X-Ray Crystal Structure and Diels–Alder Reactivity of the 3,4-Dimethyl-2H-phosphole Dimer

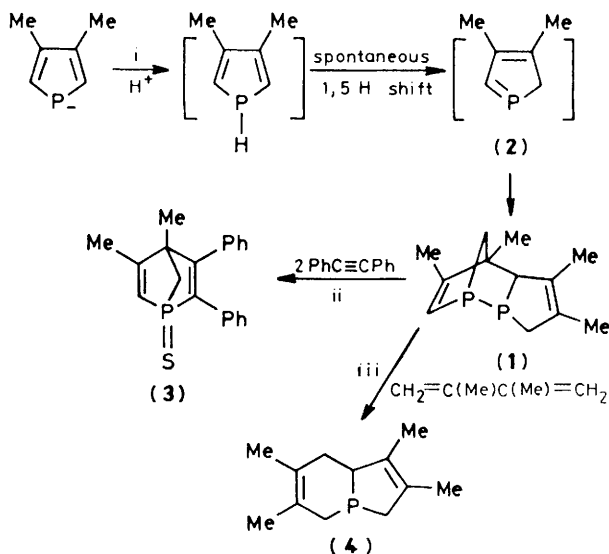Guillaume de Lauzon,[a] Claude Charrier,[a] Hubert Bonnard,[a] François Mathey,*[a] Jean Fischer,[b] and André Mitschler[b]

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The [4 + 2] P–P bonded dimer of 3,4-dimethyl-2H-phosphole has the endo geometry with long, weak P–P and C–C bridges between the two phosphole units; it can therefore act as generator of monomeric 3,4-dimethyl-2H-phosphole at ca. 100 °C and gives the expected [4 + 2] and [2 + 4] cycloadducts with diphenylacetylene and 2,3-dimethylbutadiene.

In a recent communication,[1] we described the protonation of phosphole anions which, instead of leading to the expected 1H-phospholes, gave 2H-phosphole [4 + 2] P–P bonded dimers such as (1). The formula of (1) was deduced primarily from a combination of ^{1}H, ^{13}C, and ^{31}P n.m.r. data but we were unable to establish whether the stereochemistry at the P–C junction was endo or exo. Thus, an X-ray crystal structure analysis of (1) seemed highly desirable and was carried out.† The most significant data are given in the caption to Figure

Scheme 1. Reagents and conditions: i, room temp.; ii, toluene, reflux, 6 h, then S_8; iii, 16 h, 130 °C.

1. The dimer (1) has the endo structure (as does the dimer of cyclopentadiene). The P–P bond length of diphosphines and cyclopolyphosphines is known to be remarkably constant at 2.21—2.22 Å.[2] Thus, the P–P bond of (1) [2.239(1) Å] is significantly longer than usual. Similarly, the C_2–C_7 bond bridging the two phosphole units is abnormally long [1.577(5) Å vs. 1.54 Å for ordinary C–C single bonds]. These data suggested that the dimerization of 3,4-dimethyl-2H-phosphole (2) leading to (1) was easily reversible. This hypothesis was supported by the mass spectrum of (1) [(70 eV, 80 °C): m/e 224 (M, 71%), 112 (M/2, 100%), 97 (M/2 −CH$_3$, 40%)] which showed a base peak corresponding to the monomeric 2H-phosphole. Thus, it was very tempting to use (1) to generate (2) in various [4 + 2] or [2 + 4] cycloaddition reactions at low temperature. In fact, only limited data were available in the literature on cycloaddition reactions involving P=C double bonds.[3] Since in (2) the P=C double bond was neither hindered nor stabilized by cyclic delocalization,‡ and since our previous work with 2H-
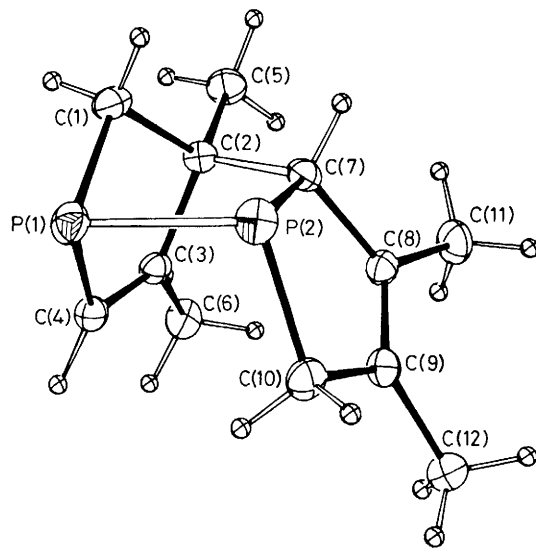
Figure 1. ORTEP drawing (60% probability ellipsoids) of (1) showing the atom numbering scheme (hydrogen atom labels are omitted). Principal bond distances are: P_1–P_2 2.239(1), P_1–C_1 1.844(4), P_1–C_4 1.812(4), P_2–C_7 1.877(4), P_2–C_{10} 1.849(4), C_1–C_2 1.542(5), C_2–C_3 1.518(5), C_3–C_4 1.337(5), C_2–C_7 1.577(5), C_7–C_8 1.508(5), C_8–C_9 1.319(5), and C_9–C_{10} 1.515(6) Å. Bond angles: C_1–P_1–C_4 87.6(2), C_7–P_2–C_{10} 92.8(1), C_1–P_1–P_2 86.0(1), C_4–P_1–P_2 97.5(1), P_1–P_2–C_7 93.3(1), P_1–P_2–C_{10} 104.5(1), P_1–C_1–C_2 102.6(2), C_1–C_2–C_7 104.2(3), P_2–C_7–C_8 103.6(2), P_2–C_7–C_2 109.8(2), and C_2–C_7–C_8 116.6(3)°.

‡ The cyclic strain occurring in the phosphole ring may even enhance the reactivity of the P=C double bond of (2).

phospholes generated at high temperature (>150 °C) showed high reactivity in both [4 + 2] and [2 + 4] cycloaddition reactions,[4] it was hoped that very rich chemistry would be found. We now report preliminary results which demonstrate that dimers such as (1) are indeed generators of 2H-phospholes such as (2) at ca. 100 °C.

In one experiment, dimer (1) was heated in refluxing toluene with a stoicheiometric amount of diphenylacetylene. After sulphurization and chromatography on silica gel (toluene eluant), the adduct (3)§ was recovered in 28% yield (not optimized). Similarly, when crude (1) was heated at 130 °C with a 4-fold excess of 2,3-dimethylbutadiene in a sealed tube, the expected [2 + 4] cycloadduct (4)¶ was obtained and was recovered in 35% yield after kugelrohr distillation at ca. 110 °C/0.1 Torr. It is interesting to note that, apart from 2H-phospholes, practically no [2 + 4] cycloaddition with a P=C double bond acting as a dienophile has ever been reported.[5]

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§ Adduct (3) has been characterized as follows: ^{1}H n.m.r. (CDCl$_3$, 80.13 MHz): δ 1.33 (s, 3H, Me), 2.07 [dd, ^{4}J(H–P) 2 Hz, ^{4}J(H–H) 1.7 Hz, 3H, Me], 2.7 [d, ^{2}J(H–P) 7.6 Hz, 2H, CH$_2$P], 6.42 [dq, ^{2}J(H–P) 27.8 Hz, 1H, CHP], and 6.8—7.4 (m, 10H, Ph); ^{13}C n.m.r. (CDCl$_3$, 20.15 MHz): δ 17.6 [d, ^{3}J(C–P) 15.6 Hz, Me], 18.6 [d, ^{3}J(C–P) 16.6 Hz, Me], 56.5 [d, ^{2}J(C–P) 20.5 Hz, Me–C sp^3], 73.3 [d, ^{1}J(C–P) 58.6 Hz, CH$_2$–P], 127—135.7 (m, Ph + CH–P), 141.6 [d, ^{1}J(C–P) 60.5 Hz, Ph–C–P], 162.1 [d, ^{2}J(C–P) 13.7 Hz, β-C sp^2], and 169.6 [d, ^{2}J(C–P) 7.8 Hz, β-C sp^2] p.p.m.; ^{31}P n.m.r. (CDCl$_3$, ext. H$_3$PO$_4$ δ +ve for downfield shifts, 32.435 MHz): δ +44.7 p.p.m.; mass spectrum (chemical ionization with CH$_4$): m/e 323 (M + 1, 100%).

¶ Adduct (4) has been characterized as follows: ^{13}C n.m.r. (CDCl$_3$): δ 14.6 [d, J(C–P) 2.9 Hz, Me], 17.2 [d, J(C–P) 2 Hz, Me], 21.0 (s, Me), 22.2 (s, Me), 29.4 [d, ^{1}J(C–P) 18.5 Hz, CH$_2$P], 34.0 [d, ^{2}J(C–P) 3.9 Hz, CH$_2$], 36.7 [d, ^{1}J(C–P) 12.7 Hz, CH$_2$P], 47.6 [d, ^{1}J(C–P) 10.7 Hz, CH–P], 125.0 [d, J(C–P) 2.9 Hz, Me–C], 128.1 [d, J(C–P) 4.9 Hz, Me–C], 131.3 [d, J(C–P) 2 Hz, Me–C], and 132.4 (s, Me–C) p.p.m.; ^{31}P n.m.r. (CDCl$_3$): δ −42.3 p.p.m.; mass spectrum (chemical ionization with CH$_4$): m/e 195 (M + 1, 100%).

References

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3 This is partly due to the fact that it is necessary to stabilize the P–C double bond in order to isolate stable compounds; this is done either by steric crowding (see *e.g.* T. C. Klebach, R. Laurens, and F. Bickelhaupt, *J. Am. Chem. Soc.*, 1978, **100**, 4886), or by cyclic delocalization (phosphorins, 1,2,3-diazaphospholes). In both cases, the reactivity of the P–C double bond is reduced. However, some cycloaddition reactions involving P=C double bonds have been reported; for [4 + 2] cycloadditions (phosphorus-containing component first) see G. Märkl and F. Lieb, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 733; G. Märkl, F. Lieb, and C. Martin, *Tetrahedron Lett.*, 1971, 1249; G. Märkl and K. H. Heier, *ibid.*, 1974, 4369; C. Jongsma, H. Vermeer, F. Bickelhaupt, W. Schäfer, and A. Schweig, *Tetrahedron*, 1975, **31**, 2931; Y. Kobayashi, H. Hamana, S. Fujino, A. Ohsawa, and I. Kumadaki, *J. Am. Chem. Soc.*, 1980, **102**, 252 (a formal [4 + 1] cycloaddition is also described, but its mechanism is probably not concerted); Y. Kobayashi, S. Fujino, and I. Kumadaki, *ibid.*, 1981, **103**, 2465; for [2 + 1] cycloadditions, see B. A. Arbuzov and E. N. Dianova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1977, 1453; B. A. Arbuzov, E. N. Dianova, and Y. Y. Samitov, *Dokl. Akad. Nauk SSSR*, 1979, **244**, 1117; for [2 + 3] cycloadditions see E. Niecke, W. W. Schoeller, and D. A. Wildbredt, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 131; R. Carrié, Y. Y. C. Yeung Lam Ko, F. De Sarlo, and A. Brandi, *J. Chem. Soc., Chem. Commun.*, 1981, 1131.

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5 As far as we know, the only exceptions are (a) the reaction of hexachlorocyclopentadiene with 1,2,3-diazaphospholes (B. A. Arbuzov and E. N. Dianova, International Conference on Phosphorus Chemistry, Halle 1979, Abstracts of papers, p. 51) and (b) the reaction of 2,3-dimethylbutadiene with 1,2,3-diazaphospholes (R. Carrié, personal communication).