Synthesis and X-ray structure of a novel 1,3-dioxo-2($\sigma^4\lambda^5$)-4,5($\sigma^3\lambda^3$)-triphospholane: a (self-)trapping aryl-metaphosphonate

Bertold Kramer, Edgar Niecke,* Martin Nieger and Robert W. Reed

Anorganisch-Chemisches Institut der Universität, 53121 Bonn, Germany

The reaction of molecular oxygen with 1-aminodiphosphene produces a novel 1,3-dioxo-2λ^5,4λ^3,5λ^3-triphospholane-2-oxide *via* the [2 + 3]-addition of 2,4,6-tri-*tert*-butylphenylmetaphosphonate to the diphosphene monoxide, the structure of which is elucidated by X-ray analysis.

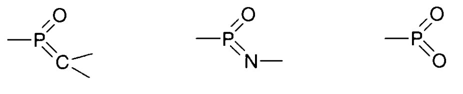
Recently several authors have shown the reaction of ozone with suitable $\sigma^2\lambda^3$-phosphaalkenes or iminophosphanes affords the corresponding oxo(ylen)phosphoranes **A**[1] and **B**.[2] While a handful of compounds of both types are known, only two methylene(oxo)-phosphoranes[3] and one imino(oxo)-phosphorane[4] have been fully characterized, including by X-ray structure analysis. The metaphosphates **C** are known as transient species, and their existence can only be inferred from trapping experiments.[5,6] While the metaphosphates **C** can be generated from a variety of precursors,[6] of great interest to us, is their formation from diphosphenes and oxygen.

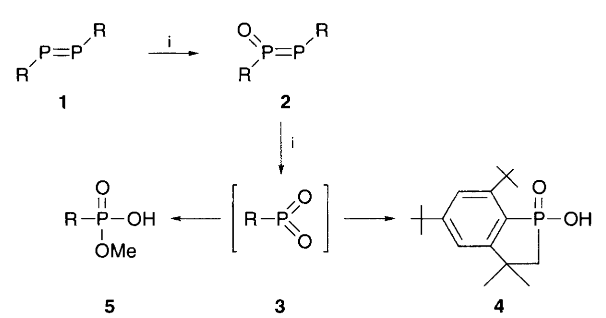
As outlined in Scheme 1, the reaction of the symmetric diphosphene **1** is reported to yield either a cyclic phosphonic acid **4** *via* C–H insertion subsequent to reaction with oxygen,[7] or a methylester **5** upon additional reaction with methanol.[8] Both **4** and **5** have been previously isolated as products from trapping reactions of the 2,4,6-tri-*tert*-butylphenylmetaphosphate **3**, and of further interest, the intermediate diphosphene monoxide **2** can be detected by ^{31}P NMR spectroscopy.[9] We report here the informative reaction of an asymmetric substituted diphosphene with oxygen which clearly demonstrates the sequential production of two reactive bis(ylene)phosphoranes, the diphosphene monoxide and **3**.

Treatment of the 1-aminodiphosphene[10] **6** with oxygen [by bubbling air through a cold (5 °C) toluene–dichloromethane solution of **6** for 6 h] results in the formation of compound **8**, which has been isolated in 33% yield. The ^{31}P NMR spectrum [δ 25.9 (J_{PP} = 215.4, 24.4 Hz), 2.3 (J_{PP} = 32.5, 24.4 Hz) and −15 (J_{PP} = 215.4, 32.5 Hz)], indicates a species with three distinct phosphorus atoms and one phosphorus–phosphorus single bond. The ^{1}H NMR data† clearly established the presence of three unique 2,4,6-tri-*tert*-butylphenyl groups and, of greatest interest, the mass spectrum‡ recorded positive ions corresponding to $O_2PC_6H_2Bu^t{}_3$-2,4,6 and 1-aminodiphosphene monoxide.

Single crystals of the major reaction product were grown slowly over a period of two months and the molecular structure was verified by X-ray crystallography to be 2,3-bis(2,4,6-tri-*tert*-butylphenyl)-4-2,4,6-tri-*tert*-butylphenylamido-1,3-dioxo-2-($\sigma^4\lambda^5$)-4,5($\sigma^3\lambda^3$)-triphospholane, **8**. It should be mentioned that the structure of an isomeric species, a 1,3,5-trioxaphosphorine, is well established.[11]

The X-ray crystal structure§ of **8** is illustrated in Fig. 1 and the pertinent metrical parameters are listed. The structure consists of a non-planar five-membered ring with one P–P bond. The three phosphorus atoms are unique with the $\sigma^4\lambda^5$-phosphorus attached to a $C_6H_2Bu^t{}_3$-2,4,6 group and not $-NHC_6H_2Bu^t{}_3$-2,4,6. The O(1) atom lies 50 pm from the plane defined by P(1), P(3), O(2) and P(2). The bulky substituents on P(1) and P(3) adopt a skewed conformation to relieve steric congestion. The phosphorus–phosphorus bond length [226.9(4) pm] is slightly longer than a normal single bond, while the remaining bond lengths and angles are as expected.


A **B** **C**



Scheme 1 *Reagents and conditions*: i, O_2, 5 °C, toluene–CH_2Cl_2; R = $C_6H_2Bu^t{}_3$-2,4,6

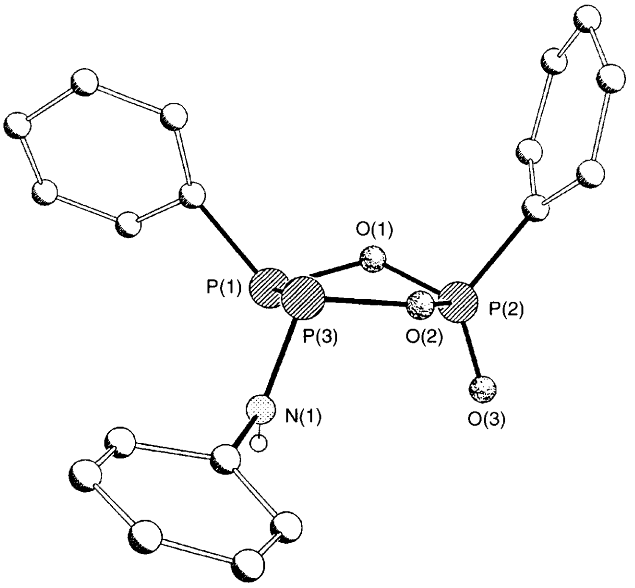
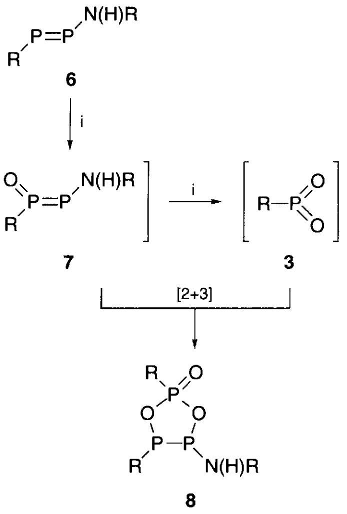


Fig. 1 Structure of **8** (Bu^t groups omitted for clarity) with important bond lengths (pm) and angles (°): P(1)–P(3) 226.9(4), P(1)–O(1) 167.7(7), P(3)–O(2) 171.8(7), P(2)–O(2) 159.5(7), P(2)–O(1) 161.0(6), P(2)–O(3) 146.7(7). P(1)–O(1)–P(2) 118.3(4), O(1)–P(1)–P(3) 95.0(2), P(2)–O(2)–P(3) 127.0(4), P(1)–P(3)–O(2) 89.1(2), O(1)–P(2)–O(2) 99.4(3)



Scheme 2 *Reagents and conditions*: i, O_2, 5 °C, toluene–CH_2Cl_2; R = $C_6H_2Bu^t_3$-2,4,6

The mechanism for the formation of **8** is outlined in Scheme 2. The first species generated from the reaction of **6** with oxygen is the monoxide **7**. This type of species is known to persist in solution and a slower reaction of **7** with oxygen to produce **3** followed by a faster [2 + 3] cycloaddition reaction affords the final product **8**. The oxidation of **7** to **3** must be the rate-determining step in this synthetic pathway and the fact that ions attributable to **7** and **3** are seen in the mass spectrum of **8** reinforces the plausibility of this mechanism.

Footnotes

† ^1H NMR (C_7D_8): 1.11 (s, br, 9 H, *p*-Bu^t), 1.28 (s, 9 H, *p*-Bu^t), 1.34 (s, 9 H, *p*-Bu^t), 1.41 (s, br, 18 H, *o*-Bu^t), 1.59 (d, 15.9 Hz, 18 H, *o*-Bu^t), 1.71 (s, 18 H, *o*-Bu^t), 3.22 (br s, 1 H, NH) 7.08, 7.56, 7.75 (s, 6 H, Ar″, Ar′, Ar).

‡ MS (70 eV/25 °C): *m*/*z* 616 ($M^+ - C_6H_2Bu^t_3$, 8%), 583 ($M^+ - C_6H_2Bu^t_3 - PO_2$, 8%), 308 [$O_2PC_6H_2Bu^t_3$, 6%), 57 ($Bu^t$, 100%).

§ *Crystal data* for **8**: colourless crystals, crystal dimension 0.3 × 0.3 × 0.5 mm^3; $C_{54}H_{88}NO_3P_3 \cdot 2\,C_6H_{12}$, $M = 1059.9$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.337(4)$, $b = 16.076(5)$, $c = 21.853(6)$ Å, $\alpha = 98.69(3)$, $\beta = 92.46(3)$, $\gamma = 106.73(3)°$, $U = 3.423$ nm^3, $Z = 2$, μ(Mo-Kα) = 0.12 mm^{-1}, $T = 293$ K, $F(000) = 1168$. 8654 reflections up to $2\theta_{max} = 44°$ were measured on a Nicolet R3m diffractometer with Mo-Kα radiation, 8381 independent reflections were used for all calculations. The structure was solved by direct methods and refined to F^2 anisotropically, the H atoms were refined with a riding model. The final quality coefficient $wR2$ was 0.341 [$R_1 = 0.114$ for 4283 reflections with $I > 2\sigma(I)$] for 615 parameters and 172 restraints. Two *para-tert*-butyl groups were disordered. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 H. Heydt, Methylene(imino, oxo, thio and selenoxo)phosphoranes, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme Verlag, Stuttgart, 1990, pp. 375–391.

2 E. Niecke and D. Gudat, Imino(oxo, thio and selenoxo)phosphoranes, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme Verlag, Stuttgart, 1990, pp. 405–410.

3 R. Appel, F. Knoch and H. Kunze, *Angew. Chem.*, 1984, **96**, 159; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 157; V. von der Gönna, M. Nieger, E. Niecke, H. Beckmann, K. Krieger, G. Ohms and G. Großmann, *XIIIth International Conference on Phosphorus Chemistry*, Jerusalem, Israel, July 16–21, 1995, Abstr. 178.

4 M. Larbig, M. Nieger, V. von der Gönna, A. Ruban and E. Niecke, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 460.

5 I. Lukes, M. Borbaruah and L. D. Quin, *J. Am. Chem. Soc.*, 1994, **116**, 1737.

6 M. Meisel, Dioxo- and Dithioxophosphoranes including the Metaphosphate Anions, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme Verlag, Stuttgart, 1900, pp. 415–442.

7 A. M.-Caminade, F. El Khativ and M. Koenig, *Phosphorus Sulfur*, 1984, **18**, 97.

8 J. I. G. Cadogan, A. H. Cowley, I. Gosney, M. Pakulski and S. Yaslak, *J. Chem. Soc., Chem. Commun.*, 1983, 1408.

9 M. Yoshifuji, K. Ando, K. Toyota, I. Shima and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, 1983, 862.

10 M. Lysek, Thesis, University of Bonn, 1987; A. V. Ruban, V. D. Romanenko, G. V. Reitel and L. N. Markowski, *Zh. Obshch. Khim.*, 1989, **59**, 2781.

11 E. Niecke, H. Zorn, B. Krebs and G. Henkel, *Angew. Chem.*, 1980, **92**, 737; *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 709; D. W. Chasar, J. F. Fackler, A. M. Mazany, R. A. Komoroski and W. J. Kroenke, *J. Am. Chem. Soc.*, 1986, **108**, 5956.

Received, 13th September 1995; Com. 5/06054K