Naphtho[1,8-*b*,*c*]phosphete and 1,2-Diphosphaacenaphthene from the Reaction of 1,8-Dilithionaphthalene with $RPCl_2$**

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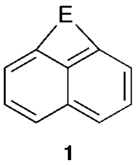
Single-atom *peri*-bridged naphthalenes **1** have a highly strained and potentially useful four-membered ring which readily undergoes a ring-enlargement reaction. The first example of **1** was reported for E = SO_2 in 1965,[1] and since then, analogues bridged by elements of Group 13 (BR, BR_2^-),[2] Group 14 (CR_2, SiR_2, and GeR_2),[3] and Group 16 (S, SO, and SO_2)[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**.



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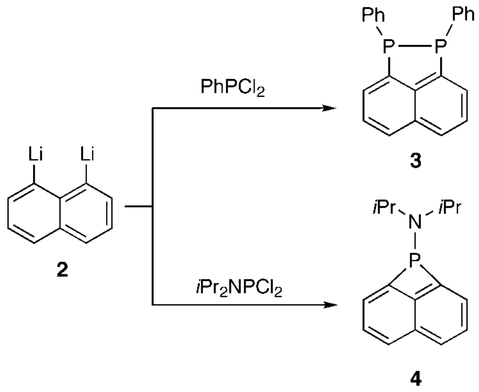
E: Group 13 (BR, BR_2^-)
Group 14 (CR_2, SiR_2, GeR_2)
Group 15 (PR: this work)
Group 16 (S, SO, SO_2)

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 $PhPCl_2$ 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 σ^3P–σ^3P-bridged naphthalene species which has a lone pair on each phosphorus atom, though two σ^4P^+–σ^3P-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, iPr_2NPCl_2, which has an electron-donating R_2N group, was employed in place of $PhPCl_2$. The reaction of **2** with iPr_2NPCl_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 and sp^2 carbon atoms.[11] The distortions observed in **4** are in line with those reported, and those predicted by theoretical calculations.[12]



Scheme 1. Reaction of **2** with $RPCl_2$.

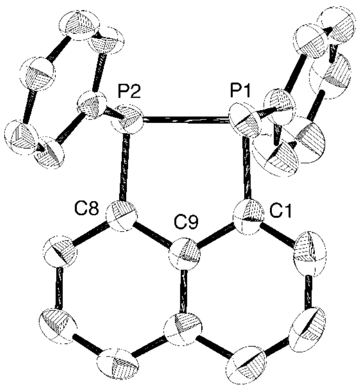


Figure 1. ORTEP drawing of **3** (thermal ellipsoids set at 50 % probability), selected bond lengths [Å] and bond angles [°]: P1-P2 2.230(1), P1-C1 1.832(4), P2-C8 1.832(4); P2-P1-C1 93.2(1), P1-P2-C8 93.4(1), P1-C1-C9 116.9(3), P2-C8-C9 116.7(3), C1-C9-C8 119.3(3).

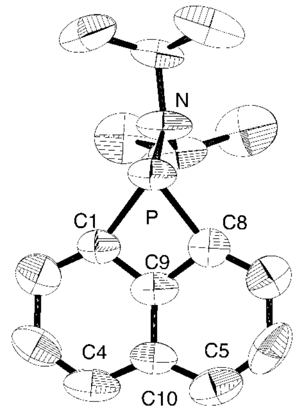


Figure 2. ORTEP drawing of **4** (thermal ellipsoids set at 50 % probability), selected bond lengths [Å] and bond angles [°]: P-N 1.654(5), P-C1 1.885(7), P-C8 1.885(7); C1-P-C8 73.1(3), P-C1-C9 89.7(4), P-C8-C9 90.4(5), C1-C9-C8 106.1(6), C4-C10-C5 131.5(8).

The reactivity of **4** was examined. Compound **4** coordinated to a $[W(CO)_5]$ fragment to form $[W(CO)_5(\mathbf{4})]$ (**5**), which was in turn treated with $[Pt(PPh_3)_4]$ and then with CO gas to give **6** (Scheme 2). The isolated product **6** has a structure in which a $[Pt(CO)(PPh_3)]$ fragment has been inserted into the strained

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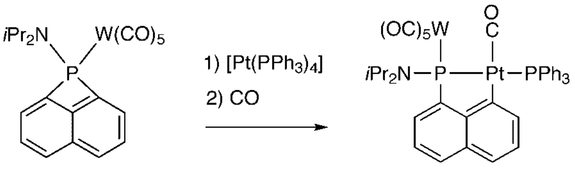
[**] This work was supported by a Grant-in-Aid for Scientific Research (No. 13640560) from the Ministry of Education, Science, Sports, and Culture, Japan. R = Ph, N*i*Pr_2.



5 **6**

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): $\delta = 7.18$ (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); $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, TMS): $\delta = 127.4$, 128.0, 128.5, 132.1, 132.2, 133.6, 138.4, 141.8, 142.0 ppm; $^{31}P\{^1H\}$ NMR (121.45 MHz, $CDCl_3$, H_3PO_4): $\delta = -8.0$ 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 iPr_2NPCl_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): $\delta = 1.18$ (d, ^3J(H,H) = 6.6 Hz, 12H; $CHMe_2$), 3.29 (m, 2H; $CHMe_2$), 7.42 (d, ^3J(H,H) = 6.6 Hz, 2H; naph), 7.52 (m, 2H, naph), 7.70 ppm (d, ^3J(H,H) = 8.2 Hz, 2H; naph); $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, TMS): $\delta = 23.8$, 47.6, 122.5, 123.8, 127.5, 129.4, 147.2 ppm; $^{31}P\{^1H\}$ NMR (121.45 MHz, $CDCl_3$, H_3PO_4): $\delta = -8.4$ ppm.

6: **5** (764 mg, 1.31 mmol), which was prepared from the reaction of **4** and $[W(CO)_5(thf)]$, was treated with $[Pt(PPh_3)_4]$ (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): $\delta = 1.20$ (d, ^3J(H,H) = 6.6 Hz, 6H; $CHMe_2$), 1.35 (d, ^3J(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); $^{13}C\{^1H\}$ NMR (125.4 MHz, $CDCl_3$, TMS): $\delta = 181.2$ (PtCO), 198.3 (*cis* WCO), 201.7 ppm (*trans* WCO); $^{31}P\{^1H\}$ NMR (121.45 MHz, $CDCl_3$, H_3PO_4): $\delta = 22.3$ (d, ^2J(P,P) = 225 Hz, ^1J(P,Pt) = 1736 Hz; PPh_3), 75.2 ppm (d, ^2J(P,P) = 225 Hz, ^1J(P,Pt) = 1706 Hz, ^1J(P,W) = 227 Hz).

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[8] Crystal data for **3**:[14] colorless crystal (0.50 × 0.15 × 0.10 mm), monoclinic, $P2_1/c$, $a = 15.8680(8)$, $b = 5.7220(1)$, $c = 19.631(1)$ Å, $\beta = 100.087(2)°$, $V = 1754.1(1)$ Å^3, $\rho_{calcd} = 1.296\ g\,cm^{-1}$, $2\theta_{max} = 55°$, $Mo_{K\alpha}(\lambda = 0.71609$ Å$)$, $T = 295$ K, 4217 reflections measured, 3824 independent reflections, 3642 ($I/\sigma(I) > 0.0$) reflections used, $\mu(Mo_{K\alpha}) = 2.47\ cm^{-1}$, 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 × 0.40 × 0.25 mm), monoclinic, $P2_1/c$, $a = 7.674(7)$, $b = 14.559(5)$, $c = 13.880(5)$ Å, $\beta = 101.15(6)°$, $V = 1521(1)$ Å^3, $\rho_{calcd} = 1.123\ g\,cm^{-1}$, $2\theta_{max} = 55°$, $Mo_{K\alpha}(\lambda = 0.71609$ Å$)$, ω-2θ scan mode, $T = 295$ K, 3954 reflections measured, 3489 independent reflections, 1458 ($I/\sigma(I) > 0.0$) reflections used, $\mu(Mo_{K\alpha}) = 1.64\ cm^{-1}$, 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**

Patrick Michel and Steven V. Ley*

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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