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Unusual reaction of 8-chloro-2-cyclohexyl-4-phenylbenzo[*e*]-1,2-oxaphosphinine-2-oxide with tetramethylenebis(magnesium bromide)

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Experimental

6-Chloro-2-cyclohexyl-4-phenylbenzo[e]-1,2-oxaphosphinine-2-oxide **2**. A solution of chlorophosphinine oxide **1** (1.83 g, 0.0057 mol) in benzene (15 ml) was added dropwise with stirring to a solution of cyclohexyl-magnesium bromide prepared from Mg (0.17 g, 0.0069 mol) and cyclo-hexyl bromide (0.84 ml, 0.0069 mol) in diethyl ether (30 ml) according to a standard procedure in an argon atmosphere. The reaction mixture was refluxed for 1 h, cooled to 20 °C and treated with water, concentrated hydrochloric acid to pH 4.0, and water again. The diethyl ether extract was evaporated and crystallised from a pentane–dichloromethane mixture. The yield of compound **2** was 2.076 g (98%), mp 153–155 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) d: 7.45 and 7.34 [2br. m, H(10), H(11), H(12)], 7.70 [br. d, H(7), $^3J_{H(8)CCH(7)}$ 8.7 Hz], 7.17 [d, H(8), $^3J_{H(7)CCH(8)}$ 8.7 Hz], 7.15 [br. s, H(5)], 6.16 [d, H(3), $^2J_{PCH}$ 24.9 Hz], 2.04 (m), 1.84 (m), 1.71 (m), 1.64 (m), 1.43 (m), 1.27 (m), 1.22 (m, C_6H_{11}). ^{13}C NMR (150.9 MHz, $CDCl_3$) (hereafter, the multiplicity of the signal in the ^{13}C-{^{1}H} spectrum is given in parentheses) δ_C: 113.69 [dd (d), C(3), $^1J_{HC(3)}$ 162.3 Hz, $^1J_{PC(3)}$ 108.3 Hz], 152.91 [m (s), C(4), $^3J_{HC(5)CC(4)}$ 3.6–4.1 Hz, $^3J_{HC(10)CC(4)}$ 3.6–4.1 Hz], 122.97 [ddd (d), C(4a), $^3J_{PCCC(4a)}$ 13.5 Hz, $^3J_{HC(3)CC(4a)}$ 7.7 Hz, $^3J_{HC(8)CC(4a)}$ 6.0–6.1 Hz], 128.48 [dd (s), C(5), $^1J_{HC(5)}$ 166.3 Hz, $^3J_{HC(7)CC(5)}$ 5.7 Hz], 128.36 [ddd (d), C(6), $^3J_{HC(8)CC(6)}$ 11.7 Hz, $^2J_{HC(5)C(6)}$ 4.1–4.2 Hz, $^2J_{HC(7)C(6)}$ 4.1–4.2 Hz], 130.83 [dm (s), C(7), $^1J_{HC(7)}$ 163.6 Hz, $^3J_{HC(5)CC(7)}$ 6.7 Hz], 120.76 [dd (d), C(8), $^1J_{HC(8)}$ 166.1 Hz, $^3J_{POCC(8)}$ 6.0 Hz], 149.29 [dddd (d), C(8a), $^2J_{POC(8a)}$ 10.1 Hz, $^3J_{HC(5)CC(8a)}$ 10.2 Hz, $^3J_{HC(7)CC(8a)}$ 10.2 Hz, $^2J_{HC(8)C(8a)}$ 4.2 Hz], 138.16 [dtd (d), C(9), $^3J_{PCCC(9)}$ 14.1 Hz, $^3J_{HC(11)CC(9)}$ 7.3 Hz, $^3J_{HC(3)CC(9)}$ 6.5 Hz], 128.20 [dm (d), C(10), $^1J_{HC(10)}$ 163.1 Hz, $^3J_{HCCC(10)}$ 6.7–7.0 Hz, $^3J_{HCCC(10)}$ 6.6–7.0 Hz], 128.63 [dd (s), C(11), $^1J_{HC(11)}$ 161.6 Hz, $^3J_{HC(13)CC(11)}$ 5.6–6.0 Hz], 129.04 [dt (s), C(12), $^1J_{HC(12)}$ 161.3 Hz, $^3J_{HC(10)CC(12)}$ 7.5 Hz], 38.60 [br. dm (d), C(13), $^1J_{HC(3)}$ 124.8 Hz, $^1J_{PC(3)}$ 105.0 Hz], 25.07 [br. tm (d), C(14), $^1J_{HC(14)}$ 128.5 Hz, $^2J_{PCC(14)}$ 3.0 Hz], 24.88 [br. tm (d), C(14), $^1J_{HC(14)}$ 128.5 Hz, $^2J_{PCC(14)}$ 3.3 Hz], 25.83 [br. tm (d), C(15), $^1J_{HC(15)}$ 127.5 Hz, $^3J_{PCCC(15)}$ 15.5 Hz], 25.56 [br. tm (d), C(16), $^1J_{HC(16)}$ 128.0 Hz, $^4J_{PCCCC(16)}$ 1.1 Hz]. ^{31}P-{^{1}H} NMR (36.5 MHz, $CDCl_3$) δ_P: 36.5 (s). MS, *m/z* (the values of *m/z* are given for ions containing the most abundant isotopes): 358 $[M]^{+\cdot}$, 323 [M – Cl], 275 [M – C_6H_{11}], 240 [M – C_6H_{11} – Cl], 228 [M – PO(C_6H_{11})], 193 [M – PO(C_6H_{11}) – Cl], 164 [M – PO(C_6H_{11}) – Cl – CO], 130 [PO(C_6H_{11})], 83 [C_6H_{11}].

2-(5-Chloro-2-hydroxyphenyl)-2-phenylethenylcyclohexylethylphosphine oxide **3**. A solution of compound **2** (2.076 g, 0.00579 mol) in benzene (6 ml) was added to the Grignard reagent obtained from magnesium (0.18 g, 0.0069 mol) and ethyl bromide (0.51 ml, 0.0069 mol) in diethyl ether (30 ml) in an argon atmosphere. The reaction mixture was refluxed for 6 h, cooled to 20 °C and treated with water, hydrochloric acid solution (3 ml in 10 ml of water) to pH 4.0 and water. The white precipitate that formed was filtered off and dried *in vacuo* (12 Torr, 100 °C). The yield of compound **3** was 2.16 g (96%), mp 85–87 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ: 1.12 (dt, 3H, Me, $^3J_{PCCH}$ 17.3 Hz, $^3J_{HCCH}$ 7.4 Hz), 1.21, 1.26, 1.35, 1.68–1.71, 1.83 and 1.93 (6m, 13H, C_6H_{11}, PCH_2), 6.30 [d, 1H, H(3), $^2J_{PCH}$ 18.8 Hz], 6.89 [d, 1H, H(5), $^4J_{H(7)CCCH(5)}$ 2.4 Hz], 7.17 [m, 1H, H(8), A part of AB spectrum, $^3J_{H(7)CCH(8)}$ 8.7 Hz], 7.20 [m, 1H, H(7), B part of AB spectrum, $^3J_{H(8)CCH(7)}$ 8.7 Hz, $^4J_{H(5)CCCH(7)}$ 2.4 Hz], 7.27 [m, 2H, H(9)], 7.32 [m, 2H, H(10), $^3J_{HCCH}$ 7.0–7.7 Hz], 7.36 [m, 1H, H(11), $^3J_{HCCH}$ 7.0–7.4 Hz], 7.78 (br. s, 1H, OH). ^{13}C NMR (150.9 MHz, $CDCl_3$) δ_C: 118.65 [br. dd (br. d), C(3), $^1J_{HC(3)}$ 152.5 Hz, $^1J_{PC(3)}$ 98.0–100.0 Hz], 157.92 [m (br. s), C(4)], 131.44 [m (br. d), C(4a), $^3J_{PCCC(4a)}$ 5.0–6.0 Hz], 129.51 [br. dd (s), C(5), $^1J_{HC(5)}$ 164.5–165.5 Hz, $^3J_{HC(7)CC(5)}$ 5.0–6.0 Hz], 125.48 [br. d (s), C(6), $^3J_{HC(8)CC(6)}$ 9.7 Hz], 129.51 [br. dd (s), C(7), $^1J_{HC(7)}$ 164.5–165.5 Hz, $^3J_{HC(5)CC(7)}$ 5.0–6.0 Hz], 123.15 [d (s), C(8), $^1J_{HC(8)}$ 162.8 Hz], 153.47 [dd (s), C(8a), $^3J_{HCCC(8a)}$ 7.2 Hz, $^3J_{HCCC(8a)}$ 6.2 Hz], 140.63 [br. m (br. d), C(9), $^3J_{PCCC(9)}$ 14.0 Hz], 127.54 [br. dm (s), C(10), $^1J_{HC(10)}$ 160.2 Hz, $^3J_{HCCC(10)}$ 6.6–7.0 Hz, $^3J_{HCCC(10)}$ 6.6–7.0 Hz], 128.56 [dd (s), C(11), $^1J_{HC(11)}$ 160.7 Hz, $^3J_{HC(13)CC(11)}$ 6.6 Hz], 129.76 [br. dm (s), C(12), $^1J_{HC}$(12) 160.0–161.0 Hz, $^3J_{HC(10)CC(12)}$ 6.6–7.0 Hz], 37.37 [br. ddm (br. d), C(13), $^1J_{HC(3)}$ 129.2 Hz, $^1J_{PC(3)}$ 81.7–82.0 Hz], 24.66 [br. tm (s), C(14), $^1J_{HC(14)}$ 128.6–129.0 Hz], 25.06 [br. tm (s), C(14), $^1J_{HC(14)}$ 128.6–129.0 Hz], 26.24 [br. tm (br. d), C(15), $^1J_{HC(15)}$ 126.5–127.5 Hz, $^3J_{PCCC(15)}$ 12.0 Hz], 25.76 [br. tm (s), C(16), $^1J_{HC(16)}$ 127.8–128.0 Hz], 129.88 [br. dm (br. d), C(17), $^1J_{PC(17)}$ 99.0–101.0 Hz], 130.76 [dm (d), C(18), $^1J_{HC(18)}$ 159.0–160.0 Hz, $^2J_{PCC(18)}$ 6.7–7.0 Hz, $^3J_{HCCC(18)}$ 6.6–7.0 Hz, $^3J_{HCCC(18)}$ 6.6–7.0 Hz], 128.13 [ddm (d), C(19), $^1J_{HC(19)}$ 160.0–161.0 Hz, $^3J_{PCCC(19)}$ 11.0 Hz, $^3J_{HCCC(19)}$ 7.0–7.3 Hz], 131.52 [br. dm (s), C(20), $^1J_{HC(20)}$ 159.5 Hz, $^3J_{HCCC(20)}$ 7.0 Hz]. ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$) δ_P: 50.5 (s). IR (ν/cm^{-1}): 536, 634, 695, 724, 768, 823, 889, 942, 1004, 1030, 1111, 1214, 1280, 1377, 1410, 1462, 1494, 1571, 1588, 2595, 2721, 2854, 2924, 3374. MS, *m*/*z*: 388 $[M]^+\cdot$, 371 $[M - OH]^+$, 353 $[M - Cl]^+$, 305 $[M - C_6H_{11}]^+$, 306 $[M - C_6H_{10}]^+$, 289 $[M - C_6H_{11} - OH]^+$, 359 $[M - C_2H_5]^+$, 229 $[M - POEt(C_6H_{11})]^+$, 228 $[M - POEt(C_6H_{11}) - H]^+$, 194 $[M - Cl - POEt(C_6H_{11})]^+$, 166 [M – – Cl – $POEt(C_6H_{11}) - CO]^+$, 158 $[POEt(C_6H_{11})]^+$, 159 $[HPOEt(C_6H_{11})]^+$, 160 $[HPOEt(C_6H_{11})H]^+$, 83 $[C_6H_{11}]^+$. Found (%): C, 67.95; H, 6.74; Cl, 9.12; P, 7.97. Calc. for $C_{22}H_{26}PO_2Cl$ (%): C, 67.95; H, 6.69; Cl, 9.14; P, 7.98.

2-(5-Chloro-2-hydroxyphenyl)-2-phenylethenylcyclohexylphenylphosphine oxide **4**. A solution of compound **2** (3.59 g, 0.01 mol) in benzene (10 ml) was added to the Grignard reagent obtained from magnesium (0.34 g, 0.0142 mol) and bromobenzene (1.49 ml, 0.0142 mol) in diethyl ether (20 ml) in an argon atmosphere. The reaction mixture was refluxed for 6 h, cooled to 20 °C and treated with water, hydrochloric acid solution (3 ml in 10 ml of water) to pH 4.0 and water. The white precipitate that formed was filtered off and dried *in vacuo* (12 Torr, 100 °C). The yield of com-pound **4** was 3.6 g (82.5%), mp 196–198 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ: 7.44 [m, H(12)], 7.30–7.35 [m, H(9)–H(11), H(18), H(19)], 6.99 and 7.01 [2m, H(7), H(8), AB spectrum, $^2J_{H(A)CCH(B)}$ 8.7 Hz], 6.83 [br. d, PCH(3), $^2J_{PCH(3)}$ 20.2 Hz], 6.32 [br. s, H(5)], 2.13 (br. m, PCH), 1.19, 1.30, 1.70, 1.78, 1.88 (5br. m, 10H, C_6H_{11}). ^{31}P-{^{1}H} NMR (162.0 MHz, [$^2H_6$]DMSO) δ_P: 29.4 (s). IR (ν/cm^{-1}): 505, 527, 553, 591, 631, 689, 665, 694, 736, 768, 808, 833, 852, 888, 917, 999, 1030, 1073, 1112, 1173, 1216, 1259, 1288, 1377, 1417, 1461, 1497, 1561, 1586, 2728, 2854, 2922, 3056, 3386. MS, *m*/*z*: 436 $[M]^+\cdot$, 419 $[M - OH]^+$, 401 $[M - Cl]^+$, 353 $[M - C_6H_{11}]^+$, 229 $[M - POPh(C_6H_{11})]^+$, 228 $[M - POPh(C_6H_{11}) - H]^+$, 208 $[POPh(C_6H_{11})]^+$, 83 $[C_6H_{11}]^+$. Found (%): C, 71.60; H, 7.03; P, 7.65. Calc. for $C_{26}H_{26}ClO_2P$ (%): C, 71.48; H, 7.00; P, 7.10.

For **9**: ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C: 116.84 [dd (d), C(3), $^1J_{HC(3)}$ 164.6 Hz, $^1J_{PC(3)}$ 155.3 Hz], 154.75 [m (d), C(4), $^2J_{PCC(4)}$ 4.2 Hz], 123.96 [ddd (d), C(4a), $^3J_{PCCC(4a)}$ 12.2 Hz, $^3J_{HC(3)CC(4a)}$ 7.6 Hz, $^3J_{HC(9)CC(4a)}$ 6.1–6.2 Hz], 128.23 [dd (s), C(5), $^1J_{HC(5)}$ 164.3 Hz, $^3J_{HC(7)CC(5)}$ 5.7 Hz], 124.53 [br. ddd (d), C(6), $^3J_{HC(8)CC(6)}$ 11.6 Hz, $^2J_{HC(5)C(6)}$ 4.1–4.2 Hz, $^2J_{HC(7)C(6)}$ 4.1–4.2 Hz, $^5J_{POCCCC(6)}$ 0.7 Hz], 130.71 [dd (s), C(7), $^1J_{HC(7)}$ 164.5 Hz, $^3J_{HC(5)CC(7)}$ 6.4 Hz], 120.81 [d (s), C(8), $^1J_{HC(8)}$ 161.8 Hz], 156.24 [dddd (d), C(8a), $^2J_{POC(8a)}$ 8.8 Hz, $^3J_{HC(5)CC(8a)}$ 8.6–8.8 Hz, $^3J_{HC(7)CC(8a)}$ 8.6–8.8 Hz, $^2J_{HC(8)C(8a)}$ 3.0 Hz], 139.79 [dtd (d), C(9), $^3J_{PCCC(9)}$ 19.7 Hz, $^3J_{HC(11)CC(9)}$ 7.4 Hz, $^3J_{HC(3)CC(9)}$ 6.4 Hz], 128.88 [dm (d), C(10), $^1J_{HC(10)}$ 159.1 Hz, $^3J_{HCCC(10)}$ 7.8–7.9 Hz, $^3J_{HCCC(10)}$ 5.8–5.9 Hz], 128.50 [ddd (s), C(11), $^1J_{HC(11)}$ 159.8 Hz, $^3J_{HC(13)CC(11)}$) 6.9–7.0 Hz, $^2J_{HCC(11)}$ 1.5 Hz], 128.84 [dt (s), C(12), $^1J_{HC(12)}$ 161.0 Hz, $^3J_{HC(10)CC(12)}$ 7.3 Hz], 47.25 [br. ddm (d), C(13), $^1J_{HC(3)}$ 130.0 Hz, $^1J_{PC(3)}$ 129.5 Hz], 28.83 [br. tm (d), C(14), $^1J_{HC(14)}$ 130.6 Hz, $^2J_{PCC(14)}$ 3.9 Hz], 28.35 [br. tm (d), C(14), $^1J_{HC(14)}$ 130.5 Hz, $^2J_{PCC(14)}$ 4.1 Hz], 26.95 [br. tm (d), C(15), $^1J_{HC(15)}$ 130.0 Hz, $^3J_{PCCC(15)}$ 19.4 Hz], 26.87 [br. tm (d), C(15), $^1J_{HC(15)}$ 130.0 Hz, $^3J_{PCCC(15)}$ 19.6 Hz], 26.38 [br. tm (d), C(16), $^1J_{HC(16)}$ 127.0 Hz, $^4J_{PCCCC(16)}$ 2.0 Hz]. IR (ν/cm^{-1}): 3059, 3028, 1959, 1877, 1808, 1763, 1574, 1545, 1464, 1377, 1343, 1275, 1244 (sh.), 1221, 1177, 1152, 1116, 1088, 1076, 1029, 1010, 954, 919, 891, 863, 835, 824, 777, 765, 743, 700, 677, 589, 562, 533, 501, 478, 432. MS, *m*/*z*: 570 $[M]^{+\cdot}$, 535 $[M - Cl]^+$, 488 $[M - C_6H_{10}]^+$, 487 $[M - C_6H_{11}]^+$, 453 $[M - Cl - C_6H_{10}]^+$, 452 $[M - Cl - C_6H_{11}]^+$, 418 $[M - 2Cl - C_6H_{10}]^+$, 417 $[M - 2Cl - C_6H_{11}]^+$, 343 $[M - C_6H_{10} - 2Cl - C_6H_3]^+$, 342 $[M - C_6H_{11} - 2Cl - C_6H_3]^+$, 260 $[C_{14}H_{10}OPCl]^+$, 259 $[C_{14}H_9OPCl]^+$, 228 $[C_{14}H_9OCl]^+$.