Supporting Information
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Phosphorus-Substituted Azulenes Accessed via Direct Hafner Reaction of a Phosphino Cyclopentadiene

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ELECTRONIC SUPPLEMENTARY INFORMATION
Diphenyl(4,6,8-trimethylazulen-2-yl)phosphine 6

The preparation of this compound was based on a method by Hansen.\(^1\) At 0 °C, to a stirred suspension of 2,4,6-trimethylpyrylium tetrafluoroborate 5 (300 mg, 1.42 mmol, 1.00 eq.) in THF (10 mL) was added by cannula lithium (diphenylphosphino)cyclopentadienide 4 (732 mg, 2.84 mmol, 2.00 eq.) in THF (10 mL), forming a deep blue/violet mixture, which was allowed to stir for 40 h before filtering through a silica plug, under atmosphere of argon. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatography (0→4% EtOAc in petroleum ether) and recrystallisation (EtOH) to give diphenyl(4,6,8-trimethylazulen-2-yl)phosphine 6 (15 mg, 0.0423 mmol, 3.0%) as purple plates (m.p. 135-137 °C); \(R_y\) 0.45 (9:1 petroleum ether/EtOAc); \(\delta_H\) (300 MHz, CDCl\(_3\)) 7.47-7.41 (4H, m, 14-CH), 7.35-7.32 (6H, m, 15,16-CH), 7.20 (2H, d, \(^3J_{PH}\) 3.1 Hz, 1,3-CH), 7.03 (2H, s, \(J_{5,7-CH}\), 2.75 (6H, s, 9,11-CH\(_3\)), 2.60 (3H, s, 10-CH\(_3\)); \(\delta_P\) (122 MHz, CDCl\(_3\)) –14.92 (12-P); \(v_{\text{max}}\) (film) 3051, 2980, 2967, 2926, 1578, 1537, 1466, 1433, 1372, 1333, 1291, 1217, 1185, 1141, 1109, 1084, 1023, 997, 909, 847, 806, 745, 721, 694, 627 cm\(^{-1}\); HRMS (ESI+) \(m/z\) calc for [C\(_{25}\)H\(_{23}\)P + H]\(^+\), 355.1616; found, 355.1631. A \(^{13}\)C-NMR spectrum could not be obtained due to instability of 6 with respect to oxidation.
Diphenyl(4,6,8-trimethylazulen-2-yl)phosphine oxide 7

The preparation of this compound was based on a method by Hansen. At 0 °C, to a stirred solution of 2,4,6-trimethylpyrylium tetrafluoroborate 5 (2.36 g, 11.2 mmol, 1.00 eq.) in THF (40 mL) was added by cannula a solution of lithium (diphenylphosphino)cyclopentadienide 4 (5.76 g, 22.5 mmol, 2.00 eq.) in THF (40 mL). After stirring for 1 h, under an atmosphere of argon, the solution was filtered through a pad of silica, washing through with ethyl acetate (40 mL), and was concentrated under reduced pressure to give the crude diphenyl(4,6,8-trimethylazulen-2-yl)phosphine 6, which on this scale could not be completely purified by column chromatography (0→2% EtOAc in petroleum ether) or recrystallisation (EtOH). Thus, at 0 °C, to a stirred solution of the impure diphenyl(4,6,8-trimethylazulen-2-yl)phosphine 6 (1.06 g, <2.98 mmol, 1.00 eq.) in THF (10 mL) was added hydrogen peroxide solution (35% wt. in H2O, 0.350 mL, 3.57 mmol, 1.20 eq.), and allowed to stir for 25 min, before the addition of Na2S2O3(aq) (10 wt. %, 10 mL) to quench excess hydrogen peroxide. The aqueous solution was extracted with CHCl3 (2 × 10 mL), and the combined organic extracts were dried over anhydrous MgSO4, and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatography (50→100% EtOAc in petroleum ether) and recrystallisation (4:1 THF/hexane) to give diphenyl(4,6,8-trimethylazulen-2-yl)phosphine oxide 7 (54 mg, 0.145 mmol, 1.3%) as purple plates (m.p. 181-183 °C); Rf 0.20 (EtOAc); δH (300 MHz, CDCl3) 7.81-7.73 (4H, m, 14-CH), 7.56-7.41 (6H, m,
15,16-CH), 7.54 (2H, d, $^3J_{Ph}$ 5.5 Hz, 1,3-CH), 7.11 (2H, s, 5,7-CH), 2.82 (6H, s, 9,11-CH$_3$), 2.63 (3H, s, 10-CH$_3$); $\delta$ C (75 MHz, CDCl$_3$) 150.1 (6-C), 149.2 (4,8-C), 136.3 (d, $^3J_{CP}$ 14.0 Hz, 3a,8a-C), 134.3 (d, $^1J_{CP}$ 110.2 Hz, 2-C), 133.7 (d, $^1J_{CP}$ 105.0 Hz, 13-C), 131.9 (d, $^2J_{CP}$ 10.2 Hz, 14-C), 131.6 (d, $^4J_{CP}$ 2.8 Hz, 16-C), 128.3 (5,7-C), 128.3 (d, $^3J_{CP}$ 12.3 Hz, 15-C), 120.2 (d, $^2J_{CP}$ 12.1 Hz, 1,3-C), 29.0 (10-C), 25.2 (9,11-C); $\delta$ P (122 MHz, CDCl$_3$) 26.3 (12-P); $\nu_{max}$(film) 3054, 2918, 2855, 1578, 1537, 1481, 1467, 1435, 1368, 1335, 1292, 1219, 1182, 1159, 1141, 1098, 1084, 1072, 1024, 940, 911, 845, 805, 745, 720, 694 cm$^{-1}$; HRMS (ESI+) m/z calc for [C$_{25}$H$_{23}$OP + H]$^+$, 371.1564; found, 371.1575.
Boranyldiphenyl(4,6,8-trimethylazulen-2-yl)phosphine 8

The preparation of this compound was based on a method by Hansen. At 0 °C, to a suspension of 2,4,6-trimethylpyrylium tetrafluoroborate 5 (1.10 g, 5.23 mmol, 1.00 eq.) in THF (30 mL) was added a solution of lithium (diphenylphosphino)cyclopentadienide 4 (2.68 g, 10.5 mmol, 2.00 eq.) in THF (30 mL). After stirring at 0 °C for 1 h, the mixture was filtered through a pad of neutral alumina under atmosphere of argon. To the stirred filtrate, at r.t., was slowly added a solution of borane-THF complex (11.0 mL, 1.0 M in THF, 2.10 eq.). After stirring for 16 h, the reaction was quenched by the addition of methanol (10 mL). The solution was then concentrated under reduced pressure to a small volume, and added to ethyl acetate (60 mL). The solution was washed with water (3 × 50 mL) and with saturated brine, and the organic layer was dried over anhydrous MgSO₄, and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatography (0→10% EtOAc in petroleum ether) to give boranyldiphenyl(4,6,8-trimethylazulen-2-yl)phosphine 8 (228 mg, 0.621 mmol, 12%) as a purple solid (m.p. 148-150 °C); Rₚ 0.53 (3:1 petroleum ether/EtOAc); δH (300 MHz, CDCl₃) 7.73-7.66 (4H, m, 14-CH), 7.51-7.41 (6H, m, 15,16-CH), 7.46 (2H, d, Jₚₕ 5.1 Hz, 1,3-CH), 7.12 (2H, s, 5,7-CH), 2.83 (6H, s, 9,11-CH₃), 2.65 (3H, s, 10-CH₃), 1.44 (3H, br d, 17-BH₃); δC (75 MHz, CDCl₃) 149.7 (6-C), 148.7 (4,8-C), 136.5 (d, Jₚₙ 11.5 Hz, 3a,8a-C), 133.0 (d, Jₚₙ 2.5 Hz, 16-C), 128.5 (d, Jₚₙ 10.2 Hz, 15-
C), 128.3 (d, $^{2}J_{CP}$ 1.2 Hz, 5,7-C), 120.8 (d, $^{2}J_{CP}$ 10.5 Hz, 1,3-C), 29.0 (10-C), 25.2
(9,11-C); δν (122 MHz, CDCl₃) 12.38-11.65 (m, 12-P); δB (96 MHz, CDCl₃) -34.5
(17-B); νmax (film) 3675, 2987, 2971, 2901, 2380 (νBH), 1578, 1537, 1483, 1468, 1435,
1408, 1394, 1377, 1333, 1290, 1218, 1187, 1140, 1102, 1027, 1066, 907, 882, 847,
809, 797, 766, 740, 690 cm⁻¹; HRMS (ESI+) m/z calc for [C₂₅H₂₆BP + Na]⁺,
391.1763; found, 391.1796.
(6-Methoxy-4,8-dimethylazulen-2-yl)diphenylphosphine oxide

The preparation of this compound was based on a method by Hansen. At -5 °C, to a stirred solution of lithium (diphenylphosphino)cyclopentadienide 4 (1.36 g, 5.31 mmol, 4.00 eq.) in THF (5.0 mL) was added portionwise 4-methoxy-2,6-dimethylpyrylium tetrafluoroborate 9 (300 mg, 1.33 mmol, 1.00 eq.), and the mixture was stirred at -5 °C for 20 min, changing in colour to deep purple. The mixture was then stirred at 60 °C for 15 h, and then allowed to cool to r.t., and poured onto crushed ice. The aqueous mixture was extracted with ethyl acetate (2 × 50 mL), and the combined organic extracts were dried over anhydrous MgSO4, and filtered. The filtrate was concentrated under reduced pressure to give crude (6-methoxy-4,8-dimethylazulen-2-yl)diphenylphosphine 10, which could not be completely purified by column chromatography (0→1% EtOAc in petroleum ether). Thus, at r.t., to a stirred solution of the impure (6-methoxy-4,8-dimethylazulen-2-yl)diphenylphosphine 10 (93 mg, <0.251 mmol, 1.00 eq.) in THF (2.0 mL) was added hydrogen peroxide (35 wt. % in H2O, 120 μL, 1.26 mmol, 5.00 eq.), and the mixture was allowed to stir for 2 h. The reaction was quenched by the addition of Na2S2O3(aq) (10 wt. % in H2O, 2.0 mL), and to this was added ethyl acetate (20 mL), and the phases were separated. The
organic layer was washed with water (3 × 10 mL), dried over anhydrous MgSO₄, and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatography (0→2% MeOH in DCM) to give (6-methoxy-4,8-dimethylazulen-2-yl)diphenylphosphine oxide 11 (11 mg, 0.0285 mmol, 2.1% overall) as a red/purple solid (m.p. 180-183 °C); Rf 0.26 (19:1 DCM/MeOH); δH (500 MHz, CDCl₃) 7.79-7.74 (4H, m, 14-CH), 7.53-7.49 (2H, m, 16-CH), 7.50 (2H, d, 3J_H 5.4 Hz, 1,3-CH), 7.46-7.43 (4H, m, 15-CH), 6.79 (2H, s, 5,7-CH), 3.96 (3H, s, 10-CH₃), 2.81 (6H, s, 9,11-CH₃); δC (126 MHz, CDCl₃) 166.9 (6-C), 149.9 (4,8-C), 134.3 (d, 1J_C 104.8 Hz, 13-C), 133.8 (d, 3J_C 14.3 Hz, 3a,8a-C), 131.9 (d, 2J_C 10.4 Hz, 14-C), 131.6 (d, 1J_C 112.2 Hz, 2-C), 131.4 (d, 4J_C 2.8 Hz, 16-C) 128.2 (d, 3J_C 12.0 Hz, 15-C), 121.1 (d, 2J_C 12.3 Hz, 1,3-C), 113.9 (5,7-C), 55.9 (10-C), 25.6 (9,11-C); δP (202 MHz, CDCl₃) 25.1 (12-P); v_max(film) 3071, 2999, 2918, 2850, 1581, 1556, 1526, 1483, 1461, 1454, 1436, 1357, 1337, 1294, 1262, 1217, 1173, 1132, 1113, 1097, 1083, 1062, 1026, 997, 965, 928, 908, 885, 836, 812, 741, 720, 693 cm⁻¹; HRMS (ESI+) m/z calc for [C₂₅H₂₃O₂P + Na]⁺, 409.1328; found, 409.1347.