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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: $\delta = 304.6$ (s) and 290.8 (s)) in about a 4:1 ratio, as well as a signal for trimethylphosphine oxide ($\delta = 39.2$). 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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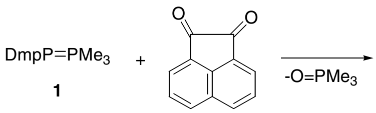

(1)

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).

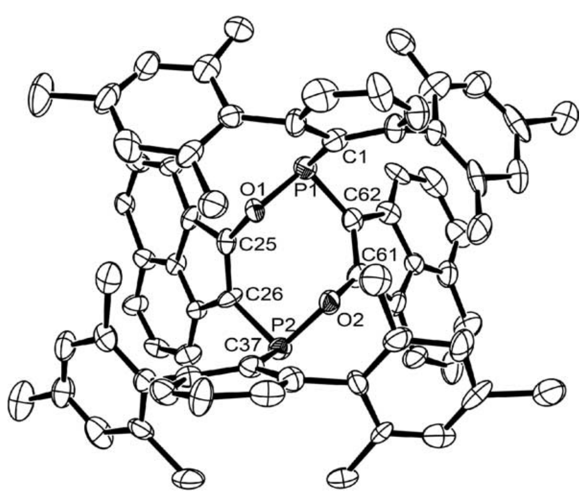

Figure 1. Crystal structure of compound **3**. Some selected bond lengths (Å) and bond angles (°): P(1)–O(1), 1.687(3); P(2)–O(2), 1.677(3); P(1)–C(62), 1.811(5); P(2)–C(26) 1.803(5); P(1)–C(1), 1.833(5); P(2)–C(37), 1.825(5); O(1)–P(1)–C(62), 98.6(2); O(2)–P(2)–C(26), 98.8(2); O(1)–P(1)–C(1), 95.8(2);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

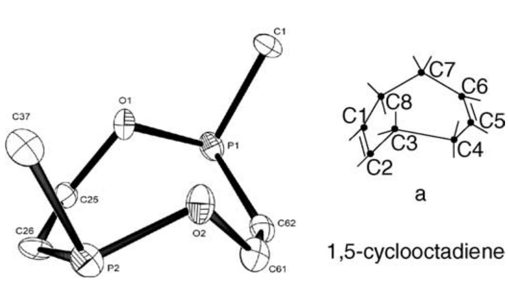

Figure 2. Structure of the eight-membered ring in **3** and schematic structure of the lowest energy configuration of 1,5-cyclooctadiene.

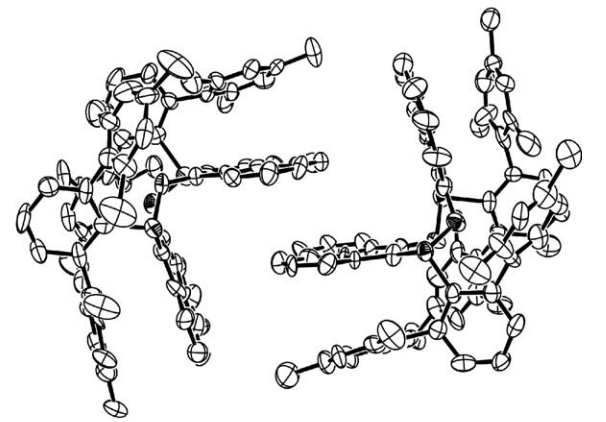

Figure 3. π–π stacking between two enantiomeric pairs of **3** in the crystal unit cell.

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 ^{1}H–^{1}H 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