

A New Reaction Involving 1,5-Diazabicyclo[4.3.0]non-5-ene as a Nucleophile and a Two Proton Donor

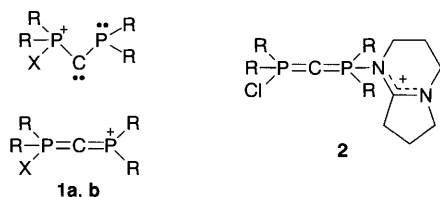
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1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) reacts at both phosphorus atoms of the (phosphino)(*P*-chlorophosphonio)carbene **1a** affording the cationic unsaturated tricyclic adduct **5**.

DBN (1,5-diazabicyclo[4.3.0]non-5-ene) is frequently used as a 'non-nucleophilic base' both in organic and inorganic syntheses.¹ However, it has been shown that this strong non-ionic base can react with a variety of main group electrophiles, including those which are relatively weak, giving rise to the formation of a range of onio-substituted derivatives.² We now report a further remarkable reaction in which DBN acts not only as a nucleophile but also as a two proton donor.

We have recently described the synthesis and spectroscopic characterisation in solution of the (phosphino)(*P*-chlorophosphonio)carbene **1a**,³ however all attempts to isolate this compound failed. *Ab initio* calculations⁴ and an X-ray crystal



Scheme 1 (Phosphino)(phosphonio)carbenes **1a** X = Cl, **1b** X = H and the expected adduct **2** of **1a** with DBN; counter anion CF₃SO₃⁻; R = NPr₂

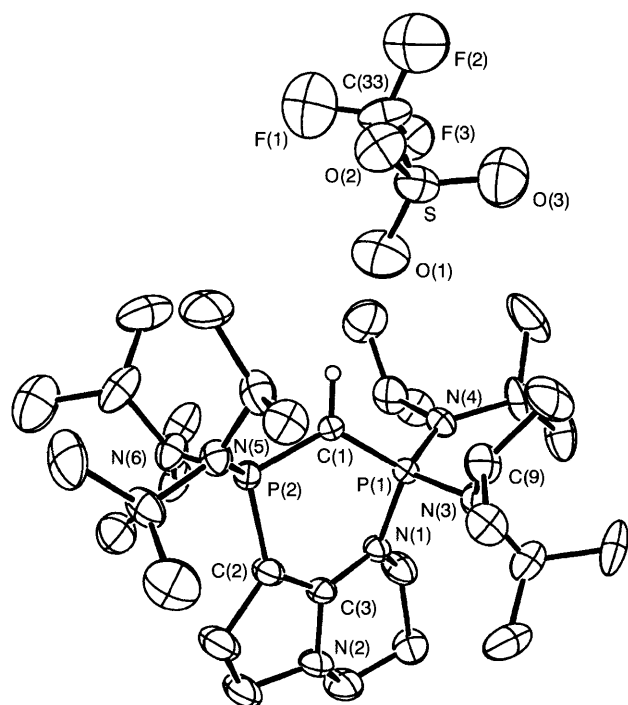
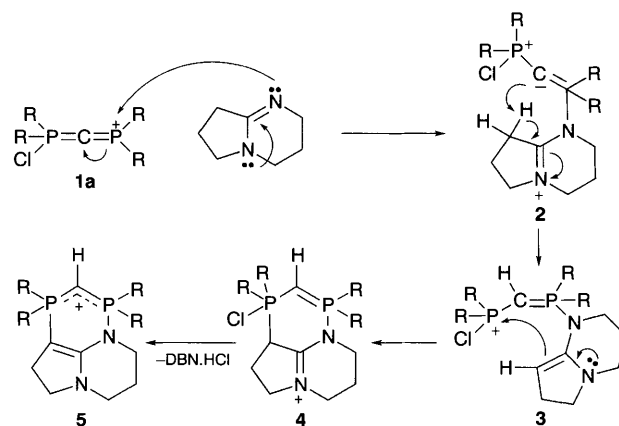


Fig. 1 Molecular structure of **5**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.660(2), P(2)–C(1) 1.719(3), P(1)–N(3) 1.654(2), P(1)–N(4) 1.636(2), P(2)–N(5) 1.666(2), P(2)–N(6) 1.685(3), P(1)–N(1) 1.705(2), P(2)–C(2) 1.751(3), N(1)–C(3) 1.384(4), C(2)–C(3) 1.358(4), C(3)–N(2) 1.387(4) Å; P(1)–C(1)–P(2) 123.6(2), C(1)–P(2)–C(2) 104.7(1), P(2)–C(2)–C(3) 123.0(2), C(3)–N(1)–P(1) 117.5(2), N(1)–P(1)–C(1) 108.7(1)°.

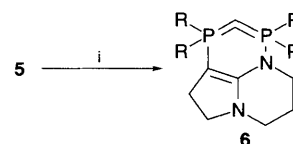
study⁵ of the *P*-hydrogeno analogue **1b** have shown that the σ^3 -phosphorus atom was planar and positively charged (Scheme 1). Therefore, by analogy with the reaction of DBU or DBN with phosphonium salts,² we believed it would be possible to isolate adduct **2**.

To a dichloromethane solution of carbene **1a** was added an excess of DBN at -78°C . The quantitative conversion to a new species was indicated by ³¹P NMR [AB system at δ +42.5 and +58.9 ($^2J_{\text{PP}} = 50.1$ Hz)]. However, the presence of a PC(H)=P sequence was indicated by a *J*-modulated ¹³C NMR spectrum (15.1, dd, $^1J_{\text{PC}} = 179.4$ and 138.2 Hz) and was confirmed by a doublet of doublets in the ¹H NMR spectrum [0.97 ($^2J_{\text{PH}} = 0.9$ and 11.2 Hz)]. Furthermore doublets at δ 68.9 ($^1J_{\text{PC}} = 151.1$ Hz) and 154.4 ($^2J_{\text{PC}} = 11.6$ Hz) in the ¹³C NMR spectrum were consistent with a PC=C fragment.†

Crystals suitable for a single-crystal X-ray diffraction study‡ were isolated in 50% yield after washing the crude reaction mixture with ether and recrystallisation from CH₂Cl₂-ether. This study revealed that instead of the expected simple carbene adduct **2**, a tricyclic species **5** had been formed (Fig. 1). There is a weak interaction of the triflate anion with the methylene proton [C(1)⋯O(1) = 3.253(4) Å, C(1)–H(C1)⋯O(1) = 153°], but not with either of the phosphorus centres. The six membered ring containing the P–C(H)–P fragment adopts a boat-like conformation. The bond distances P(1)–C(1) [1.660(2) Å] and P(2)–C(1) [1.719(3) Å] are comparable, indicating partial charge delocalisation. A localised carbon–carbon double bond



Scheme 2 Proposed mechanism for the synthesis of the tricyclic adduct **5**; R = NPr₂; counter anion CF₃SO₃⁻



Scheme 3 Reagents and conditions: i, Na⁺N(SiMe₃)₂⁻, C₆D₆; R = NPr₂

C(2)–C(3) [1.358(4) Å] is readily apparent in the five-membered ring.

This reaction is believed to proceed as expected *via* initial nucleophilic attack by DBN at the σ^3 -phosphorus centre of **1a** resulting in the formation of **2**. The basicity of the carbodiphosphorane carbon is sufficient to abstract a relatively acidic proton in the α position to the iminium function giving **3**. Cyclisation then occurs by attack of the enamine on the phosphonio centre affording **4**; lastly excess DBN easily removes HCl yielding product **5** (Scheme 2). Overall the reaction can be considered as the 1,3-di-nucleophilic attack of DBN on the (phosphino)(phosphonio)carbene **1a**. This type of reactivity is not unprecedented, Chambers *et al.* have recently reported that the related base DBU reacts in a similar manner with 2-H heptafluorobut-2-ene.⁶

Since very few cyclic carbodiphosphoranes are known,⁷ it was tempting to try to deprotonate **5** (Scheme 3). Initial attempts with classical bases proved unsuccessful, so a procedure analogous to that described by Bestmann⁸ was used. Compound **5** was treated with a slight excess of sodium hexamethyldisilyl amide in benzene, the ³¹P NMR spectrum clearly demonstrated the formation of a new species (AB system at δ +30.2 and +29.4, ²J_{PP} = 114.0 Hz). The deprotonation of **5** was apparent from the ¹³C proton coupled NMR spectrum where the signal of the PCP carbon appears as a doublet of doublets (14.9, ¹J_{CP} = 138.0 and 144.0 Hz). Compound **6** is easily reprotonated suggesting the highly basic nature of this new carbodiphosphorane, despite complete charge delocalisation in the conjugate acid **5** being precluded by the non-planar nature of the ring system.

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Footnotes

† Satisfactory elemental analyses for **5** have been obtained.

‡ *Crystal data* for **5**: C₃₃H₆₇N₆F₃P₂S₁O₃, *M* = 746.9, monoclinic, space group *P*2₁/*c* (No. 14), *a* = 10.933(2), *b* = 9.889(2), *c* = 37.426(4) Å, β = 91.19(1)°, *V* = 4045(1) Å³, *Z* = 4, *F*(000) = 1616, μ (Mo-K α) = 0.20 mm⁻¹, *D*_c = 1.226 g cm⁻³, crystal size 0.50 × 0.40 × 0.40 mm. 8801 total reflections were collected on an Enraf-Nonius CAD4 diffractometer at 293 K (graphite-monochromated Mo-K α radiation λ = 0.71073 Å, ω -2 θ scan mode, 2 θ ≤ 54°). Of these, 5141 reflections with *F*_o² > 3 σ (*F*_o²) were used for the solution (direct methods using SHELXS-86 program) and refined by full-matrix least squares analysis (using SHELX-76 program). All non-H atoms anisotropic. H atoms found on a difference Fourier map, introduced in calculations in constrained geometry [*d*(C–H) = 0.97 Å], with isotropic thermal parameters first refined, then kept fixed. Scattering factors (*f*^r, *f*^w) taken from 'International Tables for X-ray Crystallography.' Last full-matrix refinement cycle: *R*(*f*_o) = 0.040, *R*_w = 0.044 with unit weights, 5141 observations, 433 variable parameters, *S* = 1.388, max. parameter shift/esd = 0.001, max. and min. residual peaks of 0.29 and –0.26 e Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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