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SPONTANEOUS CYCLISATION OF 1-PHOSPHAHEXATRIENES INTO 1,2-DIHYDROPHOSPHININES

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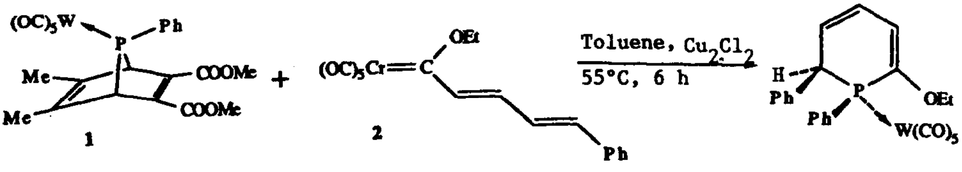
Summary : The reaction of the transient terminal phosphinidene complex $[PhP = W(CO)_5]$ with a butadienyl carbene $Cr(CO)_5$ complex yields a 1-phenyl-1,2-dihydrophosphinine $P\text{-}W(CO)_5$ complex via the spontaneous cyclisation of an intermediate 1-phenyl-1-phosphahexatriene species.

Whereas numerous [4 + 2] , [3 + 2]and [2 + 2]cycloadditions involving P=C double bonds have been recorded in the literature[1], so far only a few electrocyclic reactions have been described with similar systems. The available data concern the cyclisations of 1-phosphabutadienes and 1,4-diphosphabutadienes into the corresponding 1,2-dihydrophosphetes[2,3] and 1,2-dihydro-1,2-diphosphetes[4]. The prototypical cyclisation of hexatrienes into cyclohexadienes has, on the contrary, no equivalent in phosphorus chemistry probably because it is difficult to prepare unhindered phosphahexatrienes. We wish to report here on the first example of such a cyclisation.

In order to build the desired phosphahexatriene skeleton, we decided to use the synthesis of the P=C double bond via the condensation of a transient terminal phosphinidene complex with a carbene complex[3,5].

With this idea in mind, we studied the reaction of the 7-phosphanorbornadiene complex 1 with the butadienylcarbene complex 2[6].

The reaction was run with 4 g (6.1×10^{-3} mol) of complex 1 and 2 g (5.3×10^{-3} mol) of complex 2 with 200 mg of CuCl as a catalyst in 20 ml of toluene. After chromatography of the crude reaction product on silica gel with pentane/dichloromethane (9/1), we obtained 1.7 g of the 1,2-dihydrophosphinine complex 3[7]. According to the ^{31}P NMR spectrum of the crude reaction mixture, one isomer of 3 was very preferentially formed. Its structure was investigated by X-ray crystal structure analysis[8]. The main data are given in the caption of Figure 1. The product has a staggered conformation around the $P\text{-}C_2$ bond : $P\text{-}C_7$ approximately bisects the dihedral angle of the C_2PW_1 and C_2PC_{18} planes. This conformation probably minimizes the steric congestion. Thus, we cannot decide whether this geometry results from the disrotatory cyclisation of the major isomer of the transient 1-phosphahexatriene or if it is adopted for thermodynamic reasons.



3 (52%)

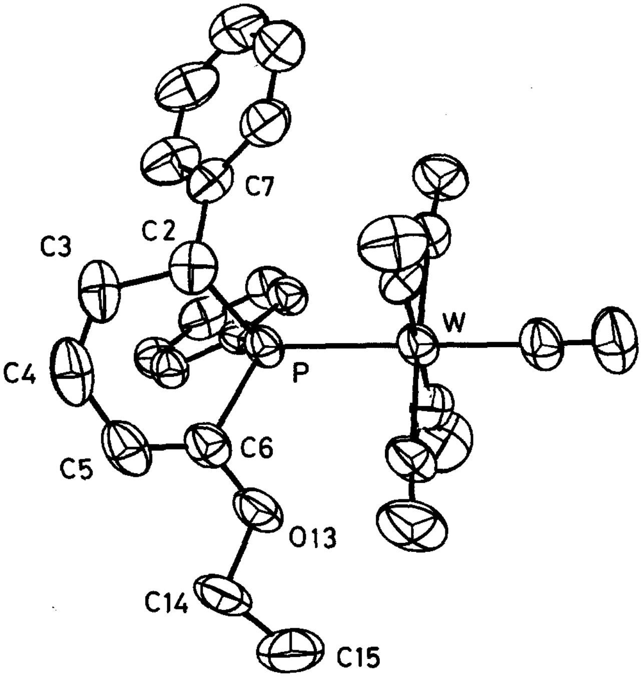


Figure 1

ORTEP representation of complex 3 with thermal ellipsoids at the 50% probability level ; hydrogen atoms are omitted. The molecule is viewed along the P_1-C_2 axis. Principal bond distances (Å) : W_1-P_1 2.522 (2) ; P_1-C_2 1.87 (1) ; P_1-C_6 1.84 (1) ; P_1-C_{18} 1.830 (8) ; C_2-C_3 1.48 (1) ; C_3-C_4 1.31 (1) ; C_4-C_5 1.46 (2) ; C_5-C_6 1.32 (1); C_6-O_{13} 1.35 (1).

Selected bond angles (deg.) : W_1-P_1-C_2 115.8 (3) ; W_1-P_1-C_6 114.0 (3) ; W_1-P_1-C_{18} 118.1 (3) ; C_2-P_1-C_6 99.6 (5) ; C_2-P_1-C_{18} 105.5 (4) ; C_6-P_1-C_{18} 101.4 (4).

Selected torsion angles (deg.) : W_1-P_1-C_2-C_7 74.85 (0) ; C_{18}-P_1-C_2-C_7 57.71 (0).

References and Notes

1. For a review on this subject, see : B.A. Arbuzov, E.N. Dianova, Phosphorus Sulfur, 26, 203 (1986).
2. B.A. Boyd, R.J. Thoma, R.H. Neilson, Tetrahedron Lett., 28, 6121 (1987).
3. N.H. Tran Huy, L. Ricard, F. Mathey, Organometallics, in press.
4. R. Appel, V. Barth, Tetrahedron Lett., 21, 1923 (1980).
5. N.H. Tran Huy, F. Mathey, Organometallics, 9, 207 (1987).
6. R. Aumann, H. Heinen, Chem. Ber., 120, 537 (1987).
7. 3 : ^{31}P NMR ($CDCl_3$) : δ 0.4 ppm, ^1J (^{31}P-^{183}W) 246.5 Hz ; ^{1}H NMR ($CDCl_3$) : δ 1.33 (t, ^3J(H-H) 7 Hz, 3H, CH_3) ; 4.02 (dq, ^4J(H-P) 2 Hz, 2H, OCH_2) ; 4.45 (m, ^3J(H-H) 3.7 Hz, ^2J(H-P) 2.7 Hz, 1H, PhCH) ; 5.58 (m, 1H, HC_3) ; 5.95 (m, 1H, HC_5) ; 6.21 (m, 1H, HC_4) ; ^{13}C NMR ($CDCl_3$): δ14.31 (CH_3) ; 51.16 (d, ^1J(C-P) 19 Hz, CHPh) ; 64.69 (d, ^3J(C-P) 6.5 Hz,OCH_2) ; 104.86 (d, ^2J(C-P) 7.5 Hz, C_5) ; 153.02 (d, ^1J(C-P) 57.5 Hz, = C-OEt) ; 197.24 (d, ^2J(C-P) 7 Hz, cis CO) ; 199.12 (d, ^2J(C-P) 23.5 Hz, trans CO) ppm ; I.R. (CH_2Cl_2) : ν(CO) 2060, 1940 cm^{-1} ; mass spectrum (E.I., 70 eV, ^{184}W) : m/z 618 (M^+, 36%), 534 (M-3CO, 100%).
8. $C_{24}H_{19}O_6PW$, F.W. = 618.24 ; monoclinic space group : P21/C (# 14) ; a = 19.132 (3) Å, b = 16.440 (2) Å, c = 16.855 (2) Å, β = 115.84 (1)° ; V = 4771.3 (2.3) Å^3 ; Z = 8 ; Dcalc = 3.442 g/cm^3 ; Radiation = Mo Kα (λ= 0.71073 Å) ; μ =100.9 cm^{-1} ; F (000) = 4800 ; Temperature = 23°C ± 1°C ; Final R = 0.053, R_ω = 0.067 ; g.o.f. = 1.31 ; Number of Unique Reflections = 6395.