

Naphtho[1,8-*b,c*]phosphete and 1,2-Diphosphaacenaphthene from the Reaction of 1,8-Dilithionaphthalene with RPhCl_2 **

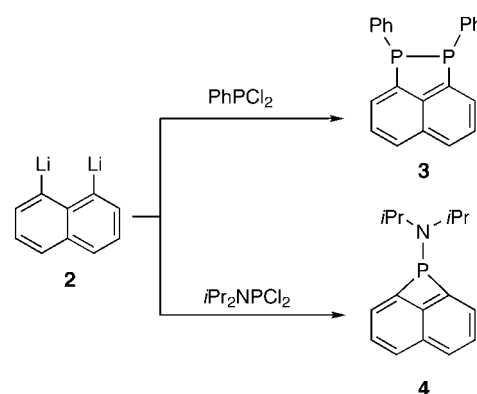
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Single-atom *peri*-bridged naphthalenes **1** have a highly strained and potentially useful four-membered ring which



readily undergoes a ring-enlargement reaction. The first example of **1** was reported for E = SO₂ in 1965,^[1] and since then, analogues bridged by elements of Group 13 (BR, BR₂⁻),^[2] Group 14 (CR₂, SiR₂, and GeR₂),^[3] and Group 16 (S, SO, and SO₂)^[4] have been reported. However, to our knowledge, no Group 15 analogues have been prepared and fully characterized to date.^[5] On the other hand, strained phosphorus heterocycles have attracted considerable interest owing not only to their unusual structures and reactivities, but also to their utility as a ligand towards a variety of transition-metal fragments.^[6] Herein we report the preparation and molecular structure of a phosphorus analogue of **1**.

1,8-Dilithionaphthalene (**2**), which is readily obtained by lithiation of 1,8-dibromonaphthalene (method A)^[7a] or of commercially available 1-bromonaphthalene, (method B),^[7b] is a convenient starting material for the preparation of **1**. The reaction of **2** with PhPCl₂ in hexane did not give the desired single-atom-bridged species (**1**, E = PPh), but instead yielded the diphosphorus-bridged species **3** as the major product (Scheme 1). The structure of **3** was determined by X-ray analysis (Figure 1).^[8] This compound is the first example of a $\sigma^3\text{P}-\sigma^3\text{P}$ -bridged naphthalene species which has a lone pair on each phosphorus atom, though two $\sigma^4\text{P}^+-\sigma^3\text{P}$ -bridged phosphonium analogues were reported recently.^[9] Although the reaction mechanism leading to **3** is not clearly understood,^[10] the presence of a P–P bond in **3** suggests that a reduction of the phosphorus centers takes place during the reaction. Thus, $i\text{Pr}_2\text{NPCl}_2$, which has an electron-donating R₂N group, was employed in place of PhPCl₂. The reaction of **2** with $i\text{Pr}_2\text{NPCl}_2$ gave the expected product **4**. The yield of **4** was improved to 75% when **2** was prepared by method A. An X-ray structure of **4** (Figure 2) indicates that bond angles are considerably distorted from standard values for tricoordinate phosphorus



Scheme 1. Reaction of **2** with RPhCl_2 .

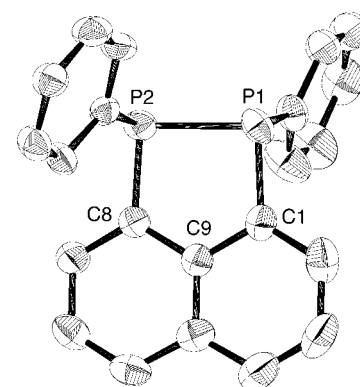


Figure 1. ORTEP drawing of **3** (thermal ellipsoids set at 50 % probability), selected bond lengths [Å] and bond angles [°]: P1–P2 2.230(1), P1–C1 1.832(4), P2–C8 1.832(4); P2–P1–C1 93.2(1), P1–P2–C8 93.4(1), P1–C1–C9 116.9(3), P2–C8–C9 116.7(3), C1–C9–C8 119.3(3).

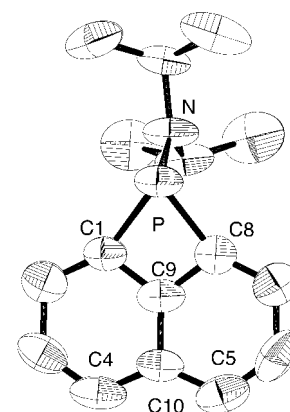


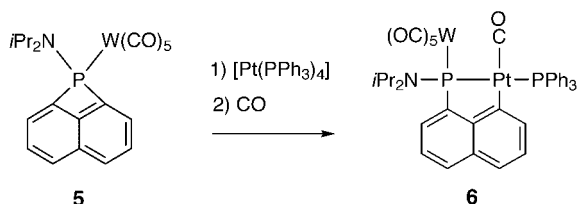
Figure 2. ORTEP drawing of **4** (thermal ellipsoids set at 50 % probability), selected bond lengths [Å] and bond angles [°]: P–N 1.654(5), P–C1 1.885(7), P–C8 1.885(7); C1–P–C8 73.1(3), P–C1–C9 89.7(4), P–C8–C9 90.4(5), C1–C9–C8 106.1(6), C4–C10–C5 131.5(8).

and sp² carbon atoms.^[11] The distortions observed in **4** are in line with those reported, and those predicted by theoretical calculations.^[12]

The reactivity of **4** was examined. Compound **4** coordinated to a [W(CO)₅] fragment to form [W(CO)₅(**4**)] (**5**), which was in turn treated with [Pt(PPh₃)₄] and then with CO gas to give **6** (Scheme 2). The isolated product **6** has a structure in which a [Pt(CO)(PPh₃)] fragment has been inserted into the strained

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Scheme 2. Insertion of the platinum fragment into a P–C bond.

P–C bond of the four-membered ring to give a 1-platina-2-phosphaacenaphthene framework.

Experimental Section^[13]

3: PhPCl_2 (6.5 mL, 48 mmol) was added at -30°C to a suspension of **2** in hexane (60 mL) which was prepared from 1-bromonaphthalene (5 mL, 36 mmol).^[7b] After vigorous stirring at -30°C for 1 h and then at 0°C for 3 h, the products were collected by filtration. The products were suspended in hexane: CH_2Cl_2 and loaded onto an Al_2O_3 column and a yellow band was collected by using CH_2Cl_2 :hexane (1:1) as the eluent. After removal of the solvents, recrystallization from diethyl ether gave a white powder, 4.88 g (59% based on PhPCl_2). ^1H NMR (300.4 MHz, CDCl_3 , TMS): δ = 7.18 (m, 10H; Ph), 7.60 (m, 2H; 3,6-naph), 7.82 (m, 2H; 1,7-naph), 7.93 ppm (d, J = 8.1 Hz 2H; 4,5-naph); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.45 MHz, CDCl_3 , TMS): δ = 127.4, 128.0, 128.5, 132.1, 132.2, 133.6, 138.4, 141.8, 142.0 ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.45 MHz, CDCl_3 , H_3PO_4): δ = -8.0 ppm.

4: A diethyl ether solution of **2**, prepared from 1,8-dibromonaphthalene (250 mg, 0.874 mmol),^[7a] was added to a solution of $i\text{Pr}_2\text{NPCl}_2$ (0.20 mL, 1.05 mmol) in diethyl ether (3 mL) at 0°C . The mixture was stirred overnight, then LiCl was removed by filtration. After evaporation of the solvents, the residue was loaded onto an Al_2O_3 column. A light yellow band was eluted with hexane, and collected. After removal of the solvents 169 mg of **4** (75%) was obtained as a white powder. ^1H NMR (300.4 MHz, CDCl_3 , TMS): δ = 1.18 (d, $^3J(\text{H,H})$ = 6.6 Hz, 12H; CHMe_2), 3.29 (m, 2H; CHMe_2), 7.42 (d, $^3J(\text{H,H})$ = 6.6 Hz, 2H; naph), 7.52 (m, 2H; naph), 7.70 ppm (d, $^3J(\text{H,H})$ = 8.2 Hz, 2H; naph); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.45 MHz, CDCl_3 , TMS): δ = 23.8, 47.6, 122.5, 123.8, 127.5, 129.4, 147.2 ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.45 MHz, CDCl_3 , H_3PO_4): δ = -8.4 ppm.

6: **5** (764 mg, 1.31 mmol), which was prepared from the reaction of **4** and $[\text{W}(\text{CO})_5(\text{thf})]$, was treated with $[\text{Pt}(\text{PPh}_3)_4]$ (1635 mg, 1.31 mmol) in toluene (90 mL) at 45°C for 3 h, and the mixture was then purged with CO gas for 10 min. The resulting solution was heated at 90°C for 2 h, followed by removal of the toluene under reduced pressure. The residue was loaded onto an Al_2O_3 column, and a yellow band was collected by elution with CH_2Cl_2 :hexane (1:4). After removal of the solvents 1252 mg (89%) of **6** was obtained. ^1H NMR (300.4 MHz, CDCl_3 , TMS): δ = 1.20 (d, $^3J(\text{H,H})$ = 6.6 Hz, 6H; CHMe_2), 1.35 (d, $^3J(\text{H,H})$ = 6.8 Hz, 6H; CHMe_2), 4.25 (m, 2H; CHMe_2), 6.77 (m, 1H), 7.30–7.60 (m, 13H), 7.73 (m, 6H), 7.87 ppm (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.4 MHz, CDCl_3 , TMS): δ = 181.2 (PtCO), 198.3 (*cis* WCO), 201.7 ppm (*trans* WCO); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.45 MHz, CDCl_3 , H_3PO_4): δ = 22.3 (d, $^2J(\text{P,P})$ = 225 Hz, $^1J(\text{P,Pt})$ = 1736 Hz; PPh_3), 75.2 ppm (d, $^2J(\text{P,P})$ = 225 Hz, $^1J(\text{P,Pt})$ = 1706 Hz, $^1J(\text{P,W})$ = 227 Hz).

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- [8] Crystal data for **3**:^[14] colorless crystal ($0.50 \times 0.15 \times 0.10$ mm), monoclinic, $P2_1/c$, $a = 15.8680(8)$, $b = 5.7220(1)$, $c = 19.631(1)$ Å, $\beta = 100.087(2)^\circ$, $V = 1754.1(1)$ Å³, $\rho_{\text{calcd}} = 1.296$ g cm⁻³, $2\theta_{\text{max}} = 55^\circ$, $\text{MoK}\alpha(\lambda = 0.71609$ Å), $T = 295$ K, 4217 reflections measured, 3824 independent reflections, 3642 ($I/\sigma(I) > 0.0$) reflections used, $\mu(\text{MoK}\alpha) = 2.47$ cm⁻¹, R/wR factors ($I/\sigma(I) > 2.0$) 0.0646/0.1324.
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- [11] Crystal data for **4**:^[14] colorless crystal ($0.75 \times 0.40 \times 0.25$ mm), monoclinic, $P2_1/c$, $a = 7.674(7)$, $b = 14.559(5)$, $c = 13.880(5)$ Å, $\beta = 101.15(6)^\circ$, $V = 1521(1)$ Å³, $\rho_{\text{calcd}} = 1.123$ g cm⁻³, $2\theta_{\text{max}} = 55^\circ$, $\text{MoK}\alpha(\lambda = 0.71609$ Å), ω - 2θ scan mode, $T = 295$ K, 3954 reflections measured, 3489 independent reflections, 1458 ($I/\sigma(I) > 0.0$) reflections used, $\mu(\text{MoK}\alpha) = 1.64$ cm⁻¹, max./min. transmission 0.998/0.746, R/wR factors ($I/\sigma(I) > 2.0$) 0.0933/0.1365.
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- [13] **2** prepared by method A is in a homogeneous diethyl ether/hexane solution,^[7a] whereas the product obtained by the method B is an adduct with N,N,N',N' -tetramethyl-1,2-ethanediamine (TMEDA) and is sparingly soluble in hexane.^[7b] Although both methods, A and B, were applied to preparation of **3** and **4**, the procedure giving a better yield is that described in the Experimental Section.
- [14] CCDC-188236 (**3**) and CCDC-188237 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Butane-2,3-diacetals of Glyceraldehyde: A Stable Alternative to Glyceraldehyde Acetonide**

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D-Glyceraldehyde acetonide **1** has been used extensively as a three-carbon building block for organic synthesis.^[1] However, it must always be freshly prepared owing to its propensity to polymerize, racemize, and form hydrates.^[2] This can result in severe problems, particularly on scale-up. Thus, a readily available, stable alternative that is accessible in both

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