[4 + 2] Cycloaddition reactions involving 1,3-diphosphacyclopentadiene and 1,2,4-triphosphacyclopentadiene: crystal and molecular structures of the exo-compounds $P_5C_5{}^tBu_5H_2$ and $P_4C_6{}^tBu_6H_2$ [1]

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Abstract

The molecular structures of the [4 + 2] cycloaddition products of (i) 1,3-diphosphacyclopentadiene with itself and (ii) with 1,2,4-triphosphacyclopentadiene are presented and mechanistic differences discussed in relation to the 'cage' product $P_6C_4{}^tBu_4H_2$ which is formed from the [4 + 2] and [2 + 2] self-cycloaddition reactions of 1,2,4-triphosphacyclopentadiene. © 1997 Elsevier Science S.A.

Keywords: Phosphorus; Cyclopentadienyl; Cycloaddition; Group 15

1. Introduction

The spontaneous generation of the five-membered anionic ring compounds $(P_2C_3{}^tBu_3)^-$ (1) and $(P_3C_2{}^tBu_2)^-$ (2) as their sodium salts occurs on treatment of $P{\equiv}C^tBu$ with Na/Hg in dimethoxyethane (dme) [1,2].

(1)   (2)
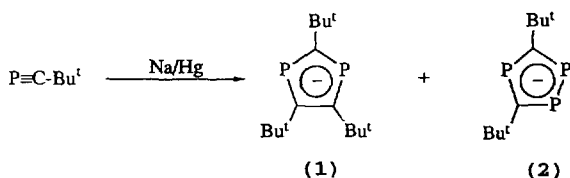
Compounds 1 and 2 can also be obtained as a mixture from the reaction of the phosphaalkene RP = C^tBuR' (R = SiMe$_3$, R' = OSiMe$_3$) with Na metal in dimethoxyethane (dme) [3]. The $(P_3C_2{}^tBu_2)^-$ ring anion can also be synthesised as a pure compound (i.e. free from the $(P_2C_3{}^tBu_3)^-$ anion). Nixon and coworkers [4] reported the synthesis of the 3,3'-diphospha-1,1'-

biphospholyl compound $P_4C_6^tBu_6$ (3) (vide infra) which is a dimer containing two P–P linked $(P_2C_3{}^tBu_3)^-$ units which reacts readily with Na (metal) in dimethoxyethane to give the $(P_2C_3{}^tBu_3)^-$ anion (1) as the sole product of the reaction.

(3)
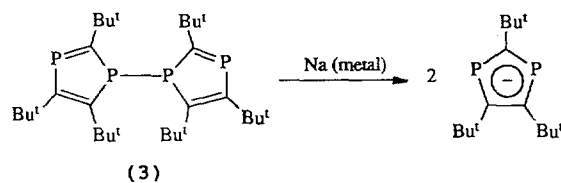
The 'metallocene-like' chemistry of these two cyclic anions is well documented in a series of papers [5–11] and reviews [12–14]; however, their organic chemistry is only just starting to develop. The pentameric 'cage' $P_5C_5{}^tBu_5$ [15] results from oxidative coupling of the two ring anions and the triruthenium carbonyl cluster complex, $[Ru_3(CO)_9(P_5C_5{}^tBu_5)]$ is also known [16].

Here we report the syntheses and structural characterisation of two [4 + 2] cycloaddition products of the protonation of ring systems 1 and 2.

2. Results and discussion

The pentaphosphorus–dicyclopentadiene compound $P_5C_5{}^tBu_5H_2$ (4) results from protonation of a mixture

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[1] This paper is dedicated to the late Professor Yuri Struchkov for his many outstanding contributions to structural organometallic chemistry and in recognition of previous collaborative studies (with JFN).
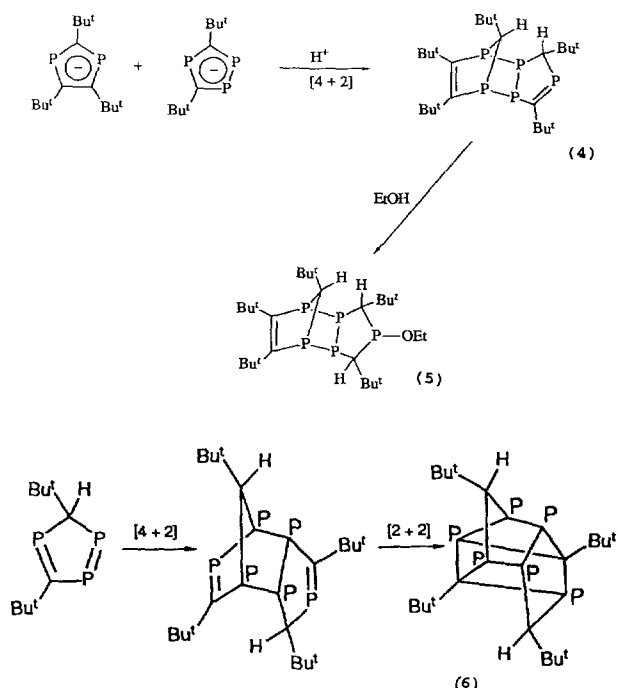
Scheme 1.

of $(P_2C_3{}^tBu_3)^-$ (1) and $(P_3C_2{}^tBu_2)^-$ (2) [17]. The product was shown to result from a [4 + 2] cycloaddition reaction, but could not be obtained in crystalline form, and its structure was elucidated by NMR and mass spectroscopic analysis and by a single crystal X-ray study of its EtOH adduct 5 [17] and also its trisulfide $P_5C_5{}^tBu_5H_3S_3(OEt)$ [18]. In contrast, protona-

tion of 2 alone gave the hexaphosphorus 'cage' compound $P_6C_4{}^tBu_4H_2$ (6) via the proposed non-isolable intermediate, shown in Scheme 1, formed by the [4 + 2] cycloaddition step, which subsequently undergoes a [2 + 2] cycloaddition reaction to yield 6 [19].

Previously [12,14], we have developed an extensive organometallic chemistry of the $(P_3C_2{}^tBu_2)^-$ and $(P_2C_3{}^tBu_3)^-$ rings attached to a variety of metals in which the rings exhibited η^5-, η^3-, and/or η^1-ligating behaviour. The latter ligation occurs only for the $(P_3C_2{}^tBu_2)^-$ ring in Pt(II) and Pd(II) systems containing stabilising R_3P ligands [20,21] and in one instance an Rh(I) complex [22]. We were therefore interested in the behaviour of the ring systems 1 and 2 towards more reactive organoplatinum(II) systems containing more readily displaceable ligands.

2.1. Synthesis of $P_5C_5{}^tBu_5H_2$ and $P_4C_6{}^tBu_6H_2$

$[PtCl_2(cod)]$ reacts with a dimethoxyethane solution of $[Na(P_2C_3{}^tBu_3)]$ and $[Na(P_3C_2{}^tBu_2)]$ rings to give a mixture of organophosphorus compounds after column chromatography. These products presumably arise via decomposition and/or protonation of unstable organometallic intermediates involving either η^1-, η^3-, or η^5-Pt(II) complexes of the di- and triphospholide ring systems. This mixture can be separated by careful column chromatography and compounds $P_5C_5{}^tBu_5$ [15], $P_5C_5{}^tBu_5H_2$ (4), $P_4C_6{}^tBu_6H_2$ (7) were fully characterised as well as the novel hexameric 'cage' compound $P_6C_6{}^tBu_6$ which has recently been discussed elsewhere
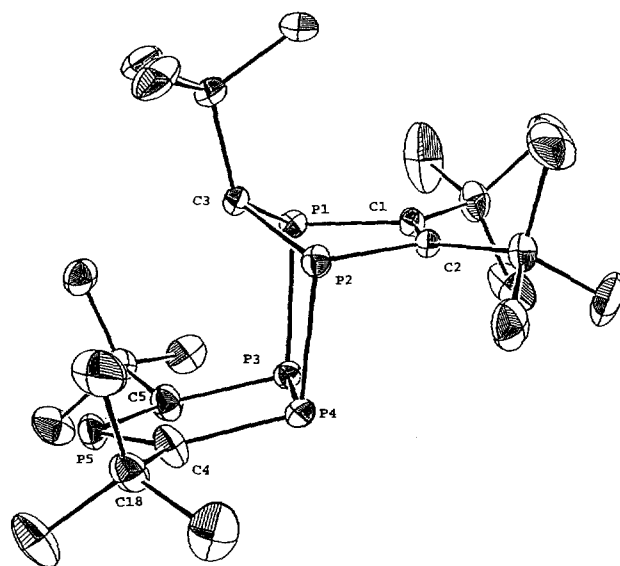
P(5)-C(5) = 1.779(3), P(5)-C(4) = 1.707(3), P(4)-C(4) = 1.840(3), P(3)-C(5) = 1.852(3), P(3)-P(4) = 2.216(1), P(2)-P(4) = 2.234(1), P(1)-P(3) = 2.227(1), P(2)-C(3) = 1.840(2), P(1)-C(3) = 1.835(3), P(2)-C(2) = 1.855(3), P(1)-C(1) = 1.853(3), C(1)-C(2) = 1.357(3), P(4)-C(4)-P(5) = 121.2(2), P(4)-C(4)-C(18) = 118.4(2), P(5)-C(4)-C(18) = 119.6(2), P(3)-C(5)-P(5) = 118.7(2), P(3)-C(5)-C(22) = 119.0(2), P(5)-C(5)-C(22) = 116.6(2), P(1)-C(3)-P(2) = 104.3(1)

Fig. 1. Molecular structure of $P_5C_5{}^tBu_5H_2$ (4) together with the atomic numbering scheme and some selected bond lengths (Å) and angles (°).

[23]. The new synthetic route to the previously known $P_5C_5^tBu_5H_2$ (4) has enabled us to obtain single crystals for the first time. A single crystal X-ray diffraction study reveals the molecular structure shown in Fig. 1, which gives selected bond lengths and angles. Atom coordinates are listed in Table 1.

The P(5)–C(4) bond distance (1.707(3) Å) is slightly longer than the expected value for a P=C double bond (1.64–1.69 Å) [4,24–29], and the P(1)–P(3), P(2)–P(4) and P(3)–P(4) bond distances (2.227(1), 2.234(1) and 2.216(1) Å respectively) lie in the range expected for a P–P single bond [4,18,30–32]. The C(1)–C(2) distance (1.357(3) Å) is typical for a C=C double bond, likewise P(5)–C(5), P(4)–C4), P(3)–C(5), P(2)–C(3), P(1)–C(3), P(2)–C(2) and P(1)–C(1) bond distances (1.779(3), 1.840(3), 1.852(3), 1.840(2), 1.835(3), 1.855(3) and 1.853(3) Å respectively) are all typical of P–C single bonds. The unsaturated C(4) atom is planar (Σ_{angles} = 359.2°).

2.2. Characterisation, crystal and molecular structure of $P_4C_6^tBu_6H_2$ (7)

The new compound $P_4C_6^tBu_6H_2$ (7), which is the expected dimer of the protonated ring 1 $P_2C_3^tBu_3H$, was characterised on the basis of (i) the observation of the parent ion m/z = 540(M)$^+$ and peaks at 270 $[P_2C_3^tBu_3H]^+$, 213 $[P_2C_3^tBu_2H]^+$ and 57 $[^tBu]^+$ in the

mass spectrum, (ii) the presence of four different phosphorus resonances in the $^{31}P\{^1H\}$ NMR spectrum, and (iii) the observation of six separate ^tBu resonances in the ^1H NMR spectrum.

The $^{31}P\{^1H\}$ NMR spectrum of 7, shown in Fig. 2, is very similar to that of 4 [17] with, as expected, one missing phosphorus resonance. Resonances are observed, corresponding to four different types of phosphorus nuclei, as an [ABMX] spin system. The four resonances (δP(X) 321.8, δP(B) 97.9, δP(A) 92.1 and δP(M) 15.1 ppm) each appear as multiplets. Only the P(A) and P(M) resonances show a direct one-bond P–P bond coupling ($^1J_{P(A)P(M)}$ 273.5 Hz). Three further $^2J_{PP}$ coupling constants are also readily identified ($^2J_{P(X)P(B)}$ 125.9, $^2J_{P(X)P(M)}$ 7.6 and $^2J_{P(A)P(B)}$ 30.5 Hz). The ^1H NMR spectrum of 7 shows six different two-proton resonances (δ 1.71 and 3.26 ppm, intensity ^1H each) as a ddd and a dddd respectively. Confirmation of the proposed structure for compound 7 comes from a single crystal X-ray diffraction study of the product and the molecular structure is shown in Fig. 3, which gives selected bond lengths and angles. Atom coordinates are given in Table 2.

As expected, the molecular structure of $P_4C_6^tBu_6H_2$ (7) is similar to that found for $P_5C_5^tBu_5H_2$ (4) [4,24–29] presented earlier. The structure of 7 shows that the P(4)–C(1) bond distance (1.676(3) Å) lies in the range expected for a P=C double bond and that the P(1)–P(3)
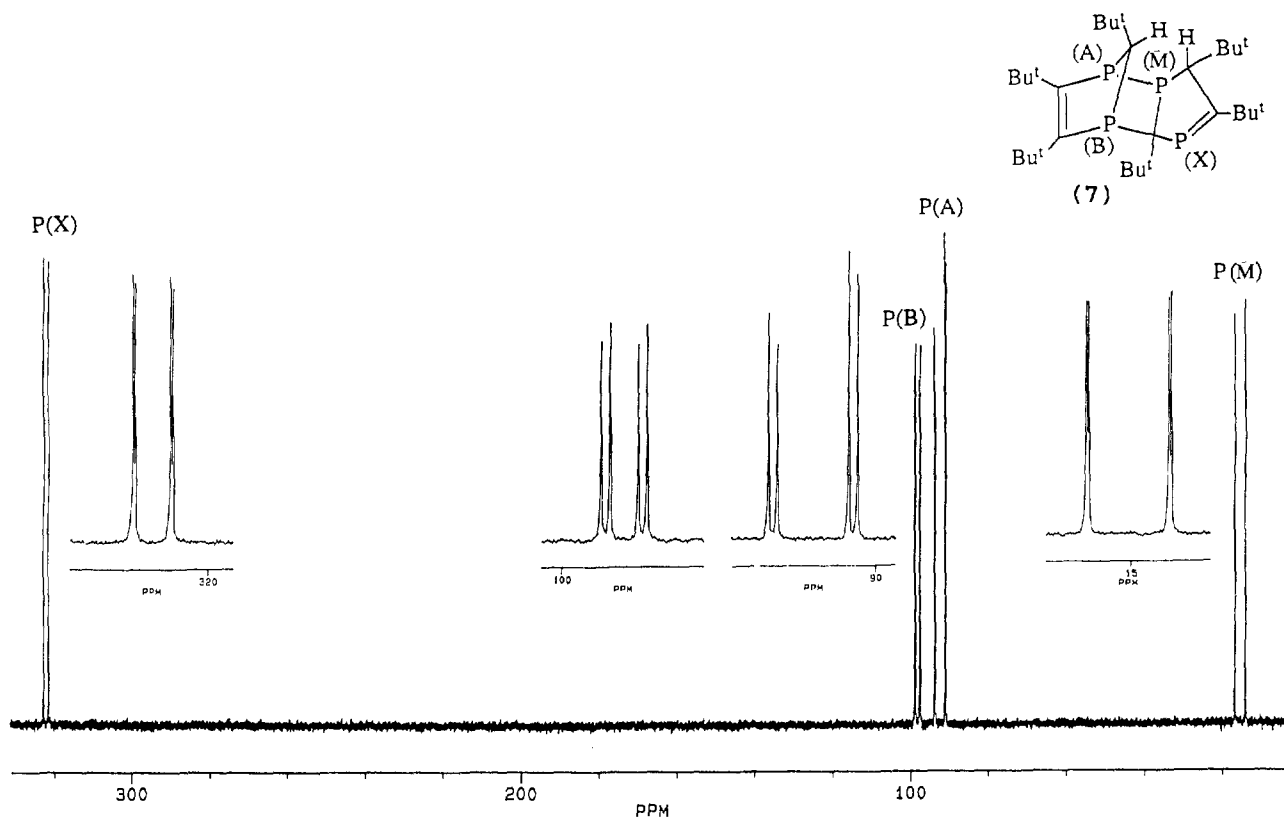

Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of $P_4C_6^tBu_6H_2$ (7) in $CDCl_3$ at 25 °C.

bond distance $(2.207(1)\,\text{Å})$ is very close to the P–P single bond distance found in compound **4**. The $C(4)=C(5)$ double bond $(1.355(4)\,\text{Å})$ in **7** is essentially identical to the related C–C bond found in compound **4** $(1.357(3)\,\text{Å})$, while the P–C single bonds (average $1.873\,\text{Å}$) are significantly longer than usual. A particularly interesting feature of compounds **4** and **7** is that they both exhibit an *exo*-structure, unlike the structurally related dimer of cyclopentadiene and the dimers of mono-phospholes (typified by $P_2C_8Me_4H_6$), which both have *endo*-structures.

It seems likely that the mechanism involved in the formation of **7** summarised in Fig. 4 involves the unstable 1-H-diphosphole which spontaneously rearranges through 1,5-proton shifts to give both the 2-H-phosphole and the 5-H-phosphole. These species presumably then undergo a spontaneous $[4 + 2]$ cycloaddition reaction with each other to give the observed dimeric product $P_4C_6{}^tBu_6H_2$ (**7**).

This proposed mechanism is based on the results of earlier protonation studies carried out by Mathey et al. [33] on phospholyl anions at low temperature and monitored by ^{31}P NMR spectroscopy. Protonation of these

Table 1

Fractional atomic coordinates and equivalent isotropic thermal parameters for $P_5C_5{}^tBu_5H_2$, **4**

Atom	x	y	z	U_{eq}
P1	0.06967(5)	0.33993(6)	−0.17156(4)	0.042(1)
P2	0.27571(5)	0.37228(6)	−0.05666(4)	0.043(1)
P3	0.02395(5)	0.43865(6)	−0.08831(4)	0.041(1)
P4	0.18156(6)	0.46762(6)	−0.00207(4)	0.043(1)
P5	0.10344(6)	0.67306(7)	−0.10081(5)	0.055(1)
C1	0.1173(2)	0.2261(2)	−0.1031(1)	0.043(1)
C2	0.2119(2)	0.2428(2)	−0.0476(1)	0.042(1)
C3	0.1981(2)	0.3994(2)	−0.1579(1)	0.041(1)
C4	0.1968(2)	0.6098(2)	−0.0263(2)	0.062(1)
C5	−0.0008(3)	0.5775(3)	−0.1288(2)	0.063(2)
C6	0.0386(2)	0.1297(3)	−0.1198(2)	0.068(2)
C7	0.0896(5)	0.0196(3)	−0.1152(2)	0.086(2)
C8	−0.0234(3)	0.1363(3)	−0.0664(3)	0.144(2)
C9	−0.0388(4)	0.1348(4)	−0.2034(3)	0.151(3)
C10	0.2819(2)	0.1743(2)	0.0217(2)	0.061(1)
C11	0.2219(4)	0.1099(3)	0.0633(2)	0.107(2)
C12	0.3546(3)	0.2473(3)	0.0853(2)	0.086(2)
C13	0.3521(3)	0.1011(3)	−0.0058(2)	0.107(2)
C14	0.2483(2)	0.3638(2)	−0.2177(1)	0.056(2)
C15	0.1787(3)	0.4004(3)	−0.2970(2)	0.078(2)
C16	0.3533(2)	0.4206(4)	−0.1985(2)	0.090(2)
C17	0.2643(3)	0.2423(3)	−0.2179(2)	0.094(2)
C18	0.3037(2)	0.6649(3)	0.0126 (2)	0.062(1)
C19	0.3529(3)	0.6263(4)	0.0947(2)	0.106(2)
C20	0.3759(3)	0.6388(3)	−0.0302(2)	0.105(2)
C21	0.2929(3)	0.7873(3)	0.0141(3)	0.103(2
C22	−0.0868(2)	0.5947(3)	−0.2086(2)	0.056(1)
C23	−0.0418(3)	0.5827(3)	−0.2716(2)	0.075(2)
C24	−0.1324(3)	0.7092(3)	−0.2121(2)	0.098(2)
C25	−0.1749(3)	0.5133(3)	−0.2211(2)	0.079(2)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 2

Fractional atomic coordinates and equivalent isotropic thermal parameters for $P_4C_6{}^tBu_6H_2$, **7**

Atom	x	y	z	U_{eq}
P1	0.24545(7)	0.34968(7)	0.31497(5)	0.033(1)
P2	0.10763(7)	0.39666(8)	0.14693(5)	0.034(1)
P3	0.18320(7)	0.52613(7)	0.35039(5)	0.032(1)
P4	0.20630(9)	0.67297(8)	0.18650(6)	0.045(1)
C1	0.3419(3)	0.7125(3)	0.2643(2)	0.040(1)
C2	0.3473(3)	0.6450(3)	0.3522(2)	0.037(1)
C3	0.2718(3)	0.3881(3)	0.1973(2)	0.034(1)
C4	0.0782(3)	0.2410(3)	0.2830(2)	0.033(1)
C5	0.0213(3)	0.2495(3)	0.1973(2)	0.033(1)
C6	0.1006(3)	0.5370(3)	0.2342(2)	0.033(1)
C7	0.3860(3)	0.7229(3)	0.4520(2)	0.053(2)
C8	0.5328(4)	0.7880(4)	0.4751(3)	0.077(2)
C9	0.3591(5)	0.6278(5)	0.5230(3)	0.089(2)
C10	0.3042(4)	0.8191(4)	0.4625(3)	0.077(2)
C11	−0.0952(3)	0.1551(3)	0.1325(2)	0.043(2)
C12	−0.0815(4)	0.0171(3)	0.1343(3)	0.061(2)
C13	−0.2313(3)	0.1639(4)	0.1526(3)	0.062(2)
C14	−0.0886(4)	0.1836(4)	0.0328(2)	0.063(2)
C15	0.0406(3)	0.1534(3)	0.3592(2)	0.044(1)
C16	0.1169(4)	0.0502(3)	0.3590(3)	0.066(2)
C17	0.0824(4)	0.2357(4)	0.4532(2)	0.062(2)
C18	−0.1061(4)	0.0939(4)	0.3569(3)	0.069(2)
C19	0.3495(3)	0.3095(3)	0.1430(2)	0.048(1)
C20	0.2838(4)	0.1672(4)	0.1277(3)	0.070(2)
C21	0.3625(4)	0.3597(5)	0.0506(3)	0.096(2)
C22	0.4847(4)	0.3279(5)	0.1957(3)	0.092(2)
C23	−0.0415(3)	0.5610(3)	0.2365(2)	0.042(1)
C24	−0.1225(3)	0.4676(4)	0.2927(3)	0.056(2)
C25	−0.1142(3)	0.5470(4)	0.1395(3)	0.060(2)
C26	−0.0298(3)	0.6953(3)	0.2811(3)	0.069(2)
C27	0.4611(3)	0.8084(3)	0.2351(3)	0.054(2)
C28	0.5849(4)	0.7600(4)	0.2519(3)	0.080(2)
C29	0.4408(4)	0.8207(5)	0.1319(3)	0.087(2)
C30	0.4826(4)	0.9443(4)	0.2825(3)	0.075(2)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

ions yields unstable 1-H-phospholes which easily rearrange via H-[1,5]-sigmatropic shifts to give 2-H-phospholes which instantly afford the expected dimers [33–35].

Although all three reactions of the $P_3C_2{}^tBu_2H$ and $P_2C_3{}^tBu_3H$ rings involve an initial $[4 + 2]$ cycloaddition step to give the tricyclic compounds (analogous to the known behaviour of cyclopentadiene itself), it is only the initially formed dimer $P_6C_4{}^tBu_4H_2$ (presumably in the *endo*-configuration) that undergoes a further intramolecular $[2 + 2]$ cycloaddition step to form the 'cage' compound **6**. Obviously the tricyclic compound **6** is also the only one that contains two most reactive $P=C$ double bonds, whereas both the other tricyclic compounds **4** and **7** contain either one $P=C$ and one $C=C$ or two $C=C$ double bonds respectively. It seems likely that steric rather than electronic factors are dominant however.

Presumably, a consequence of the additional bulky
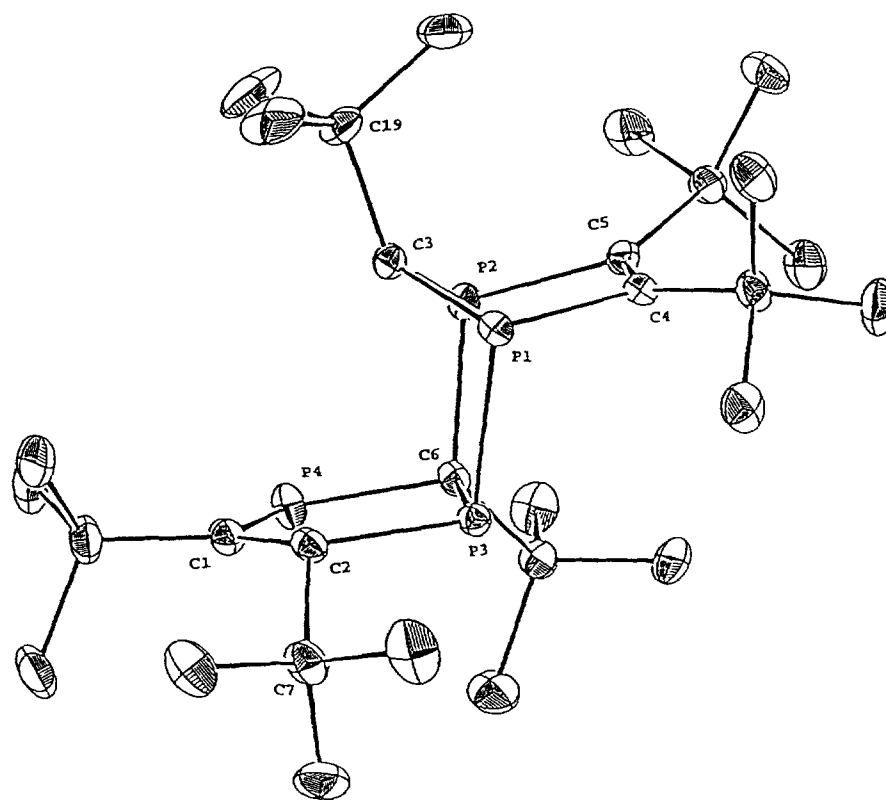
P(4)-C(1) = 1.676(3), C(1)-C(2) = 1.538(5), P(4)-C(6) = 1.861(3), P(3)-C(2) = 1.894(3), P(3)-C(6) = 1.856(3),
P(1)-P(3) = 2.207(1), P(2)-C(6) = 1.934(3), P(2)-C(3) = 1.835(3), P(1)-C(3) = 1.852(3), P(2)-C(5) = 1.888(3),
P(1)-C(4) = 1.862(3), C(4)-C(5) = 1.355(4), P(3)-C(2)-C(1) = 108.2(2), P(3)-C(2)-C(7) = 107.7(2), C(1)-C(2)-
C(7) = 122.1(2), P(1)-C(3)-P(2) = 102.3(1), P(1)-C(3)-C(19) = 117.8(2), P(2)-C(3)-C(19) = 119.7(2).

Fig. 3. Molecular structure of $P_4C_6{}^tBu_6H_2$ (7) together with the atomic numbering scheme and some selected bond lengths (Å) and angles (°).

^tBu group attached to carbon in both 4 and 7 is to force each dimeric structure into an *exo-* rather than an *endo*-configuration, thereby preventing the possibility of the final [2 + 2] cycloaddition 'cage-forming' step. It would be interesting to test this possibility utilising di- and triphosphacyclopentadienes containing smaller substituents.
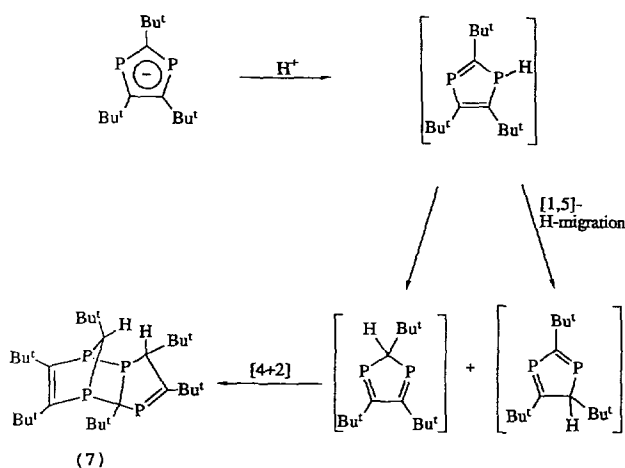

Fig. 4. Proposed mechanism for the synthesis of $P_4C_6{}^tBu_6H_2$.

2.3. X-ray diffraction studies

2.3.1. Crystal data

(i) $C_{25}H_{47}P_5$ (4), $M = 502.5$, monoclinic $P2_1/n$ (non-standard No. 14), $a = 13.662(2)$, $b = 12.326(2)$, $c = 18.629(2)$ Å, $\beta = 110.61(1)°$, $U = 2936$ Å^3, $Z = 4$, $D_c = 1.14$ g cm^{-3}. Crystal size $0.4 \times 0.3 \times 0.3$ mm^3. Data were collected at 293 K on an Enraf–Nonius CAD4 diffractometer using Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 3.2$ cm^{-1}. A total of 7399 unique reflections was measured, and 4718 with $|F^2| > 2\sigma F^2$ were used in the refinement. Non-H atoms were located by direct methods (SHELXS-86) and the structure was refined by full-matrix least-squares using Enraf–Nonius MoleN programs, non-H atoms anisotropic. The refinement converged at $R = 0.051$, $R' = 0.056$. Tables of H atom coordinates and thermal parameters and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

(ii) $C_{30}H_{56}P_4$ (7), $M = 540.7$, triclinic $P\bar{1}$ (No. 2), $a = 10.577(7)$, $b = 10.814(7)$, $c = 14.744(6)$, $\alpha = 94.44(5)$, $\beta = 96.61(4)$, $\gamma = 103.76(5)°$, $U = 1618$ Å^3, $Z = 2$, $D_c = 1.11$ g cm^{-3}. Crystal size $0.2 \times 0.2 \times$

0.1 mm^3. Data were collected at 293 K on an Enraf–Nonius CAD4 diffractometer using Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 2.4$ cm^{-1}. A total of 5686 unique reflections was measured, and 4308 with $|F^2| > 2\sigma F^2$ were used in the refinement. Non-H atoms were located by direct methods (SHELXS-86) and the structure was refined by full-matrix least-squares using Enraf–Nonius MoleN programs, non-H atoms anisotropic. The refinement converged at $R = 0.049$, $R' = 0.057$. Tables of H atom coordinates and thermal parameters and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3. Experimental

Standard procedures for the manipulation of air-sensitive materials were employed and all manipulations were carried out under an atmosphere of dry nitrogen gas or argon using Schlenk, syringe and high-vacuum line techniques with glassware that had been previously flame-dried. Solvents were dried and freshly distilled under a blanket of dinitrogen and degassed prior to use.

Mass spectra were recorded by Dr. A. Abdul-Sada using a Kratos MS-80 RF or Fison-VG Autospec spectrometer. Solution NMR spectra were recorded on Bruker ACP-250, WM360 or AMX-500 instruments. Coupling constants are in hertz and chemical shifts in parts per million. C and H microanalyses were performed on a CEC 240XA analyser by Medac Ltd., UK.

The precursors to the $P_3C_2{}^tBu_2^-$ and $P_2C_3{}^tBu_3^-$ ring anion systems [1,2], $P(SiMe_3)_3$ [36] and $Me_3SiP=C(OSiMe_3)^tBu$ [37], were made by published routes. The $[Na(P_2C_3{}^tBu_3)]$ and $[Na(P_3C_2{}^tBu_2)]$ mixture was prepared by a development of the original route devised at Sussex [38] based on related work on $[LiP_3C_2{}^tBu_3]$ by Becker et al. [39] (see also Refs. [1,2]), as detailed below.

$Me_3SiP=C(OSiMe_3)^tBu$ (5 g, 19 mmol) was stirred with Na (3 g, 130 mmol) in dme at ambient temperatures for 24 h during which time an orange colour developed, darkened and gradually became almost black. The volatile components were removed in vacuo and the oily residue washed with hexane (2 × 25 ml). $^{31}P\{^1H\}$ NMR characterisation indicated the [A$_2$] and [AB$_2$] spectra of the desired products and the oil was used without further purification. [PtCl$_2$(cod)] was made as described in Ref. [40].

3.1. Synthesis of $P_5C_5{}^tBu_5$, $P_6C_6{}^tBu_6$, $P_5C_5{}^tBu_5H_2$ (4) and $P_4C_6{}^tBu_6H_2$ (7)

To a suspension of [PtCl$_2$(cod)] (1.58 g, 4.2 mmol) in dme (40 ml) at −40 °C was slowly added a solution of $[Na(P_2C_3{}^tBu_3)]$ and $[Na(P_3C_2{}^tBu_2)]$ (4.2 mmol of each ring) dissolved in dme (10 ml). The resulting mixture

was stirred for 24 h and the solvent removed in vacuo. The dark residue was extracted into p.e. 60–80 °C and filtered through a short column (Kieselgel/p.e. 60–80 °C). The volume of this solution was reduced and the residue was chromatographed (Kieselgel/p.e. 60–80 °C) to give: (i) the pentamer $P_5C_5{}^tBu_5$ (120 mg, 6%) which was characterised by its $^{31}P\{^1H\}$ NMR and mass spectrum, (ii) the tricyclic compound $P_5C_5{}^tBu_2H_2$ (4) (95 mg, 5%) which was characterised by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy and mass spectrometry, and its structure elucidated by a single crystal X-ray diffraction study (see text), (iii) the hexamer $P_6C_6{}^tBu_6$ ($\approx 5\%$ yield), characterised by $^{31}P\{^1H\}$ NMR spectroscopy and mass spectrometry, and whose structure was confirmed by a single crystal X-ray diffraction study [23], (iv) the tricyclic compound $P_4C_6{}^tBu_6H_2$ (7) (110 mg, 10%), characterised by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^1H NMR spectroscopy, mass spectrometry and elemental analysis (Found: C, 66.5; H, 10.4. $C_{30}H_{56}P_4$ Calc.: C, 66.6; H, 10.4%). Recrystallisation of 7 from p.e. 60–80 °C at −20 °C gave yellow crystals of 7 (m.p. 153 °C (decomp.)), whose structure was confirmed by a single crystal X-ray diffraction study (see text).

3.2. Spectroscopic data for $P_4C_6{}^tBu_6H_2$ (7)

$^{31}P\{^1H\}$ NMR (101.3 MHz, chloroform-d_1, 25 °C): δ 321.8 ppm (dd, P(X), $^2J_{P(X)P(B)}$ 125.9 Hz, $^2J_{P(X)P(M)}$ 7.6 Hz); δ 97.9 ppm (dd, P(B), $^2J_{P(B)P(X)}$ 125.9 Hz, $^2J_{P(B)P(A)}$ 30.5 Hz); δ 92.1 ppm (dd, P(A), $^1J_{P(A)P(M)}$ 273.5 Hz, $^2J_{P(A)P(B)}$ 30.5 Hz); δ 15.1 ppm (dd, P(M), $^1J_{P(M)P(A)}$ 273.5 Hz, $^2J_{P(M)P(X)}$ 7.6 Hz).

$^{13}C\{^1H\}$ NMR (62.9 MHz, chloroform-d_1, 25 °C): δ 214.3 ppm (dd, $CC(CH_3)_3$, $^1J_{CP}$ 49.91 Hz, $^2J_{CP}$ 18.47 Hz); δ 164.0 ppm (d, $CC(CH_3)_3$, $^1J_{CP}$ 32.45 Hz); δ 161.2 ppm (dm, $CC(CH_3)_3$, $^1J_{CP}$ 39.48 Hz); δ 73.9 ppm (m, $CC(CH_3)_3$); δ 69.2 ppm (ddm, $CC(CH_3)_3$, $^1J_{CP}$ 52.02 Hz, $^1J_{CP}$ 40.11 Hz); δ 51.9 ppm (dd, $CC(CH_3)_3$, $^1J_{CP}$ 26.56 Hz, $^1J_{CP}$ 19.23 Hz); δ 40.9 ppm (d, $CC(CH_3)_3$, $^2J_{CP}$ 21.91 Hz); δ 40.7 ppm (d, $CC(CH_3)_3$, $^2J_{CP}$ 27.76 Hz); δ 39.1 ppm (d, $CC(CH_3)_3$, $^2J_{CP}$ 25.05 Hz); δ 38.2 ppm (dm, $CC(CH_3)_3$, $^2J_{CP}$ 22.53 Hz); δ 35.7 ppm (d, $CC(CH_3)_3$, $^3J_{CP}$ 14.12 Hz); δ 34.7 ppm (d, $CC(CH_3)_3$, $^3J_{CP}$ 18.0 Hz); δ 33.4 ppm (m, $CC(CH_3)_3$, $^3J_{CP}$ 7.15 Hz); δ 32.7 ppm (d, $CC(CH_3)_3$, $^3J_{CP}$ 10.66 Hz); δ 32.5 ppm (m, $CC(CH_3)_3$); δ 31.8 ppm (d, $CC(CH_3)_3$, $^3J_{CP}$ 15.25 Hz).

^1H NMR (250.2 MHz, benzene-d_6, 25 °C): δ 1.30 ppm (s, 9H, $CC(CH_3)_3$); δ 1.36 ppm (d, 9H, $CC(CH_3)_3$, $^4J_{CP}$ 0.91 Hz); δ 1.42 ppm (d, 9H, $CC(CH_3)_3$, $^4J_{CP}$ 2.20 Hz); δ 1.45 ppm (s, 9H, $CC(CH_3)_3$); δ 1.47 ppm (s, 9H, $CC(CH_3)_3$); δ 1.51 ppm (d, 9H, $CC(CH_3)_3$, $^4J_{CP}$ 2.56 Hz); δ 1.71 ppm (ddd, 1H, CH, $^2J_{HP}$ 6.58 Hz, $^3J_{HP}$ 2.01 Hz, $^4J_{HP}$ 0.50 Hz); δ 3.26 ppm (dddd, 1H, CH, $^2J_{HP}$ 14.26 Hz, $^2J_{HP}$ 13.16 Hz, $^3J_{HP}$ 10.42 Hz, $^4J_{HP}$ 4.20 Hz).

Mass spectrum (EI): m/z 540 $[P_4C_6{}^tBu_6H_2]^+$ (8%), 270 $[P_2C_3{}^tBu_3H]^+$, 213 $[P_2C_3{}^tBu_2H]^+$, 57 $[^tBu]^+$.

Acknowledgements

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