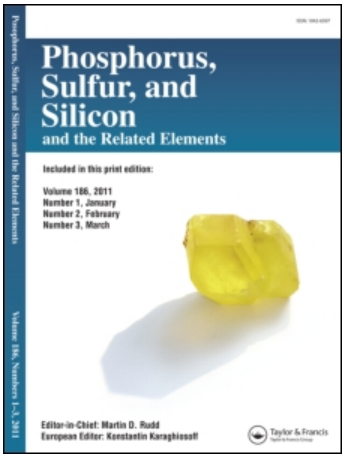

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NOVEL RINGS AND CAGES DERIVED FROM PHOSPHA-ALKYNES

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Abstract The use of the $P_3C_2Bu^t_2$ and $P_2C_3Bu^t_3$ rings in (i) the synthesis of the novel hexameric $P_6C_6Bu^t_6$ 'cage' and (ii) the first 1,2,4-triphosphacyclopentadiene and its metal complexes is described.

INTRODUCTION

The phospha-alkyne $Bu^tC{\equiv}P$ can be readily converted into the di- and triphosphacyclopentadienyl anions ($P_2C_3Bu^t_3$) and ($P_3C_2Bu^t_2$).[1]

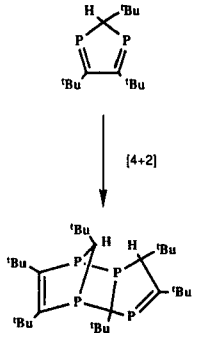
Here we present examples of the use of these rings in the generation of unusual new rings and cages containing phosphorus.

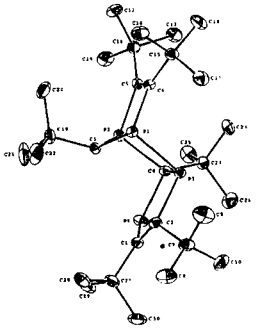
RESULTS AND DISCUSSION

Previously[2] we have shown that the $P_3C_2Bu^t_2$ ring can ligate to metals in both an η^1- and η^5- fashion whereas the $P_2C_3Bu^t_3$ ring binds in either an η^3- or an η^5- fashion. In η^1-$P_3C_2Bu^t_2$ complexes of Pt(II) of the type $[PtCl(P_3C_2Bu^t_2)(PR_3)_2]$ and $[Pt(P_3C_2Bu^t_2)_2(PR_3)_2]$ the presence of the stabilising organophosphane is important in their characterisation.[3,4]

Using the more labile $[PtCl_2(COD)]$ and a mixture of the $P_3C_2Bu^t_2$ and $P_2C_3Bu^t_3$ ring anions gave a mixture of non-metal-containing products including the known $P_5C_5Bu^t_5$[5] and $P_5C_5Bu^t_5H_2$[6] and two new compounds $P_6C_6Bu^t_6$ (A) and $P_4C_6Bu^t_6H_2$ (B). The latter, which is the previously unknown product of the [4 + 2] cycloaddition of two $P_2C_3Bu^t_3H$ rings, has been structurally characterised by a single crystal X-ray diffraction study and is depicted below.

Unlike $P_6C_4Bu^t_4H_2$, since there is a C=C and a P=C bond, the compound does not undergo a further [2 + 2] cycloaddition step to afford a cage.[7]

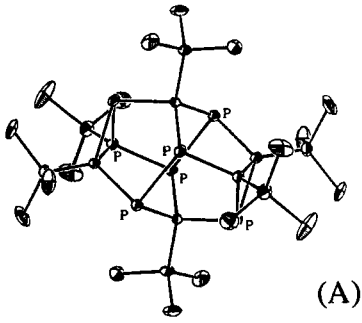




a) Bonds	
P1-P3	2.207(1)
P1-C4	1.862(3)
P2-C5	1.888(3)
P3-C2	1.894(3)
P4-C1	1.876(3)
C1-C2	1.538(5)
C2-C7	1.596(4)
C4-C5	1.355(4)
P1-C3	1.852(3)
P2-C3	1.835(3)
P2-C6	1.934(3)
P3-C6	1.858(3)
P4-C6	1.861(3)
C1-C27	1.556(4)
C3-C19	1.555(5)
C4-C15	1.551(4)

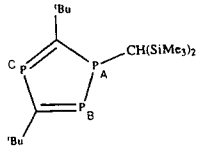
Structure of (B)

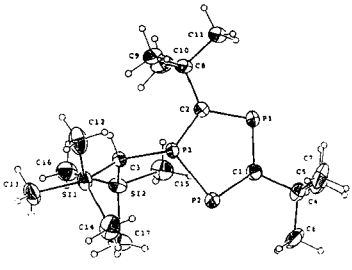
Of special interest is the molecular structure of (A), shown below, which



(A)

consists of a hexameric cage of six Bu^{t}CP units (lantern-like structure) containing two three-membered PCC rings. There is a close similarity between the C_{2h} symmetry of (A) and the D_{3d} symmetry of the known corresponding $C_{12}H_{12}$ hydrocarbon and the D_{3d} structure computed for the hypothetical P_{12} molecule. These results provide strong support for previous contentions regarding the similarity in chemical behaviour of the P and CR fragments in organic and inorganic chemistry.





A recent development is the first synthesis of a 1,2,4-triphosphacyclopentadiene by treatment of the $P_3C_2Bu^t_2$ anion with $(Me_3Si)_2CHBr$ (see above). The compound has been fully characterised by multinuclear NMR spectroscopy and a single crystal X-ray diffraction study.[8] On standing in sunlight there is a slow isomerisation involving a 1,3 shift of the $(Me_3Si)_2CH$-group from P to C.[9] The ligating potential of the new triphosphacyclopentadiene is illustrated in the Scheme shown in the paper by Nixon in this issue; all metal complexes have been fully characterised by multinuclear NMR and by single crystal X-ray diffraction studies.

Finally, an unusual cationic cage compound $P_6C_4Bu^t_4(CH_2)Me^{\oplus}$, shown below, is obtained in very low yield but has been structurally characterised by a single crystal X-ray diffraction study.[10] The mechanism of formation may involve transient formation of a dimethylphospholium salt at the sp^3 phosphorus centre.

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