), 1.57 (s, 9H, *o*-t-Bu), 7.57 [d, ^{4}J(HP2) = 4 Hz, 2H, aromatic H]. ^{13}C n.m.r. ($CDCl_3$): δ = 5.1 [d, ^{3}J(CP1) = 4.8 Hz, C(21)—C(29)], 31.2 [s, C(18)—C(20)], 32.9 [d, ^{4}J(CP2) = 6.3 Hz, C(10)—C(12) or C(14)—C(16)], 33.4 [d, ^{4}J(CP2) = 7.2 Hz, C(14)—C(16) or C(10)—C(12)], 35.0 (s, C17), 37.8 (s, C9 or C13), 38.3 (s, C13 or C9), 121.9 (s, C7 or C5), 122.9 (s, C5 or C7), 134.0 [dd, ^{1}J(CP2) = 60 Hz, ^{3}J(CP1) = 22 Hz, C3] 151.0 (s, C6) 153.1 (s, C4 or C8), 153.8 (s, C8 or C4), 172.3 [dd, ^{1}J(CP1) = 108.5 Hz, ^{1}J(CP2) = 74.0 Hz, C2]; u.v. (hexane: λ = 260 nm (ε = 14 200). m.s. (70 eV) M^+: *m/z* = 620. (**3b**), ^{31}P {^{1}H} n.m.r. (C_6D_6) δ = 343.3 (d, P2), 143.3 (d, P1) ^{2}J(P1P2) = 484 Hz. m.s. (70 eV) M^+; *m/z* = 710.

§ *Crystal structure* for (**3a**): orthorhombic, space group $P2_12_12_1$, a = 12.467 (2), b = 14.924 (5), c = 22.580 (7) Å, U = 4201(2) Å^3, Z = 4, 2701 reflections with $I > 2.5\sigma(I)$, R = 0.055, R_w = 0.052 with $\sigma = 1/[\sigma(F)^2 + 0.000414\ F^2]$. (**3a**) crystallizes with one molecule of benzene. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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