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Cycloaddition of phosphanylidene-σ⁴-phosphoranes ArP=PMe$_3$ and quinones to yield 1,3,2-dioxophospholanes†

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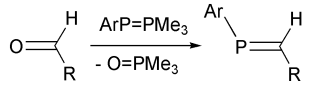
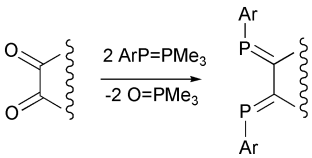
The reaction of phosphanylidene-σ⁴-phosphoranes ArP=PMe$_3$ (Ar = 2,6-Mes$_2$C$_6$H$_3$ or 2,4,6-*t*-Bu$_3$C$_6$H$_2$) with select *ortho*-quinones yields 1,3,2-dioxophospholanes, one of which shows interesting π-stacking of the aromatic groups in the solid state.

We have previously reported that reaction of the easily prepared and stable phosphanylidene-σ⁴-phosphoranes ArP=PMe$_3$ (Ar = Dmp = 2,6-Mes$_2$C$_6$H$_3$ (**1**) or Ar = Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$ (**2**)) with aldehydes affords a rapid and convenient synthesis of phosphaalkenes [eqn. (1)].[1] During this study reagents **1** and **2** were found to be unreactive towards ketones at ambient conditions. Seeking to extend this variant of the phospha-Wittig reaction[2] to new systems, it was reasoned that reaction of these reagents with more reactive C=O bonds of *o*-quinones might be more favorable. In particular, reaction of *o*-quinones might lead to easy synthesis of 1,2-diphosphaalkenes [eqn. (2)], materials which are now drawing attention as a new class of chelating ligands for transition metal catalysts.[3] Herein we report that the targeted reaction does not proceed as initially intended, but instead gives products of cycloaddition of the phosphanylidene center to *o*-quinones.



(1)

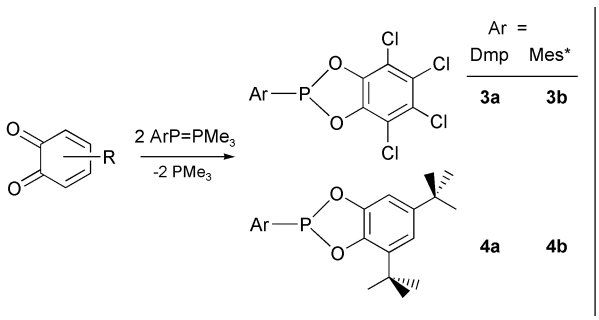


(2)

Reaction of **1** and **2** with either tetrachloro-*o*-benzoquinone or 3,5-di-*tert*-butyl-*o*-benzoquinone over a 1 hour time period in toluene yielded pale yellow–green solutions. While the reaction mixtures displayed ^{31}P NMR resonances between 194.3 and 230.1 ppm, well within the range of values determined for phosphaalkenes,[4] the resonance for PMe$_3$, not the anticipated product O=PMe$_3$, was observed. Furthermore, the reaction stoichiometry was found to be 1 : 1 for ArP=PMe$_3$: *o*-quinone (excess ArP=PMe$_3$ was left unreacted). The major products in these reactions are actually 1,3,2-dioxaphospholanes. From the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone isolated yields of 1,3,2-dioxaphospholanes are quite excellent (**4a**, 94.1%; **4b**, 98.0%; Scheme 1).‡ Reactions of **1** and **2** with tetrachloro-*o*-benzoquinone gave somewhat lower yields of the cycloadducts (40–45%). Best results for **3a** were obtained for reactions performed in toluene at reduced temperatures (−35 °C). Compound **3b** has been previously isolated in 16% yield by reaction of tetrachloro-*o*-benzoquinone with the diphosphene Mes*P=PMes*.[5]

An ORTEP diagram representing the results of crystallographic determination for **3a** is provided in Fig. 1.§ Immediately striking is the disposition of the electron deficient ring above and parallel to one of the two more electron rich mesityl rings on the Dmp unit. This intramolecular π–π stacking is evinced by a distance between rings of 3.23 Å. Although this interaction is presumed to be attractive between rings, the phosphorus atom is actually distanced from these two rings, as seen by the C(2)–C(1)–P(1) and C(6)–C(1)–P(1) bond angles of 127.0(6) and 113.6(6)°, respectively. The structural data for **3a** can also be contrasted to that found in **3b**,[5] where longer P–O and P–C bond distances and a smaller O–P–O bond angle indicate the greater steric presence of the Mes* compared to the Dmp unit. An additional feature of interest for **3a** is the manner in which molecules aggregate in the solid state by additional π-stacking between electron deficient and electron rich aromatic rings (Fig. 2) along the *c* axis of the unit cell, with an intermolecular distance of 3.70 Å between these rings. The intramolecular π-stacking is not sufficient to strongly inhibit rotation about the P–C bond in solution, as the mesityl rings are equivalent by both ^{1}H and ^{13}C NMR spectroscopy.

The results of a single crystal X-ray diffraction study of **4a** are shown in Fig. 3. In addition to lacking the electronic disparity of the two sets of aromatic rings in **3a**, steric repulsions between *tert*-butyl groups and the mesityl groups presumably also discourage the type of intramolecular π-stacking observed in **3a**. As in **3a**, the C(2)–C(1)–P(1) and C(6)–C(1)–P(1) bond angles of 128.8(4) and 111.9(4)°, respectively, are significantly different, and might indicate Menshutkin-type interactions between the phosphorus atom and the opposite mesityl ring, as have been invoked in the related *meta*-terphenyls 2,6-Ar$_2$–C$_6$H$_3$ECl$_2$ (E = As, Bi or Sb).[6]



Scheme 1

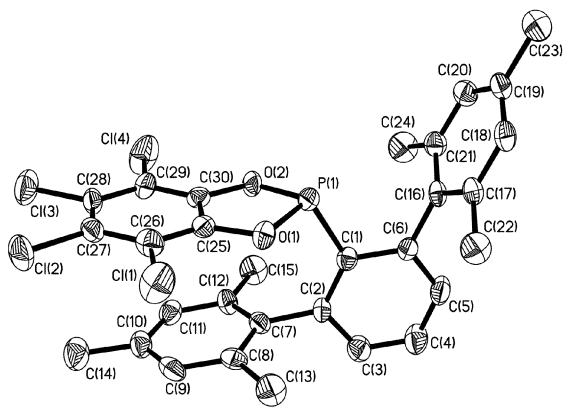


Fig. 1 Structural diagram for **3a**. Selected bond distances (Å) and angles (°): P(1)–C(1), 1.824(8), P(1)–O(1) 1.675(6); P(1)–O(1) 1.674(6); O(1)P(1)O(2), 93.5(3); C(1)P(1)O(1), 104.5(3); C(1)P(1)O(2), 104.7(3)

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b309165a/

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While the sum of angles at phosphorus (302.7°) for **3a** is slightly larger than that of compounds **4a** (297.7°) and **3b** (290.8°), each phosphorus center is pyramidal.

The present method for preparing 1,3,2-dioxophospholanes adds to the large number of reactions of *ortho*-quinones with phosphorus compounds,[7] but distinguishes itself in that reactions to produce P(III) compounds (*via* low coordinate phosphorus compounds) are not often as simple or high yielding. One can also compare the current reactions to a limited set of reactions of these *ortho*-quinones with non-carbonyl stabilized Wittig reagents $R'_2C{=}PR_3$ that yield 1,3-dioxoles.[8] Such reactions may proceed by radical or electron-transfer pathways, thus explaining the lack of C=C or P=C bond formation. Further work to increase the utility of $ArP{=}PMe_3$ for ligand synthesis is currently underway. The authors thank the National Science Foundation (CHE-0202040) for support.

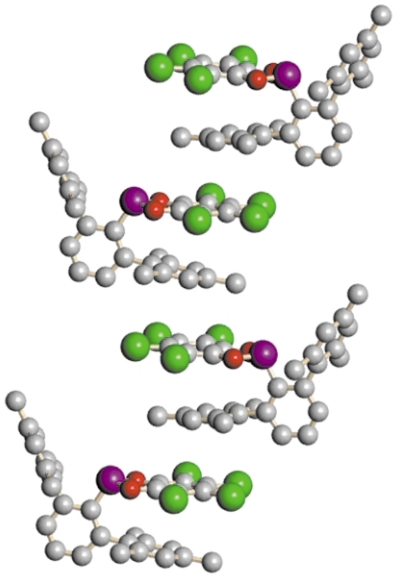

Fig. 2 Packing diagram for **3a** illustrating π-stacking in the crystal.

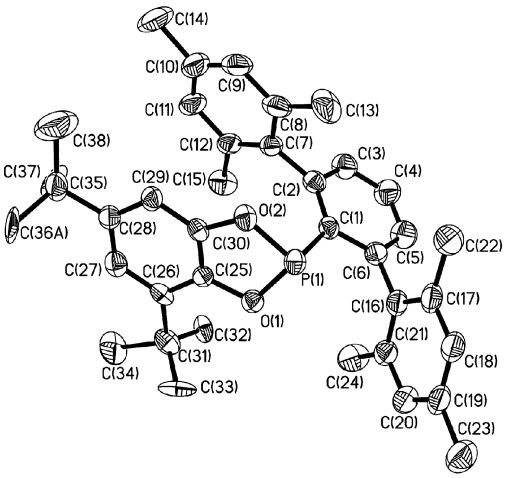

Fig. 3 Structural diagram for **4a**. Selected bond distances (Å) and angles (°): P(1)–C(1), 1.851(6), P(1)–O(1) 1.673(4); P(1)–O(1) 1.656(4); O(1)P(1)O(2), 93.4(2); C(1)P(1)O(1), 100.6(2) ; C(1)P(1)O(2) = 103.7(2)

Notes and references

‡ Selected spectroscopic data for **3–4** (See ESI for full details): **3a** mp 234–235 °C. ^{1}H NMR ($CDCl_3$): δ 2.03 (s, 12H); 2.26 (s, 6H); 6.81 (s, 4H); 7.12 (dd, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 2.0 Hz); 7.66 (t, 1H, J = 7.6 Hz). ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ 21.04 (s); 21.16 (d, J = 1.1 Hz); 127.96 (s); 130.05 (d, J = 1.8 Hz); 134.14 (s); 135.46 (d, J = 8.0); 136.15 (d, J = 2.2 Hz); 137.59 (s); 137.80 (s); 138.59 (s); 144.52 (s); 147.29 (s); 147.81 (s). ^{31}P{^{1}H} ($CDCl_3$): δ 230.1. **3b** ^{1}H NMR ($CDCl_3$): δ = 1.21 (s, 9H); 1.54 (d, 18H, J = 1.1 Hz); 7.13 (d, 2H, J = 1.1 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 217.5. **4a** mp 154–156 °C. ^{1}H NMR ($CDCl_3$): δ = 1.23 (s, 9H); 1.25 (s, 9H); 1.76 (s, 6H); 2.14 (s, 6H); 2.36 (s, 6H); 5.87 (d, 1H, J = 2.0 Hz); 6.73 (d, 1H, J = 2.1 Hz); 6.78 (s, 2H); 6.94 (dd, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 1.8 Hz); 6.99 (s, 2H,); 7.47 (t, 1H, J = 7.6 Hz). ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ 20.81 (d, J = 5.3 Hz); 21.33 (s); 21.67 (s); 29.89 (s); 31.63 (s); 34.36 (s), 34.45 (s); 108.07 (d, J = 1.6 Hz); 116.34 (s); 127.86 (s); 128.28 (s); 130.07 (s); 131.56 (s); 134.01 (s); 135.94 (d, J = 2.0 Hz); 136.64 (s); 136.86 (d, J = 1.7 Hz); 137.32 (d, J = 4.6 Hz); 143.69 (s); 144.30 (s); 144.69 (s); 146.94 (s); 147.06 (s). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 194.3. **4b** mp 100–101 °C. ^{1}H NMR ($CDCl_3$): δ 1.12 (s, 9H); 1.20 (s, 9H); 1.24 (s, 9H); 1.52 (s, 18H); 6.65 (d, 1H, J = 1.9 Hz); 6.75 (d, 1H, J = 2.2 Hz); 7.01 (d, 2H, J = 1.0 Hz). ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$): δ 30.23 (s); 31.02 (s); 31.57 (s); 34.14 (d, J = 9.2 Hz); 34.36 (s); 34.44 (s); 34.54 (s); 39.49 (d, J = 2.7 Hz); 108.03 (s); 115.70 (s); 121.21 (s); 134.22 (s); 141.28 (s); 142.41 (s); 144.00 (s); 146.94 (d, J = 7.4 Hz); 149.54 (s); 156.62 (d, J = 6.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 195.9.

§ Crystal data for **3a**. $C_{30}H_{25}Cl_4O_2P$, M = 590.27, monoclinic, a = 8.451(3), b = 24.614(8), c = 14.068(4) Å, α = 90.00, β = 105.55(2), γ = 90.00, U = 2819.1(14) Å^3, T = 293 K, space group $P2(1)/c$, Z = 4, μ(Mo–Kα) = 0.503 mm^{-1}, 4432 reflections measured, 1851 unique (R_{int} = 0.0618) which were used in all calculations. Final R_1 = 0.0800, $wR(F^2)$ was 0.1900 (all data). CCDC 216923.

Crystal data for **4a**. $C_{38}H_{45}O_2P$, M = 564.71, monoclinic, a = 13.623(2), b = 11.2320(17), c = 22.372(3) Å, α = 90.00, β = 98.531(12), γ = 90.00, U = 3385.4(9) Å^3, T = 293 K, space group $P2(1)/c$, Z = 4, μ(Mo–Kα) = 0.111 mm^{-1}, 5315 reflections measured, 2896 unique (R_{int} = 0.0342) which were used in all calculations. Final R_1 = 0.0930, $wR(F^2)$ was 0.2680 (all data). CCDC 216924. http://www.rsc.org/suppdata/cc/b3/b309165a/ for crystallographic data in .cif format.

1 S. Shah and J. D. Protasiewicz, *Chem. Commun.*, 1998, 1585.
2 (*a*) P. Le Floch, A. Marinetti, L. Ricard and F. Mathey, *J. Am. Chem. Soc.*, 1990, **112**, 2407; (*b*) P. Le Floch and F. Mathey, *Synlett*, 1990, 171; (*c*) S. Shah and J. D. Protasiewicz, *Coord. Chem. Rev.*, 2000, **210/1**, 181.
3 Some recent reports: (*a*) A. S. Ionkin and W. Marshall, *Chem. Commun*, 2003, 710–711; (*b*) A. S. Ionkin and W. Marshall, *Heteroat. Chem.*, 2002, **13**, 662–666; (*c*) T. Minami, H. Okamoto, S. Ikeda, R. Tanaka, F. Ozawa and M. Yoshifuji, *Angew. Chem., Int. Ed.*, 2001, **40**, 4501; (*d*) M. Yoshifuji, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 28813.
4 R. Appel, F. Knoll and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731.
5 M. Freytag, P. G. Jones, R. Schmutzler and M. Yoshifuji, *Heteroat. Chem.*, 2001, **12**, 300.
6 B. Twamley, C. D. Sofield, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1999, **121**, 3357.
7 F. H. Osman and F. A. Al-Samahy, *Chem. Rev.*, 2002, **102**, 629.
8 For example: (*a*) V. B. Z. V. A. Voleva, A. L. Khristyuk, V. V. Ershov and N. S. Enikolopyan, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)*, 1983, **32**, 402; (*b*) M. M. B. L. S. Sidky, *Phosphorus Sulfur Relat. Elem.*, 1984, **19**, 27; (*c*) W. M. Abdou, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1992, **66**, 2.