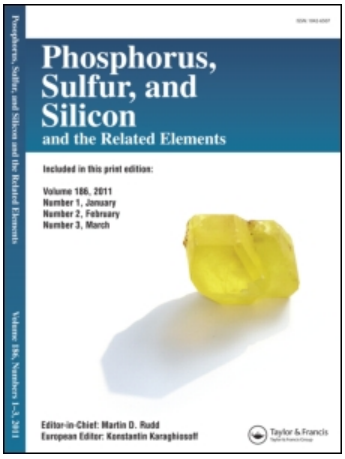


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Inorganic Rings and Cages Derived from Phospha-Alkynes and Arsa-Alkynes

John F. Nixon[a]
[a] School of Chemistry and Molecular Sciences, University of Sussex, Sussex, UK

To cite this Article Nixon, John F.(1994) 'Inorganic Rings and Cages Derived from Phospha-Alkynes and Arsa-Alkynes', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 87 — 91
To link to this Article: DOI: 10.1080/10426509408021801
URL: http://dx.doi.org/10.1080/10426509408021801

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 87–91
Reprints available directly from the publisher
Photocopying permitted by license only

INORGANIC RINGS AND CAGES DERIVED FROM PHOSPHA-ALKYNES AND ARSA-ALKYNES

JOHN F. NIXON*
School of Chemistry and Molecular Sciences, University of Sussex, Brighton, E. Sussex, BN1 9QJ, UK

Abstract The versatility of phospha-alkynes, RC≡P, and their arsenic analogues in the synthesis of novel inorganic ring and cage compounds is discussed.

INTRODUCTION

Previously we have shown that the phospha-alkyne $Bu^tC{\equiv}P$ can be readily cyclodimerised at metal centres to afford η^4-ligated 1,3-diphosphacyclobutadiene $P_2C_2Bu^t_2$ ring systems.[1-3]

An important early observation[4] was the spontaneous generation of the five-membered anionic ring compounds $P_2C_3Bu^t_3$ and $P_3C_2Bu^t_2$ by treatment of $Bu^tC{\equiv}P$ with alkali metals in diglyme. The novel 'cage' compounds $P_4C_4Bu^t_4$[5,6] and $P_5C_5Bu^t_5$[7] have also been described, as well as penta- and hexa-phospha metallocenes of the type $[M(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ (M = Fe, Cr) and $[M'(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ (M = Fe, Ni).[8-10]

Here we report significant extensions to the synthetic utility of phospha-alkynes and their arsenic analogues.

RESULTS AND DISCUSSION

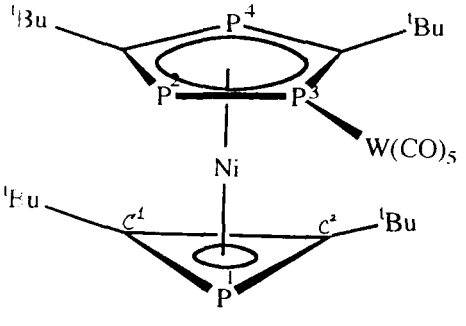
Using the technique of metal-vapour synthesis we have co-condensed a variety of metals drawn from both the transition and lanthanide series with $Bu^tC{\equiv}P$ and have been able to spontaneously synthesise complexes containing both the $P_2C_2Bu^t_2$, $P_3C_2Bu^t_2$, and $P_2C_3Bu^t_3$ ring systems. Clearly, these results, which are the first of their kind, offer enormous synthetic potential.

Thus Mo(vapour) and W(vapour) give the complexes $[M(\eta^4\text{-}P_2C_2Bu^t_2)_3]$ (M = Mo, W), the former having been fully characterised by a single crystal X-ray

diffraction study.[11] Using Co(vapour) two products have been obtained, one being characterised by a single crystal X-ray diffraction study and by multinuclear NMR spectroscopy as the 18e system $[Co(\eta^4\text{-}P_2C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$. The second product is a dinuclear cobalt complex not yet fully characterised.[12]

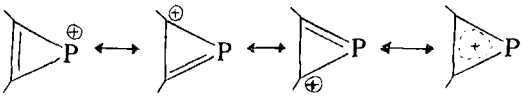
Interestingly, using Fe(vapour) and Cr(vapour) respectively, we obtain $[M(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ (M = Fe, Cr). Although the Fe complex is known, the corresponding 16e chromium derivative is new. There is no evidence for the known $[M(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ (M = Fe, Cr) complexes in these reactions, suggesting that steric effects may influence the course of the reaction.

Of special importance is the reaction of $Bu^tC{\equiv}P$ with Ni(vapour) which gives rise to equimolar amounts (*ca.* 40% yield) of two red compounds of identical molecular formula $[NiP_4C_4Bu^t_4]$, (A) and (B). Compound (A) is readily identified as the known 1,3-diphosphacyclobutadiene nickel(0) complex $[Ni(\eta^4\text{-}P_2C_2Bu^t_2)_2]$ made previously by Binger and Regitz and their co-workers by reduction of Ni(II) salts in a conventional cyclodimerisation of Bu^tCP. The new compound (B) has been shown by spectroscopic methods (mass spectroscopy, multinuclear NMR spectroscopy) to be $[Ni(\eta^3\text{-}PC_2Bu^t_2)(\eta^5\text{-}P_3C_2Bu^t_2)]$, which represents the first example of the stabilised long sought after 3-membered ring phosphirenyl cation which is the simplest 2π aromatic ring containing phosphorus. Although (B) could not be structurally characterised by a single crystal X-ray diffraction study, treatment with $[W(CO)_5THF]$ readily afforded $[Ni(\eta^3\text{-}PC_2Bu^t_2)(\eta^5\text{-}P_3C_2Bu^t_2)W(CO)_5]$ whose structural parameters are shown below.[13] The structure can be discussed in terms of the



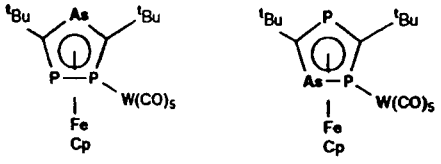
Ni-P1	2.207(5)	Ni-P2	2.397(5)
Ni-P3	2.354(5)	Ni-P4	2.354(5)
Ni-C1	2.02(2)	Ni-C2	2.04(2)
Ni-C11	2.24(2)	Ni-C12	2.12(2)
P1-C1	1.78(2)	P1-C2	1.82(2)
P2-P3	2.111(7)	C1-C2	1.33(3)

resonance forms depicted here.



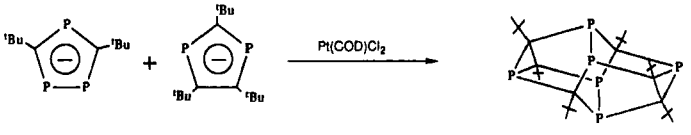
Using Yb(vapour) we have synthesised the diamagnetic green 'bent' sandwich compound $[Yb(\eta^5\text{-}P_2C_3Bu^t_3)_2]$ and have obtained both ^{171}Yb and ^{31}P NMR spectroscopic data as well as observing a parent ion in the mass spectrum. Of special interest is its ready reaction with $NiBr_2$ in an ether solvent to afford $[Ni(\eta^3\text{-}P_2C_3Bu^t_3)(\eta^5\text{-}P_2C_3Bu^t_3)]$ in which the two rings undergo a dynamic exchange in solution at room temperature. We have also synthesised this complex by more conventional means.[14]

The mixed arsenic-phosphorus ring system 1-arsa-3,4-diphosphacyclopentadienyl anion $(C_2Bu^t_2AsP_2)^-$ is readily synthesised by reaction of $LiAs(SiMe_3)_2$ with $Bu^tC{\equiv}P$.[15] Two equivalents of this anion react with $[Fe(mesitylene)_2^{2+}]$ to give the diarsatetraphosphaferrocene complex $[Fe(\eta^5\text{-}C_2Bu^t_2AsP_2)_2]$ which has been characterised by NMR and mass spectroscopic studies. The anion also reacts with $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)^+]$ to give $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2Bu^t_2AsP_2)]$ which, when treated with $[W(CO)_5THF]$, gives the bimetallic complex $[Fe(\eta^5\text{-}C_5H_5)\text{-}(\eta^5\text{-}C_2Bu^t_2AsP_2)W(CO)_5]$. Both complexes have been characterised spectroscopically and in the case of the latter a single crystal X-ray study has been carried out.



Further ligation modes of the triphospha- and arsadiphosphacyclopentadienyl ions lead to novel triple-decker sandwich compounds containing two Ru atoms of the type $[C_5Me_5Ru(\eta^5\text{-}P_3C_2Bu^t_2)RuC_5Me_5]^+$ and $[C_5Me_5Ru(\eta^5\text{-}P_2AsC_2Bu^t_2)\text{-}RuC_5Me_5]^+$.[15,16,17]

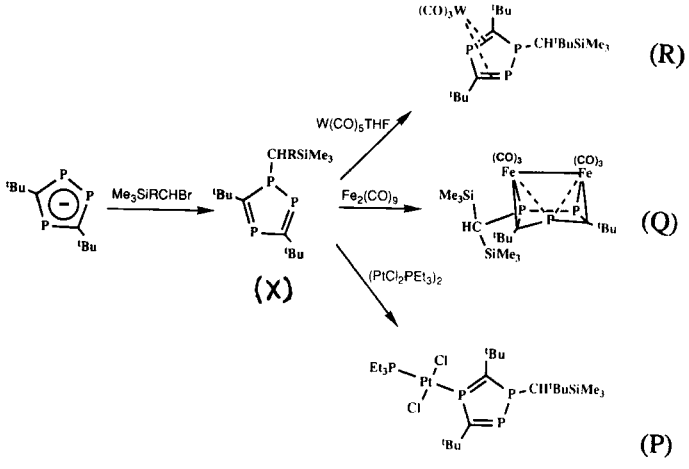
As mentioned in the introduction, the tetramer and pentamer of Bu^tCP are both known but very recently we have obtained a new non-'cage' isomer of the tetramer and structural evidence for the novel <u>hexamer</u> $P_6C_6Bu^t_6$ shown below using a synthesis



involving a labile Pt(II) precursor and a mixture of the $P_3C_2Bu^t_2$ and $P_2C_3Bu^t_3$ ring anions.[18]

This is a particularly interesting molecule in view of the related $C_{12}H_{12}$ and P_{12} cluster (the latter only discussed theoretically) which have similar structural and bonding features.

Finally $Li^+[P_3C_2Bu^t_2]^-$ reacts with $BrHC(SiMe_3)_2$ to give the 1,2,4-triphosphole (X) shown below which represents the first example of this type of organophosphorus compound.[20] Subsequent treatment with $[PtCl_2(PEt_3)]_2$, $[Fe_2(CO)_9]$, and $[W(CO)_5THF]$ affords (P), (Q), and (R) respectively, in which the new ring system is differently ligated to the metal centres. Complex (R) represents a formally $16e^-$ system. Detailed ^{31}P NMR spectroscopic and single X-ray diffraction studies have been used to elucidate the structural features of the resulting products.



The reaction of (X) with BuLi followed by $FeCl_2$ affords two products $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^4\text{-}P_3C_2Bu^t_2HCH(SiMe_3)_2)]$ (Y) and $[Fe(\eta^4\text{-}P_3C_2Bu^t_2HCH\text{-}(SiMe_3)_2)_2]$ (Z) whose novel structures have been established by single crystal X-ray diffraction studies.[20,21]

ACKNOWLEDGEMENT

I wish to thank my co-workers, Professor F. G. N. Cloke, V. Caliman, Dr K. R. Flower, Dr J. A. Johnson, Dr P. B. Hitchcock, J. Perry, and D. Vickers. We thank the SERC and CNPq (Brazil) for financial support for this work.

REFERENCES

1. P. B. Hitchcock, M. J. Maah and J. F. Nixon, J. Chem. Soc., Chem. Commun., 737 (1986).
2. P. B. Hitchcock, M. J. Maah and J. F. Nixon, J. Chem. Soc., Chem. Commun., 844 (1987).
3. P. B. Hitchcock, M. J. Maah and J. F. Nixon, Heteroatom. Chem., 2, 253 (1991).
4. R. Bartsch and J. F. Nixon, Polyhedron, 8, 2407 (1989).
5. T. Wettling, J. Schneider, O. Wagner, C. G. Kreiter and M. Regitz, Angew. Chem., Int. Edn. Engl., 28, 1013 (1989).
6. T. Wettling, B. Geissler, R. Schneider, S. Barth, P. Binger and M. Regitz, Angew. Chem., Int. Edn. Engl., 31, 758 (1992).
7. R. Bartsch, P. B. Hitchcock and J. F. Nixon, J. Organometal. Chem., 375, C31 (1989).
8. R. Bartsch, P. B. Hitchcock and J. F. Nixon, J. Chem. Soc., Chem. Commun., 1146 (1987).
9. R. Bartsch, P. B. Hitchcock and J. F. Nixon, J. Organometal. Chem., 356, C1 (1988).
10. R. Bartsch, P. B. Hitchcock and J. F. Nixon, J. Organometal. Chem., 373, C17 (1989).
11. F. G. N. Cloke, K. R. Flower, P. B. Hitchcock, J. F. Nixon and D. Vickers, J. Chem. Soc., Chem. Commun., 489 (1994).
12. F. G. N. Cloke, K. R. Flower, P. B. Hitchcock, J. F. Nixon and D. Vickers, unpublished results.
13. A. G. Avent, F. G. N. Cloke, K. R. Flower, P. B. Hitchcock, J. F. Nixon and D. Vickers, Angew. Chem., Int. Edn. Engl., in press.
14. F. G. N. Cloke, K. R. Flower, C. Jones, R. M. Matos, P. B. Hitchcock and J. F. Nixon, J. Organometal. Chem., in press.
15. R. Bartsch, P. B. Hitchcock, J. A. Johnson, R. M. Matos and J. F. Nixon, Phosphorus and Sulfur, 77, 45 (1993).
16. S. I. Al-Juaid, P. B. Hitchcock, J. A. Johnson and J. F. Nixon, J. Organometal. Chem., in press.
17. P. B. Hitchcock, J. A. Johnson and J. F. Nixon, paper in preparation.
18. V. Caliman, P B. Hitchcock, J. F. Nixon, M. Hofmann and P. v. R. Schleyer, Angew. Chem., Int. Edn. Engl., in press.
19. J. Perry, P. B. Hitchcock and J. F. Nixon, unpublished results.
20. V. Caliman, P B. Hitchcock and J. F. Nixon, unpublished results.
21. V. Caliman, C. Jones, P. B. Hitchcock and J. F. Nixon, unpublished results.