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A cyclic diphosphinite by a formal [4+4] cycloaddition reaction of β-phosphaenone

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Abstract—Unstable β-phosphaenones formed by reaction of the phosphanylidene-σ^4-phosphorane DmpP = PMe_3 (Dmp = 2,6-dimesitylphenyl) with acenaphthenequinone dimerize in hexane by a formal [4+4] cycloaddition reaction to form a cyclic diphosphinite. X-ray crystallographic analysis and variable temperature ^{1}H NMR spectra of the cyclic diphosphinite are presented.

1. Introduction

The reactions of Wittig reagents with *ortho*-quinones have been investigated and it has been shown that the specific products of the reactions are dependent on the structure of the Wittig reagents and 1,2-dicarbonyl compounds. Common reactions include bis- or mono-Wittig reactions that form 1,2-dialkenes or enones[1–3] and cycloadditions that form 1,3-dioxolanes.[4,5] These three kinds of products may be stable products or undergo further reaction with nearby functional groups.

Phosphaenones and *ortho*-diphosphaalkenes are examples of phosphorus analogues of enones and 1,2-dialkenes. Because of the reactivity of low-coordinate phosphorus compounds, bulky groups are often introduced for purposes of kinetic stabilization. Some *ortho*-diphosphaalkenes have been prepared and used as bidentate ligands for transition metal catalysis.[6–10] Based on these reports, it was envisioned that phosphanylidene-σ^4-phosphoranes (ArP = PMe_3) might be of utility for the preparation of related ligands by reaction with 1,2 dicarbonyl compounds. This idea was inspired by the success of phospha-Wittig reaction to prepare phosphaalkenes (ArP = C(H)R) from ArP = PMe_3 and aldehydes.[11] In one extension of our reactivity studies of phosphanylidene-σ^4-phosphoranes, we have recently reported that they can react with *ortho*-quinones to yield 1,3,2-dioxaphospholanes.[12] In this report, we describe a novel permutation of such reactions that shows that the analogous reaction with acenaphthenequinone yields an eight-membered cyclic diphosphinite.

2. Results and discussion

A yellow solution of phosphanylidene-σ^4-phosphorane DmpP = PMe_3 **1** and acenaphthenequinone (1:1) in $CHCl_3$ transforms rapidly at room temperature to a red color. Analysis of the reaction mixture by ^{31}P NMR spectroscopy reveals exclusive formation of a new material **2** appearing to have two isomers (^{31}P NMR: δ = 304.6 (s) and 290.8 (s)) in about a 4:1 ratio, as well as a signal for trimethylphosphine oxide (δ = 39.2). Performing the reaction with a 2:1 ratio of DmpP = PMe_3 and acenaphthenequinone yields the same material **2**, O = PMe_3, and unreacted DmpP = PMe_3 after 1 day, indicating the optimal stoichiometry is 1:1. Reaction times greater than 2 days led to mixture of unidentified products. Workup of a 1:1 reaction mixture by removal of solvent under reduced pressure yielded a residue that was extracted with hexane and filtered. Orange crystals of a new compound **3** were thus obtained from hexane (yield: 39%) (Eq. 1). These crystals are not air stable and change from red orange to yellow orange and lose transparency after about 2.0 h in the air.

Keywords: β-Phosphaenones; Phosphanylidene-σ^4-phosphorane; Cycloaddition reaction; Cyclic diphosphinite.
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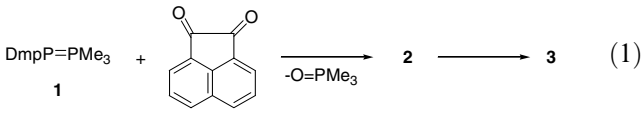


The phoshorus-31 NMR chemical shift for compound **3** at δ 138.8 ppm is no longer consistent with a material containing a P = C unit. Proton NMR spectra were broad and uninformative (vide infra), and it was thus necessary to perform a crystal structure analysis to identify **3**.

An ORTEP representation of the crystal structure analysis of **3**·*n*-C_6H_{14} is shown in Figure 1. The molecule of **3** has pseudo C_2-symmetry around the rotation axis passing through the center of the eight-membered ring. The shape of the eight-membered heterocyclic ring is similar to that of the lowest energy configuration of 1,5-cyclooctadiene (Fig. 2).[13] The acenaphthylene groups from two enantiomeric pairs within the unit cell (related by the inversion center) are parallel to each other at a distance of 3.60 Å, which suggests π–π stacking interaction between the two moieties (Fig. 3).

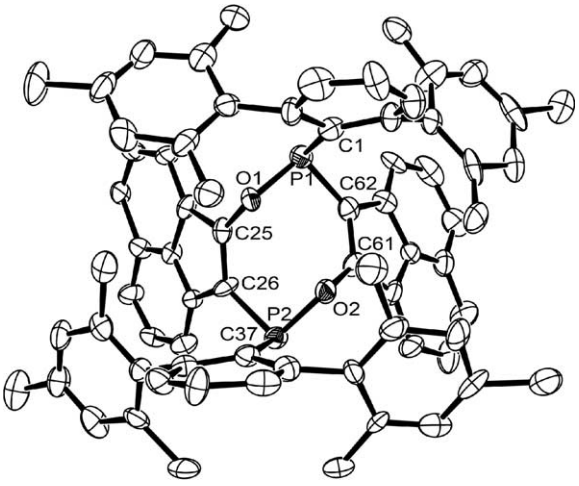


Figure 1. Crystal structure of compound **3**. Some selected bond lengths (Å) and bond angles (°): P(1)–O(1), 1.687(3); P(2)–O(2), 1.677(3); P(1)–C(62), 1.811(5); P(2)–C(26) 1.803(5); P(1)–C(1), 1.833(5); P(2)–C(37), 1.825(5); O(1)–P(1)–C(62), 98.6(2); O(2)–P(2)–C(26), 98.8(2); O(1)–P(1)–C(1), 95.8(2); O(2)–P(2)–C(37), 96.1(2); C(25)–O(1)–P(1), 115.3(2); C(62)–P(1)–C(1), 106.6(2); C(37)–P(2)–C(26), 105.9(2).

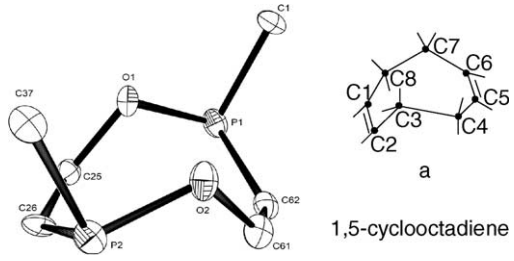


Figure 2. Structure of the eight-membered ring in **3** and schematic structure of the lowest energy configuration of 1,5-cyclooctadiene.

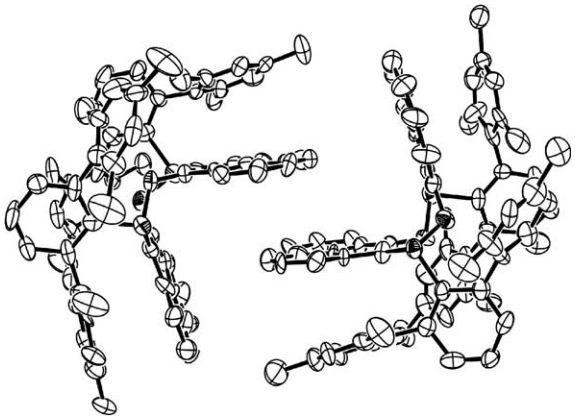


Figure 3. π–π stacking between two enantiomeric pairs of **3** in the crystal unit cell.

The crowded nature of **3**, in particular, the proximity of the two rather large Dmp units, is responsible for hindered rotation about some bonds and corresponding broad proton NMR signals for the aromatic and methyl protons in the Dmp groups. Resonances for the aromatic protons of acenaphthylene, however, are sharp, and assignment of these signals was confirmed by 2D ^1H–^1H COSY NMR spectroscopy in acetone-d_6. Variable temperature spectra in the higher boiling solvent C_6D_5Br allowed spectra to be recorded up to 110 °C (Fig. 3) and some analysis of the fluxional behavior. Overlap of the Dmp aromatic signals with the acenaphthylene protons made analysis of these particular resonances difficult, but from these spectra it is clear that the nearly baseline broadened methyl resonances sharpened on heating to nearly resolve into 2 signals in a 1:2 ratio (Fig. 4, bottom). For a static structure, six different methyl resonances would be expected.

Two different fluxional processes could be present for **3**. First, inversion at phosphorus might interconvert the RR and SS enantiomers. Pyramidal phosphorus compounds have higher inversion barrier than that of their nitrogen analogues.[14] However, the bulky substituents can lower inversion barriers by ground state destabilization.[15] Such a process might be expected to pass through the meso form (RS or SR). No evidence of a second ^{31}P NMR signal was observed, thus a possible inversion process might also involve a ring flip that simultaneously inverts both chiral centers. Interconversion of the RR and SS enantiomers would not, however, explain the broadening of the Dmp methyl resonances. The second, more likely process is that rotation about the P1–C1 (or P2–C37) bonds is hindered. In the absence of rotation, six independent resonances are expected. Fast rotation would lead to exchange of three pairs of methyl groups (pairs, a, b, and c, Chart 1) and yield three signals in the fast exchange limit. The observed spectrum at 110 °C, however, reveals the presence of two broad signals at δ 2.3 and 1.9 ppm in a 1:2 ratio for the methyl protons. As the fast exchange limiting spectrum could not be obtained in this case, a firm assignment of the fluxional process for **3** is thus not yet available. It should be mentioned that a process

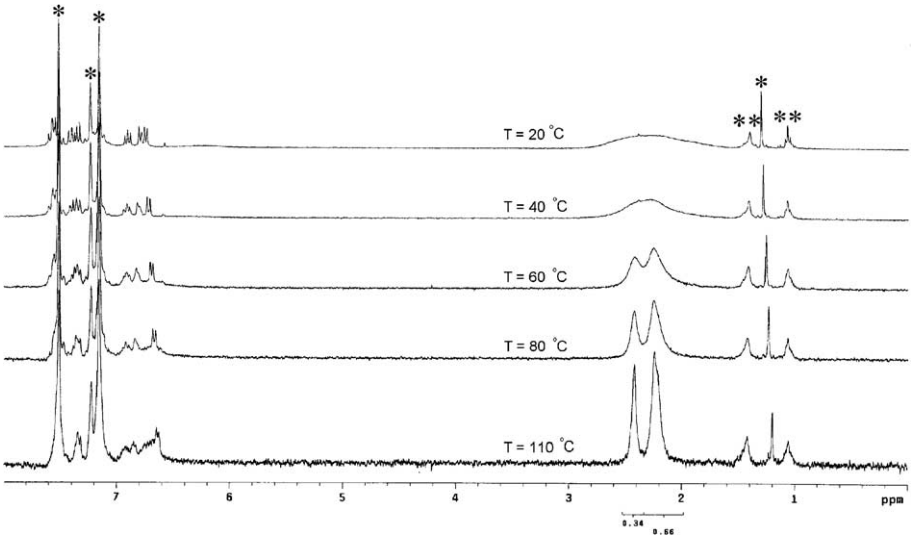


Figure 4. Variable temperature ^{1}H NMR (300 MHz) spectra for compound **3** in C_6D_5Br (signals at 7.15, 6.88, 6.80 indicated by ∗ are residual protons in C_6D_5Br, and signal at 1.20 ppm is due to solvent impurities. Signal at 1.40 and 1.05 indicated by ∗∗ are due to hexane co-solvent from crystals of compound **3**·(n-C_6H_{14})$_{0.5}$).

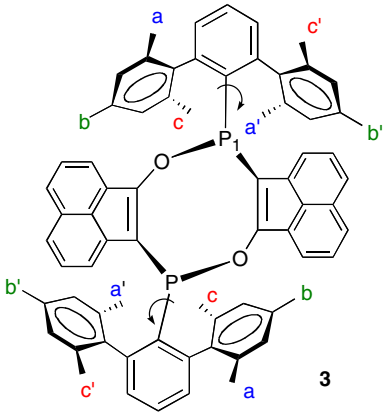
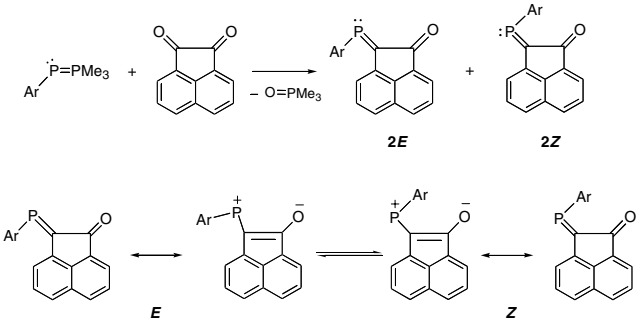


Chart 1.



Scheme 1. Formation of β-phosphaenones and resonance structures.

involving dissociation of **3** into β-phosphaenone monomers is not consistent with the comparatively sharp resonances observed for acenaphthylene protons.

The ^{31}P NMR chemical shifts for the two isomers of **2** fall within the broad range of values (δ 257–335 ppm) reported for β-phosphaenones. These materials have ^{31}P NMR shifts that show deshielding of the phosphorus nucleus compared to non-conjugated phosphaalkenes.[16–18] Other phosphaenones have also been reported to exist as two isomers (*E*,*Z*) as shown by ^{31}P NMR spectroscopy.[16,17] The *Z*-isomers typically resonate at a lower field than the *E*-isomers. As suggested previously, interconversion of such *Z*/*E* isomers may be facilitated by the contribution of the zwitterionic structures portrayed in Scheme 1.[16] A small thermodynamic preference of 1.1 kcal/mol for the *Z* isomer was predicted by molecular modeling (*SPARTAN '04*, PM3).

The phosphorus-31 NMR chemical shift for compound **3** of δ 138.8 ppm is similar to chemical shifts observed in 10-membered heterocyclic phosphorochloridites[19,20] and N-substituted chlorodiazadiphosphetidine derivatives.[21]

A reasonable mechanism accounting for formation of **3** involves a formal [4+4] cycloaddition of two β-phosphaenones. Once acenaphthenequinone reacts with the first equivalent of the DmpP = PMe_3 by a phospha-Wittig reaction to give these phosphaenones, it appears that addition of the second equivalent is discouraged by the presence of large Dmp unit on the phosphaenone. As **3** was isolated as a racemate and no evidence of a meso form was observed, a facile equilibrium between **2*Z*** and **2*E*** (presumably **2*E*** having more accessible C=O unit is more reactive for cycloaddition) might also account for selective formation of the presumably more stable form of **3**. Similar mechanisms were proposed for some enones, which dimerized by Diels–Alder type reactions.[1,3,22,23] Other reported phosphaenones have been synthesized via the reaction of chloro(phosphinidene) methyllithium/magnesium reagents with carbonyl chlorides.[16–18]

Attempts to extend the chemistry reported herein to the phosphanylidene-σ^4-phosphorane Mes*P = PMe_3 (Mes* = 2,4,6-tri-*tert*-butylphenyl) unveiled that reactions

with acenaphthenequinone (1:1) in $CHCl_3$ or THF do produce a single isomer (*E* or *Z*) of the analogous β-phosphaenones (^{31}P NMR $\delta = 300$ and 287 ppm, respectively) and $O = PMe_3$. However, isolation of products from these reactions were thwarted by the presence of much Mes*P = PMes* and other unidentified species.

3. Conclusion

In conclusion, an eight-membered cyclic diphosphinite was synthesized by the reaction of acenaphthenequinone and phosphanylidene-σ^4-phosphorane DmpP = PMe_3. Its structure was established by X-ray analysis and NMR spectroscopy. Acenaphthenequinone thus behaves differently from tetrachloro-*o*-benzoquinone and 3,5-di-*tert*-butyl-*o*-benzoquinone toward phosphanylidene-σ^4-phosphoranes. This finding is similar to that found for the reaction of acenaphthenequinone with a Wittig reagent,[2] where an enone and its dimer were isolated from the reaction when two equivalents of ylide were used. However, the β-phosphaenones formed in the present reaction are not stable and isolation of the phosphaenone failed. An unusual cyclic diphosphinite was obtained instead.

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Supplementary data

A supplementary experimental section is provided that includes full experimental detail for synthesis of **3** and NMR spectra of **3**. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC 267415). Copies of this information can be obtained free of charge via www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.tetlet.2005.06.131.

References and notes

1. (a) Osman, F. H.; El-Samahy, F. A. *Chem. Rev.* **2002**, *102*, 629; (b) Soliman, F. M.; Khalil, Kh. M.; Abd-El-Naim, G. *Phosphorus Sulfur Silicon Relat. Elem.* **1988**, *35*, 41.
2. Boulos, L. S.; Hennawy, I. T. *Phosphorus Sulfur Silicon Relat. Elem.* **1993**, *84*, 173.
3. Abdou, W. M.; Ganoub, N. A. F.; Abdel-Rahman, N. M. *Phosphorus Sulfur Silicon Relat. Elem.* **1991**, *61*, 91.
4. Fylaktakidou, K. C.; Gautam, D. R.; Hadjipavlou-Litina, D. J.; Kontogiorgis, C. A.; Litinas, K. E.; Nicolaides, D. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3073.
5. (a) Voleva, V. B.; Zhorin, V. A.; Khristyuk, A. L.; Ershov, V. V.; Enikolopyan, N. S. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1983**, *32*, 402; (b) Sidky, M. M.; Boulos, L. S. *Phosphorus Sulfur Silicon Relat. Elem.* **1984**, *19*, 27; (c) Abdou, W. M. *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *66*, 285.
6. Appel, R.; Winkhaus, V.; Knoch, F. *Chem. Ber.* **1987**, *120*, 243.
7. Märkl, G.; Kreitmeier, P.; Nöth, H.; Polborn, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 927.
8. (a) Yoshifuji, M.; Toyota, K.; Murayama, M.; Yoshimura, H.; Okamoto, A.; Hirotsu, K.; Nagase, S. *Chem. Lett.* **1990**, 2195; (b) Toyota, K.; Tashiro, K.; Yoshifuji, M.; Nagase, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2297; (c) Toyota, K.; Tashiro, K.; Yoshifuji, M. *Angew. Chem.* **1993**, *105*, 1256; (d) Yamada, N.; Abe, K.; Toyota, K.; Yoshifuji, M. *Org. Lett.* **2002**, *4*, 569.
9. Maerkl, G.; Hennig, R.; Noeth, H.; Schmidt, M. *Tetrahedron Lett.* **1995**, *36*, 6429.
10. Ikeda, S.; Ohhata, F.; Miyoshi, M.; Tanaka, R.; Tatsuya, M.; Fumiyuki, O.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4512.
11. (a) Marinetti, A.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1382; (b) Le Floch, P.; Mathey, F. *Synlett* **1990**, *171*; (c) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793; (d) Shah, S.; Protasiewicz, J. D. *Coord. Chem. Rev.* **2000**, *210/1*, 181; (e) Shah, S.; Protasiewicz, J. D. *Chem. Commun.* **1998**, 1585.
12. Chen, X.; Smith, R. C.; Protasiewicz, J. D. *Chem. Commun.* **2004**, 146.
13. Hovis, J. S.; Hamers, R. J. *J. Phys. Chem. B* **1997**, *101*, 9581.
14. Baechler, R. D.; Andose, J. D.; Stackhouse, J.; Mislow, K. *J. Am. Chem. Soc.* **1972**, *94*, 8060.
15. Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 3090.
16. Yoshifuji, M.; Ito, S.; Toyato, K.; Yasunnami, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1206.
17. van der Sluis, M.; Bickelhaupt, F.; Veldman, N.; Kooijman, H.; Spek, A. L.; Eisfeld, W.; Regitz, M. *Chem. Ber.* **1995**, *128*, 465.
18. van der Sluis, M.; Wit, J. B. M.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 174.
19. Balakrishna, M. S.; Panda, R.; Mague, J. T. *Inorg. Chem.* **2001**, *40*, 5620.
20. Balakrishna, M. S.; Panda, R. *Phosphorus Sulfur Silicon Relat. Elem.* **2003**, *178*, 1391.
21. Vijjulatha, M.; Kumaraswamy, S.; Kumara Swamy, K. C.; Engelhardt, U. *Polyhedron* **1999**, *18*, 2557.
22. Abd El-Rahman, N. M.; Boulos, L. S. *Molecules* **2002**, *7*, 81.
23. Boulos, L. S.; Abd El-Rahman, N. M. *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *68*, 241.