

Supporting Information

Phosphorus Peri-bridged Acenaphthenes: Efficient Syntheses, Characterisation and Quaternization Reactions

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Experimental

General procedure for the synthesis of compounds **3** and **4**: 5,6-Dibromoacenaphthene^[1] (1.56 g, 5.0 mmol) was dispersed in thf (20 mL) and cooled to -78 °C. At this temperature nBuLi (2M solution in hexanes, 2.5 mL, 5.0 mmol) was added dropwise and then the mixture was stirred for additional 2h at low temperature during which time the solid dissolved totally and the formation of a dark yellow solution was observed. The cold solution was then transferred using cannula to the cooled (-78 °C) solution of appropriate dichlorophosphine (5.0 mmol) in thf (20 mL) and the mixture was stirred overnight. The next day the thf was evaporated in vacuo and replaced with diethyl ether. The precipitated lithium chloride was filtered off and the solvent was removed in vacuo to yield a yellow solid which was used in the next step without further purification. **3**: ³¹P{¹H} nmr (121.5 MHz, CDCl₃, H₃PO₄): δ_P = 88.5 (s); **4**: ³¹P{¹H} nmr (121.5 MHz, CDCl₃, H₃PO₄) δ_P = 107.7 (s).

5: A solution of **3** (1.09 g, 2.0 mmol) in thf (20 mL) was cooled to -78 °C and MeLi (1.25 mL of 1.6M solution in hexanes, 2.0 mmol) was added dropwise. The reaction mixture was left to warm to room temperature and was stirred overnight. The thf was replaced with diethyl ether, the precipitated lithium chloride was filtered off, and the volatiles were evaporated in vacuo to give 0.72 g (84%) of pure **5** as a slightly yellow solid, m. p. 178-182 °C (with decomp.) (Found C, 83.64; H, 9.11. C₃₀H₃₇P requires C, 84.07; H, 8.70%); δ_H (300.1 MHz, CDCl₃, TMS) 1.13 (s, 9H, p-tBu), 1.57 (m, 18H, o-tBu), 3.23 (m, 4H, 2×CH₂), 7.09-7.13 (m, 4H, 4×H arom.), 7.42 (d, ³J=6.8 Hz, 2H, H(2) and H(7) on acenaphthene); δ_C (75.5 MHz, CDCl₃, TMS) 31.6 (s, p-tBu), 32.7 (s, 2×CH₂), 34.2 (d, ⁴J_{CP} = 10.0 Hz, 6×CH₃ of o-tBu), 34.7 (s, q at p-tBu), 39.8 (d, ³J_{CP} = 2.7 Hz, 2×q at o-tBu), 122.8 (s, C(3) and C(6) on acenaphthene), 123.6 (s, CH on Mes*), 128.0 (s, C(2) and C(7) on acenaphthene), 132.8 (s, q), 133.7 (s, q), 135.8 (d, J_{CP} = 3.0 Hz, q), 140.2 (d, J_{PC} = 19.5 Hz, q), 145.4 (s, q), 148.0 (s, q), 152.0 (d, J_{CP} = 5.70 Hz, q); δ_P (121.5 MHz, CDCl₃, H₃PO₄) 134.1 (s); m/z (EI+) 428.3 (M⁺).

6: A solution of **4** (0.96 g, 2.80 mmol) in thf (40 mL) was cooled to -100 °C (internal temperature control). At this temperature a pentane solution of t-BuLi (1.75 mL of 1.6M solution, 2.80 mmol) was added dropwise, taking care that the temperature did not increased above -100 °C. The reaction mixture was left to warm up to room temperature and was stirred overnight. Thf was replaced with diethyl ether (80 mL), the precipitated lithium chloride was filtered off and the volatiles were evaporated in vacuo to give **6** (0.52 g, 80 %) as a yellow solid (Found C, 78.42; H, 6.78.^[2] C₁₆H₁₇P requires C, 79.98; H, 7.13%); δ_H (300.1 MHz, CDCl₃, TMS) = 1.10 (d, ³J_{PH} = 13.5 Hz, 9H, tBu), 3.32 (s, 4H, 2×CH₂), 7.14 (m, 2H, H(3) and H(6)), 7.22 (d, ³J_{HH} = 6.6 Hz, 2H, H(2) and H(7)); δ_C (75.5 MHz, CDCl₃, TMS) 26.3 (d, ²J_{CP} = 15.4 Hz, CH₃ in tBu), 29.2 (d, ¹J_{CP} = 6.7 Hz, q in tBu), 31.6 (s, 2×CH₂), 121.4 (d, ³J_{CP} = 1.47 Hz, C(3) and C(6) in acenaphthene), 124.4 (s, C(2) and C(7) in acenaphthene), 131.9 (d, J_{CP} = 22.0 Hz, q), 142.8 (s, C(4) and C(5) in acenaphthene), 145.0 (d, J_{CP} = 15.2 Hz, q), 146.6 (d, J_{CP} = 8.5 Hz, q); δ_P (121.5 MHz, CDCl₃, H₃PO₄) 150.8 (s); m/z (CI+) 240.1 (M⁺).

8: MeI (0.22 mL, 3.5 mmol) was added dropwise to a solution of **5** (0.43 g, 1 mmol) in thf (20 mL) and the mixture was stirred overnight. The precipitate was filtered off, washed with thf (5 mL) and dried in vacuo to give **8** (0.37 g, 65%) as a yellow powder (Found C, 64.54; H, 7.37. C₃₁H₄₀IP requires C, 65.26; H, 7.07 %);³ δ_H (300.1 MHz, CDCl₃, TMS) 1.18 (s, 9H, p-tBu), 1.70 (s, 18H, 2×o-tBu), 3.26 (d, ²J_{HP} = 3.2 Hz, 3H, CH₃), 3.49 (m, 4H, 2×CH₂), 7.43 (d, ⁴J_{HP} = 5.2 Hz, 2H, 2× m-CH), 7.52 (m, 2H), 7.84 (m, 2H); δ_C (75.5 MHz, CDCl₃, TMS) 23.9 (d, ¹J_{CP} = 29.3 Hz, CH₃), 31.1 (s, p-tBu), 33.6 (s, 2×CH₂), 34.2 (s, 2×o-tBu), 35.4 (s, q in p-tBu), 40.5 (d, ³J_{CP} = 3.3 Hz, 2×q in o-tBu), 125.9 (d, ³J_{CP} = 13.8 Hz, C(3) and C(6) in acenaphthene), 127.0 (d, ³J_{CP} = 13.2 Hz, 2× m-CH), 128.5 (s, q), 129.7 (s, C(2) and C(7) in acenaphthene), 129.8 (s, q), 138.0 (d, J_{CP} = 18.8, q), 147.7 (d, J_{CP} = 4.3 Hz, q), 152.2 (d, J_{CP} = 3.5 Hz, q), 156.7 (d, J_{CP} = 4.1 Hz, q), 158.2 (d, J_{CP} = 8.8 Hz, q); δ_P (121.5 MHz, CDCl₃, H₃PO₄) 95.4 (s); m/z (ES+) 475.3 (M+MeOH).

9: BH₃·Me₂S (2.52 mL of 1M solution in dichloromethane, 2.52 mmol) was added dropwise to a solution of **6** (0.55g, 2.29 mmol) in CH₂Cl₂ (15mL) at -78 °C. The mixture was allowed to warm to room temperature and stirred overnight. Volatiles were evaporated in vacuo and the residue was purified by column chromatography (silica gel, elution with dichloromethane:hexane, 2:3). Yield 0.25 g (43%) of **9** as a colorless, air stable solid (m. p. 175-177 °C) (Found C, 74.78; H, 8.68. C₁₆H₂₀BP

requires C, 75.62; H, 7.93); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc) 2969m, 2948m, 2924m, 2386s, 2344s, 1120s, 1049s, 845s; δ_{H} (300.1 MHz, CDCl_3 , TMS) 1.18 (br s, 3H, BH_3), 1.20 (d, $^3J_{\text{HP}} = 15.7\text{ Hz}$, 9H, tBu), 3.38 (m, 4H, $2\times\text{CH}_2$), 7.26 (m, 2H), 7.38 (m, 2H); ^{11}B nmr (128.4 MHz, CDCl_3 , NaBH_4): $\delta = -38.5$ (d, $^1J_{\text{BP}} = 89.3\text{ Hz}$); δ_{C} (75.5 MHz, CDCl_3 , TMS) 26.0 (d, $^2J_{\text{CP}} = 4.5\text{ Hz}$, CH_3 in tBu), 33.4 (s, $2\times\text{CH}_2$), 33.7 (d, $J_{\text{CP}} = 14.3\text{ Hz}$, q), 129.9 (d, $J_{\text{PC}} = 9.2\text{ Hz}$, $2\times\text{CH}$), 126.6 (s, $2\times\text{CH}$), 129.5 (d, $^1J_{\text{CP}} = 51.9\text{ Hz}$, q), 135.3 (d, $J_{\text{CP}} = 9.4\text{ Hz}$, q), 147.0 (d, $J_{\text{CP}} = 2.31\text{ Hz}$, q), 147.4 (d, $J_{\text{CP}} = 7.9\text{ Hz}$, q); δ_{P} (121.5 MHz, CDCl_3 , H_3PO_4): 157.7 (br m); m/z (ES+) 277.1 (M+Na).

X-ray Crystallography. Data for **8** and **9** were collected using the St Andrews Robotic diffractometer (Saturn724 CCD) at 125 K with graphite monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$).⁴ Data for **5** were collected using a Rigaku (Saturn92 CCD) at 173 K with Cu-K α radiation ($\lambda = 1.54178\text{ \AA}$), using copper rotating anode, obtaining as complete a dataset as could be collected.⁴ All intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXL).⁵ Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries.

References

- ¹ W. D. Neudorff, D. Lentz, M. Anibarro and A. D. Schlüter, *Chem. Eur. J.*, 2003, **9**, 2745-2757.
- ² Compound **6** decomposes slowly in solution at room temperature, attempts to purify it by recrystallization from variety of organic solvents (including alkane solvents) resulted in partial decomposition.
- ³ The sample was slightly contaminated with co-crystallized CDCl_3 solvent.
- ⁴ a) Rigaku (2006). Crystal Structure, Version 3.8. Single Crystal Structure Analysis Software. Rigaku/MS, 9009 TX, USA 77381-5209. Rigaku, Tokyo 196-8666, Japan; b) Rigaku (2004). CrystalClear. Version 1.36. Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan; c) Rigaku (2006) SCXmini Benchtop Crystallography System software 1.0; Rigaku Americas Corp: 9009 New Trails Drive, The Woodlands, TX 77381-5209 USA.
- ⁵ G. M. Sheldrick (2008). SHELXL97. *Acta Cryst. A* 64, 112-122.