The Cycloaddition Reaction of 1,3-Diphospha-2,4,5-tri-t-butylcyclopentadiene and 1,2,4-Triphospha-3,5-di-t-butylcyclopentadiene: Crystal and Molecular Structure of the Ethanol Adduct of $P_5C_5Bu^t{}_5H_2$

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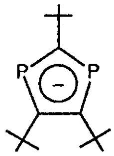
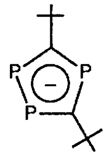
Protonation of a 1 : 1 mixture of the anions $(P_2C_3Bu^t{}_3)^-$, **1** and $(P_3C_2Bu^t{}_2)^-$, **2**, affords the corresponding di- and tri-phosphacyclopentadienes **3** and **4** which undergo a [4 + 2] cycloaddition reaction to form $P_5C_5Bu^t{}_5H_2$ **5** whose structure has been elucidated by NMR spectroscopy and a single crystal X-ray study of its EtOH adduct $P_5C_5Bu^t{}_5H_3$ (OEt), **6**; in the [4 + 2] cycloaddition reaction the diphosphacyclopentadiene acts as the diene and the triphosphacyclopentadiene as the dieneophile, unlike the corresponding self-cycloaddition reaction of the triphosphacyclopentadiene there is no subsequent [2 + 2] cycloaddition of the C=C and P=C bonds in **5** to give a cage structure.

There is considerable current interest in the organic chemistry and coordination chemistry of compounds containing phosphorus–carbon multiple bonds.[1,2] Phosphaalkynes, RC≡P, have played a particularly important role in the development of both these areas[3] and very recently their potential as building blocks for synthesis of cages containing phosphorus and carbon has been described.

To date organophosphorus cages containing four,[4,5] five[5,6]



1



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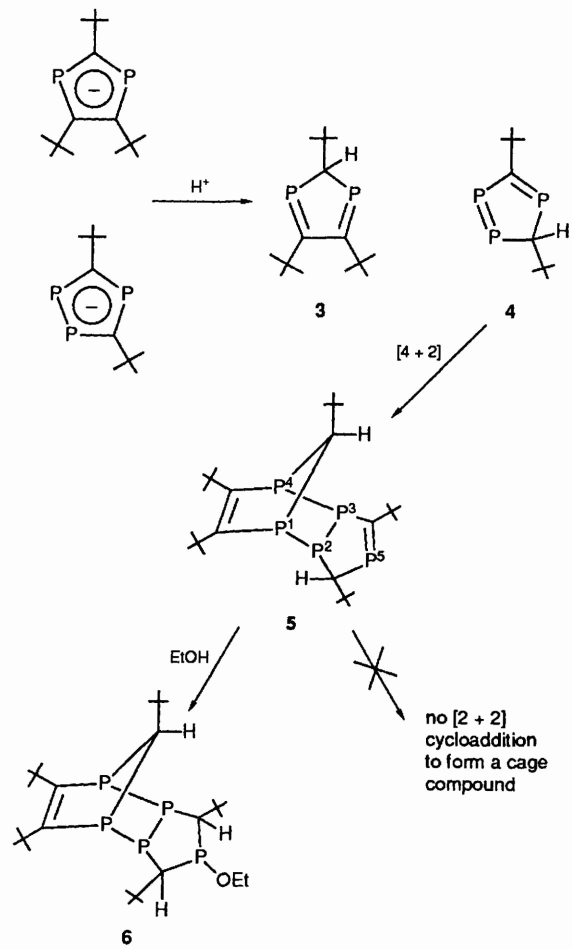
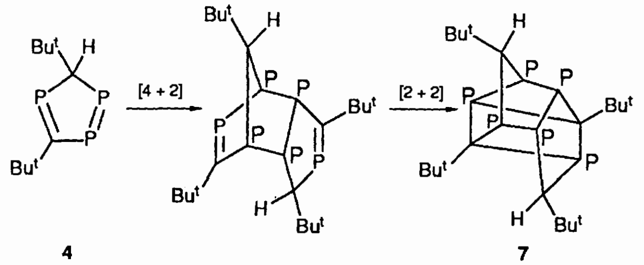


no [2 + 2] cycloaddition to form a cage compound

Scheme 1



Scheme 2

and six[7] phosphorus atoms have been reported and structurally characterised. We now report that protonation of a mixture of the sodium salts of the diphospha- and triphosphacyclopentadienyl anions **1** and **2** with CH$_3$CO$_2$H leads to the formation of the colourless compound P$_5$C$_5$Bu$^t_5$H$_2$, **5**, (*m/z* = 502)† whose ^{31}P(^{1}H) NMR spectrum† is only consistent with the proposed structure since the chemical shift of P(5) (315.5 ppm) lies in the region characteristic of C=P– double bonds.

The interesting features summarised in reaction Scheme 1 are (i) the intermediacy of P$_2$C$_3$Bu$^t_3$H **3** and P$_3$C$_2$Bu$^t_2$H **4** and (ii) in the [4 + 2] cycloaddition reaction the diphosphacyclopentadiene acts as the diene and the triphosphacyclopentadiene is the dieneophile. (iii) The spontaneous [2 + 2] cycloaddition reaction of intermediate **5** to give a 'cage' compound does not occur, unlike our previous report of the corresponding reaction involving two triphosphacyclopentadienes **4** to give **7** (see Scheme 2), indicating that this type of [2 + 2] cycloaddition reaction is facilitated more by P=C bonds than by C=C bonds.

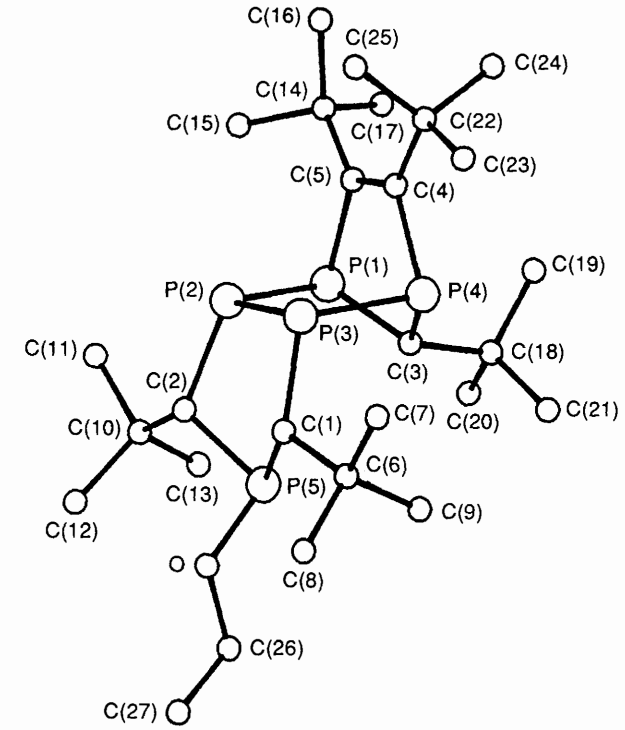


Fig. 1

Confirmation of the proposed structure of **5** comes from a single crystal study of the product formed when the above reaction was carried out in ethanol to afford colourless crystals of P$_5$C$_5$Bu$^t_5$H$_3$(OEt), **6**, the molecular structure of which was determined by a single crystal X-ray study and is shown in Fig. 1.‡ Compound **6** clearly arises from addition of EtOH across the P=C double bond of **5**, suggesting that many similar addition reactions of these polyphosphorus compounds will be possible.

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References

1 R. Appel and F. Knoll, *Adv. Inorg. Chem.*, 1989, **33**, 259 and references therein.
2 M. Regitz and P. Binger, *Angew. Chem., Intl. Ed. Engl.*, 1988, **27**, 1484 and references cited therein.
3 J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327; M. Regitz, *Chem. Rev.*, 1990, **90**, 191.
4 T. Wettling, F. Schreider, O. Wagner, C. G. Kreiter and M. Regitz, *Angew. Chem., Intl. Ed. Engl.*, 1989, **28**, 1013.
5 D. Zhu, R. Schaufele, K. Pritzkow and U. Zenneck, *Angew. Chem., Intl. Ed. Engl.*, 1989, **28**, 900.
6 R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Organomet. Chem.*, 1989, **375**, C31.
7 R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1989, 1046.

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† ^{31}P NMR **5** (rel H$_3$PO$_4$): δp 64.9, 11.0, −7.7, 61.7, 315.5, $J_{2,5}$ 17.5, $J_{3,5}$ 4.5, $J_{1,2}$ 306.0 Hz, $J_{4,3}$ 300.4, $J_{3,2}$ 305.1, $J_{2,4}$ 20.5, $J_{1,3}$ 0 Hz; *m/z* 502 (M$^+$), 431 [(Bu^{t}CP)$_4$P]$^+$, 402 [(Bu^{t}CP)$_4$H$_2$]$^+$, 364 [(Bu^{t}CP)$_3$P$_2$H$_2$]$^+$, 301 [(Bu^{t}CP)$_3$H]$^+$, 169 [(Bu^{t}CP)(Bu^{t}C)]$^+$, 69 (Bu^{t}C)$^+$, 57 (Bu^t)$^+$.

‡ *Crystal data:* C$_{27}$H$_{53}$OP$_5$, $P2_1/n$, a = 11.652(2), b = 19.848(3), c = 14.399(4) Å, β = 107.02(2)°, Z = 4, μ(Mo-Kα) = 3.0 cm^{-1}; 2574 reflections with $F^2 > 3\sigma(F^2)$ used in the refinement to R = 0.043, R_w = 0.055. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.