

Remarkable carbene-induced transformation of 2,4,6-tri-*tert*-butyl-1,3,5-triphospha-benzene, $P_3C_3Bu^t_3$, to the 1,2,4-triphosphole, $P_3C_2Bu^t_2CBu^t(\text{carbene})$. Crystal and molecular structure of the planar triphosphole complex $[Mo(CO)_3(\eta^5-P_3C_2Bu^t_2CBu^t(\text{carbene}))]$ [carbene = $C(N(Me)C(Me) = C(Me)N(Me))$] †

Scott B. Clendenning,^a Peter B. Hitchcock,^a John F. Nixon^{*a} and László Nyulászi^b

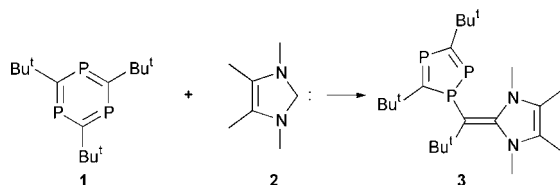
^a School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, Sussex, UK, BN1 9QJ. E-mail: j.nixon@sussex.ac.uk

^b Department of Inorganic Chemistry, Technical University of Budapest, H-1521 Budapest Gellért tér 4, Hungary

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Treatment of 2,4,6-tri-*tert*-butyl-1,3,5-triphospha-benzene, $P_3C_3Bu^t_3$, with the stable carbene 1,3,4,5-tetramethylimidazol-2-ylidene affords the planar 1,2,4-triphosphole, $P_3C_2Bu^t_2CBu^t(\text{carbene})$, [carbene = $C(N(Me)C(Me) = C(Me)N(Me))$] which has been structurally characterised as its η^5 -ligated $[Mo(CO)_3]$ complex; theoretical calculations are presented on the mechanism of this novel reaction.

The synthesis and ligating properties of compounds containing P–C multiple bonds is of considerable current interest.^{1–4} The availability^{5–7} of 2,4,6-tri-*tert*-butyl-1,3,5-triphospha-benzene $P_3C_3Bu^t_3$ **1** has enabled its chemistry to be developed and we recently described an unusual [1+4]-cycloaddition reaction with a stable silylene.⁸ We now describe the remarkable reaction of **1** with the stable ‘Arduengo’ type carbene 1,3,4,5-tetramethylimidazol-2-ylidene **2**⁹ which involves extrusion of a CBu^t fragment from the six-membered aromatic ring to quantitatively afford the 1,2,4-triphosphole, $P_3C_2Bu^t_2CBu^t(\text{carbene})$ **3** (carbene = 1,3,4,5-tetramethylimidazol-2-ylidene). (Scheme 1) This type of behaviour is unprecedented and has no parallel in conventional organic chemistry.



To our knowledge, contractions from aromatic six-membered rings to aromatic five-membered rings are unknown in organic chemistry. In sulfur chemistry, reactions with electrophiles are known to cause six- to five-membered ring contractions in nonaromatic systems with S–S bond formation.^{10,11} While ring expansion of arenes¹² and aromatic phosphabenzene^{13,14} are known to occur with carbenes, no ring contractions have been reported to date.

Thus, addition of the 1,3,5-triphospha-benzene **1** to the carbene **2** in solutions of benzene, toluene or THF immediately led to a deep red solution of the 1,2,4-triphosphole **3** which could be isolated as an air and moisture-sensitive red oil. ‡ **3** is highly soluble in benzene, toluene, THF and diethyl ether but only sparingly soluble in saturated hydrocarbon solvents.

The structure of **3** was established by its mass spectrum and its characteristic ¹H, ¹³C and ³¹P NMR spectra, the latter exhibiting a very similar pattern of lines to that of the known, structurally characterised, triphosphole $P_3C_2Bu^t_2CH-$

($SiMe_3$)₂.¹⁵ The ³¹P NMR spectrum of the triphosphole **3** consists of three doublets of doublets in the unsaturated region at δ 209.2, 163.3 and 121.4 with the expected large ¹J(PP) coupling of 519.6 Hz, indicating a highly delocalised π -system, and the two smaller ²J(PP) couplings of 40.3 and 27.2 Hz. While the ¹³C and ¹H NMR spectra are in good agreement with the proposed structure, several accidental coincidences should be noted. Though chemically inequivalent, in both the ¹³C and ¹H NMR spectra, the two N-methyl groups and two carbene backbone methyl groups appear as singlets at their respective chemical shifts.

Confirmation of the proposed structure came from a single crystal X-ray diffraction study of the η^5 -ligated molybdenum tricarbonyl complex **4** which was made by treatment of **3** with $[Mo(CO)_3(\text{cycloheptatriene})]$ at room temperature. ‡ Crystals suitable for single crystal X-ray diffraction were grown at –25 °C from a saturated toluene solution layered with light petroleum (bp 40–60 °C). §

The molecular structure of **4**, shown in Fig. 1, reveals the following interesting features which are strongly indicative of a significantly delocalised system: (i) the sum of the bond angles at the tricoordinate phosphorus P(2) is 358.5°, (ii) the sum of the bond angles within the triphosphole ring is 539.97°, (iii) the C(14)=C(19) bond is 1.452(3) Å, (iv) the P(2)–C(14) bond outside the triphosphole ring is very short [1.7130(19) Å], (v) the P–C bond distances within the triphosphole ring are almost identical, [1.760(2), 1.7623(19), 1.763(2) and 1.774(2) Å, respectively].

The molybdenum tricarbonyl complex **4** was also characterised by ³¹P, ¹³C and ¹H NMR spectroscopy and mass

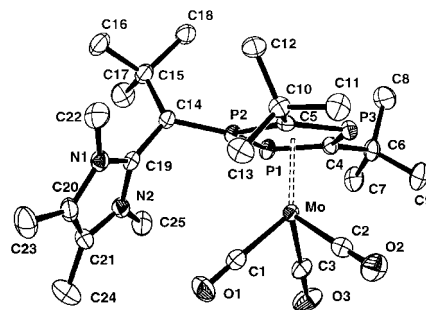


Fig. 1 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): P(1)–C(4) 1.774(2), P(1)–P(2) 2.1214(7), P(2)–C(14) 1.7130(19), P(2)–C(5) 1.760(2), P(3)–C(5) 1.7623(19), P(3)–C(4) 1.763(2), Mo–M(1) 1.986(2), C(1)–O(1) 1.161(3), C(14)–C(19) 1.452(3), N(1)–C(19) 1.361(2), N(1)–C(20) 1.388(3), N(1)–C(22) 1.456(3), N(2)–C(19) 1.356(3), N(2)–C(21) 1.388(3), N(2)–C(25) 1.461(3), C(20)–C(21) 1.350(3); C(4)–P(1)–P(2) 95.20(6), C(14)–P(2)–C(5) 129.43(9), C(5)–P(2)–P(1) 104.64(7), C(5)–P(3)–C(4) 101.40(9), P(3)–C(4)–P(1) 122.73(11), P(2)–C(5)–P(3) 116.00(10), C(19)–C(14)–C(15) 119.50(16), C(15)–C(14)–P(2) 119.68(14), C(14)–P(2)–P(1) 124.44(7).

† Electronic Supplementary information (ESI) available: spectroscopic data for **3** and **4**, B3LYP/6-31+G* level generated structure of **3**, and reaction of **3** with $[PtCl_2(PR_3)_2]$. See <http://www.rsc.org/suppdata/cc/b0/b001285h/>

spectrometry. As was observed in the η^5 -ligated $\text{Mo}(\text{CO})_3$ complex of the triphosphole $\text{P}_3\text{C}_2\text{Bu}^t_2\text{CH}(\text{SiMe}_3)_2$,¹⁶ we observe a large upfield shift for the ring phosphorus resonances as well as an inversion in the chemical shifts of the two formally unsaturated P centres. Furthermore, the ¹³C and ¹H NMR spectra of **4** revealed that the chemical shift coincidences of methyl groups in the parent triphosphole mentioned above, were no longer present.

We have investigated the mechanism of the above transformation of **1** to **3** by theoretical calculations¹⁷ at the B3LYP/6-31+G* level. The parent 1,3,5-triphosphabenzene, $\text{P}_3\text{C}_3\text{H}_3$, and the diaminocarbene, $\text{C}(\text{NH}_2)_2$, were used initially to model the entire reaction path. In order to take the most important steric effects into account, additional new calculations were performed at all the minima (product and intermediates), to find the corresponding structures derivable from 2,4-dimethyl-6-*tert*-butyl-1,3,5-triphosphabenzene and 1,3-dimethylimidazol-2-ylidene. Since no significant changes were observed in the relative energies of the minima on the reaction path, apart from some destabilisation of the first intermediate, we consider that the transition structures are not significantly affected.

From the reaction of the diaminocarbene and the triphosphabenzene a complex **5** (Fig. 2) is obtained in which the charge of the carbon atom of the diaminocarbene unit becomes more positive by 0.6 than in the free diaminocarbene, while each of the three phosphorus ring atoms become more negative by *ca.* 0.2 electrons. Thus **5** can be described as an ylid in which the negative charge is delocalised over the PCPCP unit. Intermediate **7** is formed from **5** via the transition state **6TS** as a result of a ring closure and the product **9** is formed via transition state **8TS**. Despite a careful search, no transition state linking **5** directly to **9** was found. Furthermore, the Gibbs free energies of **5**, **6TS**, **7**, **8TS** and **9** are lowered by 4.4, 3.0, 6.6, 4.7 and 21.5 kcal mol⁻¹, respectively, from that of the reactants and since the transition structures lie just slightly higher in energy than the intermediates, the reaction should proceed smoothly.

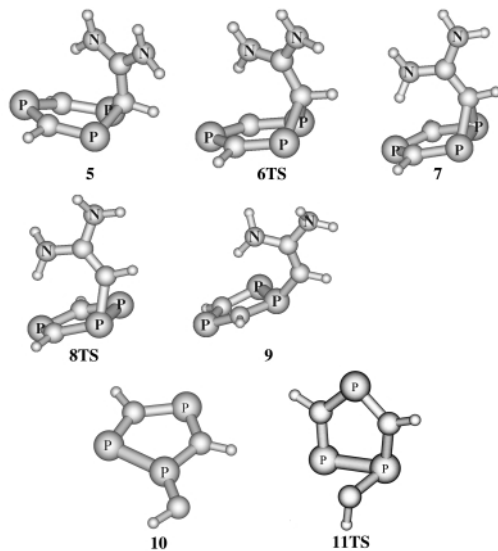


Fig. 2 B3LYP/6-31+G* level generated structures of intermediates and transition states generated in the transformation of **1** to **3**.

The structure of the experimentally observed **3** has also been optimised at the B3LYP/6-31G* level (neglecting the two β methyl groups on the imidazole ring). The calculated structural parameters are very similar to those obtained for the molybdenum complex **4**, except that the tricoordinate phosphorus atom is somewhat less planar (Σ bond angles 348.6°). The calculated C(14)=C(19) bond length for the uncomplexed triphosphole system is 1.413 Å and the P(2)–C(14) bond length is 1.780 Å, while the remaining bonding distances are even closer to those obtained from the X-ray structure.

Finally, of special interest is the reversible nature of the triphosphabenzene–(triphosphole–carbene) interconversion. Thus treatment of **3** with $[\text{PtCl}_2(\text{PR}_3)]_2$ ($\text{PR}_3 = \text{PMe}_3$ or PMe_2Ph),

at room temperature over 4 days leads to removal of the carbene, forming mixtures of the Pt(II) complexes *trans*- $[\text{PtCl}_2(\text{PR}_3)(\text{carbene})]$, *cis*- $[\text{PtCl}_2(\text{PR}_3)_2]$ and $[\text{PtCl}_2(\text{carbene})_2]$ with simultaneous regeneration of the triphosphabenzene ring **1**, as the major product, as evidenced by ³¹P NMR spectroscopy. Mechanistic information comes from theoretical calculations on the parent system which suggest that triphosphabenzene, $\text{P}_3\text{C}_3\text{H}_3$, which arises from loss of the carbene $\text{C}(\text{NH}_2)_2$ from **9** by metal complexation, results from the isomerisation of the planar compound **10** (Fig. 2), which has a singlet ground state and is less stable than triphosphabenzene by 59.3 kcal mol⁻¹. The Gibbs free energy of the transition state **11TS** for this reaction lies 17.5 kcal mol⁻¹ higher than that of **10**.

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Notes and references

‡ Preparations: $\text{P}_3\text{C}_2\text{Bu}^t_2\text{CBu}^t(\text{carbene})$ **3**: to a solution of $\text{C}\{\text{N}(\text{Me})\}_2\text{C}_2\text{Me}_2$ (63.6 mg, 0.512 mmol) in THF (5 mL) was added a solution of $\text{P}_3\text{C}_3\text{Bu}^t_3$ (153.8 mg, 0.512 mmol) in THF (5 mL) with stirring. The resulting red solution was stirred for 2 h before removing the solvent *in vacuo* to afford a red oil in quantitative yield by ¹H and ³¹P NMR spectroscopy.

$[\text{Mo}(\text{CO})_3\text{P}_3\text{C}_2\text{Bu}^t_2\text{CBu}^t(\text{carbene})]$ **4**: to a solution of $\text{C}\{\text{N}(\text{Me})\}_2\text{C}_2\text{Me}_2$ (83.0 mg, 0.668 mmol) in benzene (10 mL) was added a solution of $\text{P}_3\text{C}_3\text{Bu}^t_3$ (200.7 mg, 0.668 mmol) in benzene (10 mL) with stirring. The resulting red solution was stirred for 1 h prior to the addition of a red solution of $[\text{Mo}(\text{CO})_3(\text{cycloheptatriene})]$ (190.3 mg, 0.699 mmol) in benzene (10 mL) with no colour change. After a further 72 h stirring, the reaction mixture was filtered and the solvent removed *in vacuo* to give an orange solid, which was washed with hexane (10 mL) at –50 °C to afford **4** as a fine orange powder (313.1 mg, 78%).

§ Crystal data for **4**: $\text{C}_{25}\text{H}_{39}\text{MoN}_2\text{O}_3\text{P}_3$, $M = 604.3$, triclinic, space group $P1$ (no. 2), $a = 10.5667(3)$, $b = 10.9262(3)$, $c = 13.8900(4)$ Å, $\alpha = 90.436(2)$, $\beta = 96.562(2)$, $\gamma = 114.401(2)^\circ$, $U = 1448.18(7)$ Å³, $Z = 2$, $D_c = 1.39$ Mg m⁻³, crystal dimensions $0.4 \times 0.3 \times 0.2$ mm, $F(000) = 628$, $T = 173(2)$ K, Mo-K α radiation ($\lambda = 0.71073$ Å) Data collection: Kappa CCD. Of the total 5046 independent reflections measured, 4645 having $I > 2\sigma(I)$ were used in the calculations. The final indices [$I > 2\sigma(I)$] were $R1 = 0.024$, $wR2 = 0.058$ and $R1 = 0.028$, $wR2 = 0.059$ (for all data). CCDC 182/1651. See <http://www.rsc.org/suppdata/cc/b0/b001285h/> for crystallographic files in .cif format.

- 1 K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, John Wiley, Chichester, 1998, pp. 366 and references therein.
- 2 J. F. Nixon, *Coord. Chem. Rev.*, 1995, **145**, 201.
- 3 J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327.
- 4 *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart, 1990, p. 496 and references therein.
- 5 P. Binger, S. Leininger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann and C. Kruger, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2227.
- 6 F. Tabellion, A. Nachbauer, S. Leininger, C. Peters, M. Regitz and F. Preuss, *Angew. Chem., Int. Ed.*, 1998, **37**, 1233.
- 7 R. Gleiter, H. Lange, P. Binger, J. Stannek, C. Kruger, J. Bruckmann, U. Zenneck and S. Kummer, *Eur. J. Inorg. Chem.*, 1998, 1619.
- 8 S. B. Clendenning, B. Gehrhuis, P. B. Hitchcock and J. F. Nixon, *Chem. Commun.*, 1999, 2451.
- 9 A. J. Arduengo III, *Acc. Chem. Res.*, 1999, **32**, 913 and references therein.
- 10 C. G. Marcellus, R. T. Oakley, A. W. Cordes and W. T. Pennington, *Can. J. Chem.*, 1984, **62**, 1822.
- 11 J. E. Ellis, J. H. Fried, I. T. Harrison, E. Rapp and C. H. Ross, *J. Org. Chem.*, 1977, **42**, 2891.
- 12 J. March, *Advanced Organic Chemistry*, John Wiley, Chichester, 4th edn., 1992, p. 869 and references therein.
- 13 G. Keglevich, *Synthesis*, 1993, **93**, 931.
- 14 G. Keglevich, *Rev. Heteroat. Chem.*, 1996, **14**, 119.
- 15 V. Caliman, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1995, 1661.
- 16 V. Caliman, P. B. Hitchcock, J. F. Nixon, L. Nyulaszi and N. Sakarya, *Chem. Commun.*, 1997, 1305.
- 17 Quantum chemical calculations were carried out using the Gaussian 98 package (Gaussian 98, Revision A.5).