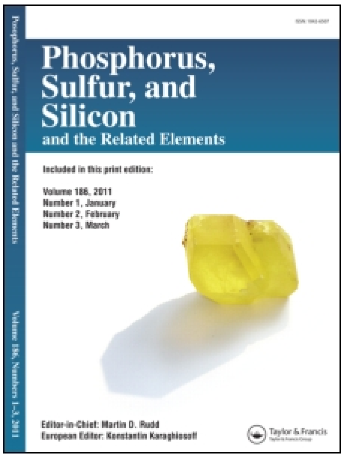

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Nixon, John F.(2002) 'Novel Chemistry of the Aromatic 1,2,4-Triphospholyl and 1,3,-Diphospholyl Anions, P 3 C 2 t Bu 2 and P 2 C 3 t Bu 3 , and the 1,3,5-Triphosphabenzene, P 3 C 3 t Bu 3', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1517 — 1522

To link to this Article: DOI: 10.1080/10426500212266

URL: http://dx.doi.org/10.1080/10426500212266

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1517–1522
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1042-6507/02 \$12.00 + .00
DOI: 10.1080/10426500290093801

NOVEL CHEMISTRY OF THE AROMATIC 1,2,4-TRIPHOSPHOLYL AND 1,3,-DIPHOSPHOLYL ANIONS, $P_3C_2{}^tBu_2$ AND $P_2C_3{}^tBu_3$, AND THE 1,3,5-TRIPHOSPHABENZENE, $P_3C_3{}^tBu_3$

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(Received July 29, 2001; accepted December 25, 2001)

Oxidative coupling of the $P_3C_2{}^tBu_2$ anion with I_2 affords a convenient synthetic route to the remarkable hexaphosphapentaprismane cage $P_6C_4{}^tBu_4$, which undergoes ready insertion reactions of carbene like fragments such as S, Se, Te, SnR_2 specifically into the P—P bond, which in turn connects the two $P_3C_2{}^tBu_2$ fragments. Di- and tri-phospholyl compounds $MP_3C_2{}^tBu_2$ (M = Ga, In, Tl), $M'(P_3C_2{}^tBu_2)_2$ (M′ = Zn, Cd, Hg), and [1 + 4] cyclo-additions of the triphosphabenzene, $P_3C_3{}^tBu_3$, and extrusion of the ${}^tBuC$ or P moieties from the 6-membered ring are presented.

INTRODUCTION

The past decade has seen the rapid development of a rich new area of organometallic chemistry in which one or more phosphorus atoms replace CH- fragments in the more familiar unsaturated organic ligands. There is now an extensive range of phosphaorganometallic compounds containing phospha-alkynes, phosphaalkenes, phosphadienes, phosphaallyls, phosphacyclobutadienes, phosphacyclopentadienyls, and phospha-arenes, as well as tetraphosphacubanes and tetraphospha barrelenes. The area has recently been comprehensively reviewed.

In collaboration with M. Al- Ktaifani, S. B. Clendenning, G. Clentsmith, F. G. N. Cloke, M. D. Francis, B. Gehrhus, P. B. Hitchcock, J. R. Hanks, M. F. Lappert, D. J. Wilson (Sussex University), Prof. R. West (Wisconsin, USA), Prof. H. G. Schnoekel (Karlsruhe, Germany) and Prof. K. Lammertsma (Amsterdam, Netherlands) and their coworkers.

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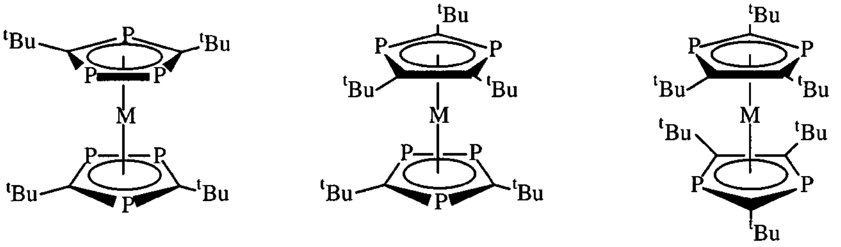
At Sussex University, we have shown that the phosphaalkyne, ^{t}BuCP, can play a key role in the generation of a wide variety of novel phospha-organometallic compounds containing 1,3-diphosphacyclobutadiene, 1,2,4-triphosphacyclopentadienyl, 1,3-diphosphacyclopentadienyl, 1,3,5-triphosphabenzene, and 1,3,5,7-tetraphosphabarrelene ring systems. We have focussed our attention on the organometallic chemistry of the aromatic 1,2,4-triphospholyl and 1,3-diphospholyl anions, $P_3C_2{}^tBu_2{}^-$ and $P_2C_3{}^tBu_3{}^-$, respectively, and also the neutral 1,3,5-triphosphabenzene, $P_3C_3{}^tBu_3$.

The present paper gives a brief overview of further (and often unexpected) developments in this area and outlines research carried out in collaboration with several other groups. Theoretical studies underpinning the work have been carried out by Professor Jenny Green (Oxford, UK) and Professor Laszlo Nyulaszi (Budapest, Hungary).

The availability of the $P_3C_2{}^tBu_2$ and $P_2C_3{}^tBu_3$, ring anions, formed directly by treatment of ^{t}BuCP or $P_3C_3{}^tBu_3$ with alkali metals, has enabled us to readily generate a variety of tri-, tetra-, penta-, and hexaphospha metallocenes typified by some examples shown below. Compounds were usually obtained by treatment of the appropriate anion with suitable metal halides; however, an important alternative synthetic route involves the direct interaction of the phosphaalkyne ^{t}BuCP, using the technique of metal-vapour synthesis (work carried out in collaboration with my Sussex colleague, Professor Geoff Cloke).

Recently we have turned our attention to polyphospholyl derivatives of the main group elements, particularly to the 1,2,4-triphospholyl and 1,3-diphospholyl half-sandwich compounds of the Group 13 elements, e.g., $InP_3C_2{}^tBu_2$ and $InP_2C_3{}^tBu_3$, which we are studying as potential single source precursors for indium phosphide, InP.

These types of compounds can be made either by metal vapor synthesis or, more conveniently, from the corresponding $P_2C_3{}^tBu_3$ (**1**) and $P_3C_2{}^tBu_2$ (**2**) anions. We have now extended the study to

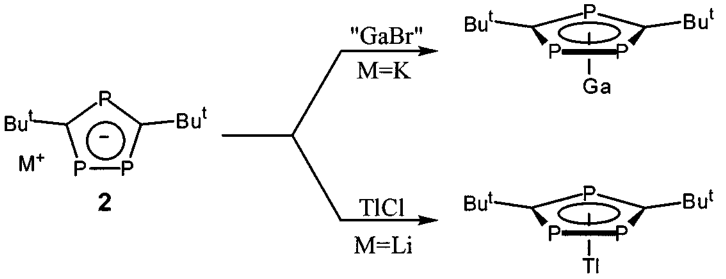


M = Ti, Mn, Cr, Fe, Ru

M = V, Cr, Fe, Ru

M = Sc, Ni, Pd, Pt, Yb

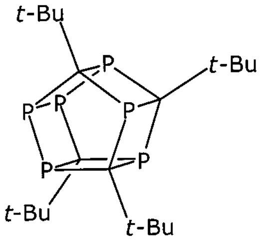
FIGURE 1



2 **3** **4**

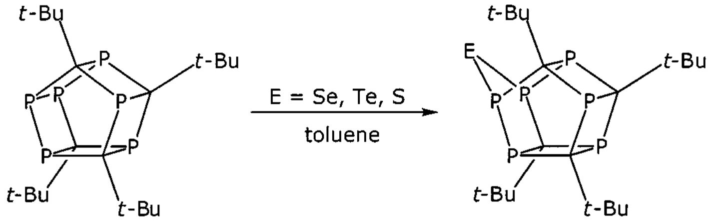
FIGURE 2

the corresponding Tl(I) and Ga(I) derivatives. Thus, treatment of a metastable toluene/thf solution of GaBr (made in Professor Schnoekel's laboratory, Karlsruhe, Germany) with $KP_3C_2{}^tBu_2$ led to the monomeric triphospholyl gallium(I) complex Ga(η^5 -$P_3C_2{}^tBu_2$) (**3**). The corresponding thallium complex Tl(η^5-$P_3C_2{}^tBu_2$) (**4**) was prepared at Sussex in a similar manner by treatment of TlCl with $[Li(tmeda)_2]$ $[P_3C_2{}^tBu_2]$. Both **3** and **4** are monomeric in solution and the gas phase and were characterized by mass spectrometry and multinuclear nmr spectroscopy. X-ray structure analyses of both complexes showed them to consist of weakly interacting monomeric half-sandwich units in the solid state. Using Group 10 halides leads to surprisingly different results. With Zn and Cd dihalides, the corresponding η^1 ligated complexes $[M\ (P_3C_2{}^tBu_2)_2]$, (M = Zn, Cd) were obtained, and both were structurally characterized as their bis- and tris- pyridine adducts. However, when two equivalents of $KP_3C_2{}^tBu_2$ were treated with one equivalent of $HgCl_2$ in THF under the influence of daylight over 24 h, precipitation of elemental mercury results together with the formation of the remarkable hexaphosphapentaprismane cage compound, $P_6C_4{}^tBu_4$. Carrying out the reaction in the dark for 10 h gave the remarkable, fully structurally characterized trimercury cluster compound $[P_6C_4{}^tBu_4Hg]_3$. ^{31}P NMR spectroscopic



5

FIGURE 3



6(E=S) **7** (E=Se) **8** (E=Te)

FIGURE 4

studies on reaction mixtures suggest that other oligomers of the type $[P_6C_4{}^tBu_4Hg]_n$ may be also present in solution, but these compounds have not yet been isolated.

We now report that oxidative coupling of the $P_3C_2{}^tBu_2$ anion **2** with I_2 at room temperature affords a much more convenient alternative synthetic route to the hexaphosphapentaprismane cage compound, $P_6C_4{}^tBu_4$ (**5**). Interestingly, several years ago we had described the oxidative coupling reacion of **a mixture** of the two $P_3C_2{}^tBu_2$ and $P_2C_3{}^tBu_3$ anions to afford the phosphaalkyne pentamer, $P_5C_5{}^tBu_5$. The latter cage, however, has a distinctly different molecular structure to **5** and does not exhibit any of the unusual reactivity features of its isoelectronic partner $P_6C_4{}^tBu_4$. Reactivity features of its isoelectronic partner, $P_6C_4{}^tBu_4$, are discussed below.

A remarkable feature of the chemistry of the hexaphosphapentaprismane is its propensity to undergo ready **insertion reactions** of "carbene-like" fragments such as S, Se, and Te, **specifically** into the P—P bond that connects the two $P_3C_2{}^tBu_2$ fragments.

We have likened this opening and closing of the cage behavior to that of the fictional shark "Jaws." The resulting expanded cage compounds $EP_6C_4{}^tBu_4$ (E = S, Se, Te) (**6–8**) have all been fully structurally characterized by single crystal X-ray diffraction studies, and their

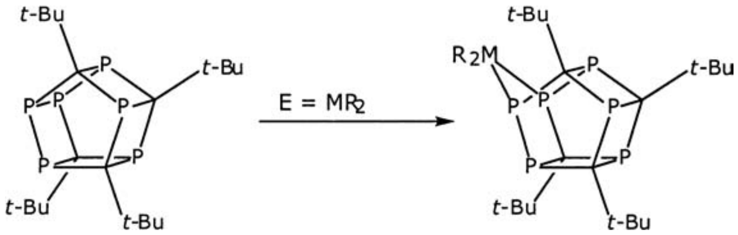


FIGURE 5

= $(Me_3Si)_2N$—)

2. the germylene GeR_2 (R = $(Me_3Si)_2N$—)
3. the plumbylene PbR'_2 (R′ = $C_6H_3)(NMe_2)_2{}^-$

In all cases, quantitative yields of the inserted products $R_2MP_6C_4{}^tBu_4$, (M = Sn) (**9**), (M = Ge) (**10**), (M = Pb) (**11**) are obtained, all of which being fully structurally characterized.

The molecular structure of the germanium compound **10** is shown in Figure 6.

Especially noteworthy is the reaction of $P_6C_4{}^tBu_4$ with the zerovalent platinum carbene-like fragment $[Pt(PPh_3)_2]$, where, remarkably, the insertion reaction also occurs **exclusively** in spite of the availability of the presence of six phosphorus lone pairs in the cage. The reaction pathway might have been expected to simply involve Lewis acid-base type coordination chemistry, leading to an intact $P_6C_4{}^tBu_4$ cage η^1-ligated to the platinum(0) centre, as is the case in many complexes of the type $[Pt(PPh_3)_2(PR_3)_2]$. The behavior of the $P_6C_4{}^tBu_4$ cage towards a metal centre is unprecedented.

Finally, we find that the 1,3,5-triphosphabenzene, $P_3C_3{}^tBu_3$, readily made using the Regitz et al. vanadium imide catalyzed cyclotrimerisation of ${}^tBuCP$ route, undergoes [1 + 4] cyclo-addition of

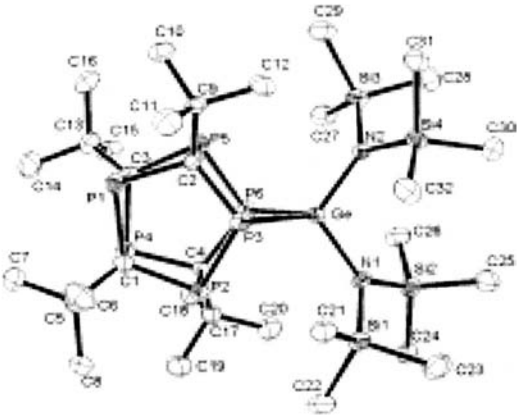


FIGURE 6

the stable silylene $C_6H_4N_2(CH_2Bu^t)_2Si$ but ring contraction reactions with Arduengo-type carbenes and certain amide anions. For example, the carbene $Me_2C_2N_2Me_2C$: leads to extrusion of the ^tBuC moeity from the 6-membered ring to afford the aromatic 5-membered 1,2,4-triphosphole(carbene) ring; furthermore, the reaction is reversible. Theoretical studies (LN) have established the mechanism of these novel reactions.

ACKNOWLEDGMENTS

We thank the EPSRC (JFN, FGNC, MDF, JRH, DJW), the Royal Society (JFN-LN), the Canadian Government (SC), and the AEC of Syria, Damascus, P.O. Box 609, (M.Al-K) for financial support.

REFERENCE

[1] K. B. Dillon, F. Mathey, and J. F. Nixon, *Phosphorus: The Carbon Copy* (Wiley, New York, 1998).