

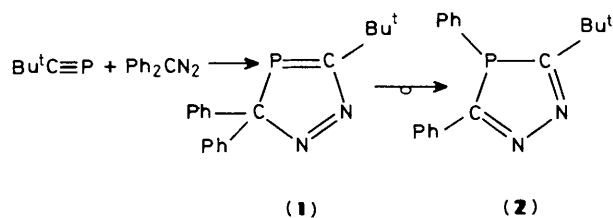
Reaction of a Phospha-alkyne with Diphenyldiazomethane: a Novel 1,2-Phenyl Migration from Carbon to Phosphorus

Alan H. Cowley,* Stephen W. Hall, Richard A. Jones,* and Christine M. Nunn

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, U.S.A.

The reaction of Ph_2CN_2 with $\text{Bu}^t\text{C}\equiv\text{P}$ affords a [2 + 3] cycloadduct, which isomerises *via* a novel 1,2-phenyl migration from carbon to phosphorus.

It has been demonstrated previously that diazoalkanes undergo [2 + 3] cycloaddition reactions with phospha-alkynes.¹ However, in each instance the diazoalkane featured a C–H bond and the initial adduct rearranged to a diazaphosphole *via* shift of hydrogen from carbon to nitrogen. We have found that if a diazoalkane without C–H bonds is used, the reaction takes a different course. We also present the first spectroscopic evidence for the initially formed [2 + 3] cycloadduct.



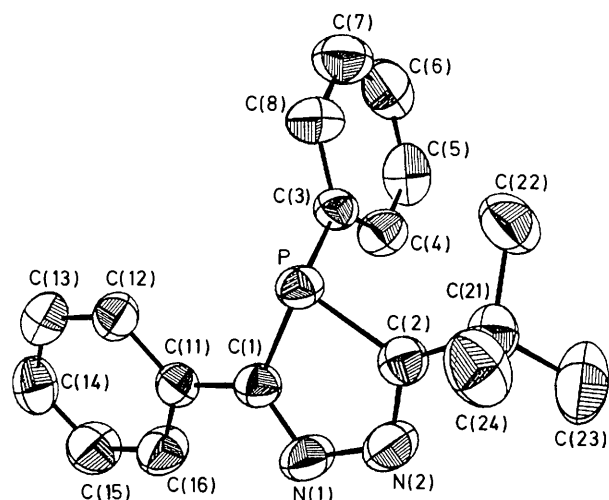


Figure 1. View (ORTEP) of the molecule (2) showing the atom numbering scheme; important lengths (Å) and angles (°): P–C(1) 1.813(2), P–C(2) 1.817(3), P–C(3) 1.818(3), C(1)–N(1) 1.292(3), C(2)–N(2) 1.287(3), N(1)–N(2) 1.425(3); C(1)–P–C(2) 85.9(1), C(1)–P–C(3) 104.9(1), C(2)–P–C(3) 106.6(1).

Treatment of $\text{Bu}^t\text{C}\equiv\text{P}^2$ with an equimolar quantity of Ph_2CN_2 in n-hexane at 0°C for 15 min produces a red solution. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum (121.5 MHz) of this solution (s, δ +253 p.p.m.) is consistent with the two-co-ordinate phosphorus environment in structure (1). After a further 15 min stirring at 0°C, the mixture assumes a pale yellow colour. Filtration, and concentration and cooling of the filtrate to –20°C results in crystals of the rearrangement product (2) (m.p. 98–99°C) of composition $\text{C}_{18}\text{H}_{19}\text{N}_2\text{P}$.† The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of (2) (C_6D_6 ; 121.5 MHz) comprises a singlet (δ +19 p.p.m.) in the region expected for tertiary phosphines. A further indication of the tri-co-ordinate nature of the phosphorus centre is provided by the fact that $^1J_{\text{PC}}$ for the

CBu^t (27 Hz)‡ is much smaller than those of diazaphospholes and other two-co-ordinate phosphorus systems. Moreover, the medium-resolution mass spectrum of (2) reveals a peak at m/z 108 (P–Ph).

An X-ray analysis confirms the structure assignment for (2). It is clear that a Ph group has migrated to phosphorus (Figure 1).§ All three P–C bond distances are identical within experimental error and indicative of single bonds. The carbon–nitrogen and nitrogen–nitrogen bond distances correspond to bond orders of two and one, respectively.

We thank the National Science Foundation and the Robert A. Welch Foundation for financial support.

Received, 8th February 1988; Com. 8/00529J

References

- 1 Y. Y. C. Yeung Lam Ko, R. Carrié, A. Mench, and G. Becker, *J. Chem. Soc., Chem. Commun.*, 1984, 1634; W. Rösch, U. Vogelbacher, T. Allspach, and M. Regitz, *J. Organomet. Chem.*, 1986, **306**, 39; T. Allspach, M., Regitz, G. Becker, and W. Becker, *Synthesis*, 1986, 31.
- 2 G. Becker, G. Gressner, U. Uhl, *Z. Naturforsch., Teil B*, 1981, **36**, 16; G. Becker, *Z. Anorg. Allg. Chem.*, 1974, **430**, 66.

‡ For compound (2): $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. (C_6D_6 ; 75.4 MHz; ambient temp.) δ 36.55 [d, $^2J_{\text{PC}}$ 3.8 Hz, $\text{CC}(\text{CH}_3)_3$], 37.77 [d, $^2J_{\text{PC}}$ 17 Hz, $\text{CC}(\text{CH}_3)_3$], 179.56 (d, $^1J_{\text{PC}}$ 15.1 Hz, CC_6H_5), and 190.35 [d, $^1J_{\text{PC}}$ 27 Hz, $\text{CC}(\text{CH}_3)_3$]; ^1H n.m.r. (C_6D_6 ; 300 MHz; ambient temp.) δ 1.19 (9H, s, Bu^t).

§ *Crystal data:* $\text{C}_{18}\text{H}_{19}\text{N}_2\text{P}$, $M = 294.30$, monoclinic, space group $P2_1n$ (No. 14), $a = 9.805(2)$, $b = 16.290(4)$, $c = 11.119(2)$ Å, $\beta = 111.15(2)^\circ$, $U = 1656.2$ Å³, $Z = 4$, $D_c = 1.180$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.56$ cm⁻¹; 3222 Unique reflections measured with an Enraf-Nonius CAD-4 diffractometer over the range $3.0 \leq 2\theta \leq 50.0$ (θ – 2θ scan mode). An anisotropic decay correction was made but no absorption correction was applied. The structure was solved by direct methods and refined (difference Fourier, full-matrix least-squares) using 1919 reflections with $I > 3.0 \sigma(I)$. The final residuals were $R = 0.0373$ and $R_w = 0.0355$. 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.

† A satisfactory elemental analysis was obtained for the product (2).