Supporting Information

Double [3+2]-dimerisation cascade synthesis of bis(triazolyl)diphosphanes, a new scaffold for bidentate diphosphanes

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VI.1. 4,4′-BIS(DIPHENYLPHOSPHINOXY)-1,1′-DIBENZYL-5,5′-BIS-1,2,3-TRIAZOLE 11.1 26
I. General information

All reactions were carried out under an argon or nitrogen atmosphere using standard Schlenk techniques otherwise stated. Solvents were carefully dried by conventional or were purified with an MBRAUN Solvent Purification System. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded with a Bruker Avance 500 FT-NMR or a Bruker Avance 400 spectrometer. The resonances were calibrated relative to the residual solvent peaks and are reported with positive values downfield from TMS. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. For all characterized compounds, the peak assignments in the $^1$H and $^{13}$C NMR spectra were based on COSY, HSQC and HMBC 2D experiments. HRMS were obtained from dichloromethane solutions with a Xevo G2 Q TOF spectrometer by the electrospray method or with a LC-TOF spectrometer (Micromass).

II. Synthesis of bistriazolyl phosphane oxides 8.1-8.7

II.1. General procedure

In a round bottom flask, ethynyldiphenylphosphane oxide (250 mg, 1.1 mmol) was dissolved in acetonitrile (3 mL). Then the corresponding azide (3.3 mmol) and aqueous cesium carbonate solution at 2 mol.L$^{-1}$ (1.65 mL) were added followed by copper bromide (158 mg, 1 mmol). The resulting mixture was stirred at room temperature in an open vessel for 12 hours. After complete reaction as monitored by TLC, the solvent was removed under reduced pressure and the residue was dissolved in dichloromethane, washed with aqueous ammonia solution (10%, 3 x 10mL), brine, then dried over magnesium sulfate and the solvent was evaporated under reduced pressure. The product was isolated as specified below.

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II.2. 4,4'-bis(diphenylphosphonyl)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole dioxide, 8.1

The compound was isolated as a white solid after recrystallization from ethanol; Yield : 49%; $^1$H NMR (400,13 MHz, CDCl$_3$) δ 8.13 - 7.97 (m, 4H), 7.65 - 7.41 (m, 10H), 7.39 - 7.08 (m, 12H), 6.91 - 6.77 (m, 4H), 5.51 (d, J = 14.7 Hz, 2H), 4.70 (d, J = 14.7 Hz, 2H); $^{13}$C NMR (100,61 MHz, CDCl$_3$) δ 141.18 (d, J = 10.4 Hz), 132.88 (s), 132.36 (d, J = 2.8 Hz), 132.04 (d, J = 2.8 Hz), 131.65 (d, J = 10.0 Hz), 131.39 (dd, J = 55.3 Hz, J = 109.07 Hz), 131.23 (d, J = 10.9 Hz), 130.85 (d, J = 241.7 Hz), 128.92(s), 128.83 (s), 128.62 (d, J = 12.6 Hz), 128.54 (d, J = 12.8 Hz), 128.15 (s), 53.13 (s); $^{31}$P NMR (161.97 MHz, CDCl$_3$) δ 16.80 (s); HRMS (EI): m/z Calcd. for C$_{65}$H$_{68}$N$_2$O$_2$P$_2$ [M+H]$^+$/2:717.22; Found: 717.2306; mp : 224.5-227.4°C.

II.3. 4,4'-bis(diphenylphosphonyl)-1,1'-dibutyl-5,5'-bis-1,2,3-triazole dioxide, 8.2

The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); Yield : 42%; $^1$H NMR (400,13 MHz, CDCl$_3$) δ 7.96 (dd, J = 7.6 Hz, J = 12.1 Hz, 4H), 7.61 - 7.35(m, 10H), 7.33 - 7.21 (m, 2H), 7.20 - 7.08 (m, 4H), 4.23 - 4.40 (m, 2H), 4.13 - 4.01 (m, 2H), 1.92-1.78(m, 2H), 1.77 - 1.64 (m, 2H), 1.22 - 1.08 (m, 4H), 0.78 (t, J = 7.4 Hz, 6H); $^{13}$C NMR (100,61 MHz, CDCl$_3$) δ 140.82 (d, J = 130,0 Hz), 133.27 (d, J = 2.7 Hz), 131.98 (d, J = 2.7 Hz), 131.66 (d, J = 10,0 Hz), 131.57 (dd, J = 29 Hz, J = 110.3 Hz), 131.27 (d, J = 10.9 Hz), 130.42 (d, J = 21.9 Hz), 129.57 (d, J = 12.7 Hz), 129.47 (d, J = 13,0 Hz), 49.40 (s), 30.17 (s), 19.84 (s), 13.31 (s); $^{31}$P NMR (161.97 MHz, CDCl$_3$) δ 15.6,5 (s); HRMS (EI): m/z Calcd. for C$_{38}$H$_{38}$N$_2$O$_2$P$_2$ [M+H]$^+$/3:469.25; Found: 469.2607; mp : 172.2-172.7°C.

II.4. 4,4'-bis(diphenylphosphonyl)-1,1'-diisobutyl-5,5'-bis-1,2,3-triazole dioxide, 8.3

The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); Yield : 23%; $^1$H NMR (400,13 MHz, CDCl$_3$) δ 8.05 - 7.92 (m, 4H), 7.61 - 7.44 (m, 10H), 7.38 - 7.27 (m, 2H), 7.23 - 7.14 (m, 4H), 4.20 (dd, J = 7.5 Hz, J = 13.9 Hz, 2H), 3.88 (dd, J = 7.4 Hz, J = 13.9 Hz, 2H), 2.10 (t, J = 6.87 Hz, J = 6.87 Hz, J = 2.7 Hz, 6H), 0.81 (d, J = 6.7 Hz, 6H), 0.73 (d, J = 6.6 Hz, 6H); $^{13}$C NMR (100,61 MHz, CDCl$_3$) δ 140.87 (d, J = 131.2 Hz), 133.26 (d, J = 41.9 Hz), 132.27 (d, J = 2.7 Hz), 132.00 (d, J = 2.8 Hz), 131.71 (d, J = 10.0 Hz), 131.22 (d, J = 10.8 Hz), 130.67 (d, J = 22 Hz), 128.58 (d, J = 12.6 Hz), 128.08 (d, J = 13.0 Hz), 56.97 (s), 28.02 (s), 20.16 (s), 20.03 (s); $^{31}$P NMR (161.97 MHz, CDCl$_3$) δ 16.5 (s); HRMS (EI): m/z Calcd. for C$_{38}$H$_{38}$N$_2$O$_2$P$_2$ [M+H]$^+$/3:649.25; Found: 649.2618; mp : 237.1-238.0 °C.

II.5. 4,4'-bis(diphenylphosphonyl)-1,1'-dicyclocHexyl-5,5'-bis-1,2,3-triazole dioxide, 8.4

The compound was isolated as a white solid after sublimation; Yield : 6%; $^1$H NMR (400,13 MHz, CDCl$_3$) δ 7.95 - 7.89 (qt, 3H), 7.51 - 7.38 (m, 11H), 7.27 - 7.21 (m, 6H), 3.70 (tt, J = 11.74 Hz,3.70 Hz, 2H), 2.53 - 2.56 (m, 2H), 2.11 - 2.02 (m, 2H), 1.91 - 1.83 (m, 2H), 1.75 - 1.66 (m, 4H), 1.56 - 1.48 (m, 4H), 1.18 - 1.11 (m, 2H), 0.99 - 0.89 (m, 2H), 0.84 - 0.74 (m, 2H); $^{13}$C NMR (100,61 MHz, CDCl$_3$) δ 140.47 (d, J = 132.1 Hz), 133.13 (d, J = 40.3 Hz), 132.23 (d, J = 2.9 Hz), 131.94 (d, J = 2.8 Hz), 131.79 (d, J =
II.6. 4,4'-bis(diphenylphosphinoxy)-1,1'-bis(benzyloxyacetyl)-5,5'-bis-1,2,3-triazole dioxide, 8.5

The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); Yield : 28%; \(^{1}H\) NMR (400.13 MHz, CDCl\(_3\)) \(\delta\) 7.97 - 7.89 (m, 4H), 7.59 - 7.52 (m, 2H), 7.51 - 7.39 (m, 8H), 7.34 - 7.28 (m, 8H), 7.25 - 7.19 (m, 4H), 7.17 - 7.09 (m, 4H), 5.40 (d, \(J = -17.8\) Hz, 2H), 5.18 (d, \(J = -17.8\) Hz, 2H), 5.05 (d, \(J = -12.1\) Hz, 2H), 4.99 (d, \(J = -12.1\) Hz, 2H); \(^{13}C\) NMR (100.61 MHz, CDCl\(_3\)) \(\delta\) 165.89 (s), 141.10 (d, \(J = 129.7\) Hz), 134.58 (s), 132.54 (d, \(J = 2.7\) Hz), 132.3 (dd, \(J = 20.8\) Hz, \(J = 110.9\) Hz), 132.19 (d, \(J = 2.7\) Hz), 131.83 (d, \(J = 10.2\) Hz), 131.82 (d, \(J = 21.7\) Hz), 131.21 (d, \(J = 10.9\) Hz), 128.77 (d, \(J = 12.6\) Hz), 128.75 (s), 128.72 (s), 128.55 (s), 128.5 (d, \(J = 13.0\) Hz), 68.04 (s); \(^{31}P\) NMR (161.97 MHz, CDCl\(_3\)) \(\delta\) 17.36 (s); HRMS (EI): \(m/z\) Calcd. for C\(_{80}H_{72}N_{8}O_{19}P_{2} [M+H]^+: 833.23; Found: 833.2400; \(\delta\): 157.4-157.9 °C.

II.7. 4,4'-bis(diphenylphosphinoxy)-1,1'-bis(methoxyacetyl)-5,5'-bis-1,2,3-triazole dioxide, 8.6

The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); Yield : 20%; \(^{1}H\) NMR (400.13 MHz, CDCl\(_3\)) \(\delta\) 7.92 - 7.84 (m, 4H), 7.50 - 7.32 (m, 10H), 7.24 - 7.18 (m, 2H), 7.09 - 7.03 (m, 4H), 5.29 (d, \(J = -17.8\) Hz, 2H), 5.06 (d, \(J = -17.8\) Hz, 2H), 3.58 (s, 6H); \(^{13}C\) NMR (100.61 MHz, CDCl\(_3\)) \(\delta\) 166.45 (s), 147.07 (d, \(J = 129.0\) Hz), 132.57 (d, \(J = 2.78\) Hz), 132.19 (d, \(J = 2.8\) Hz), 131.82 (d, \(J = 10.9\) Hz), 131.6 (dd, \(J = 23.4\) Hz, \(J = 110.81\) Hz), 131.17 (d, \(J = 10.9\) Hz), 130.93 (s), 128.78 (d, \(J = 12.8\) Hz), 128.5 (d, \(J = 13.0\) Hz), 62.99 (s), 49.89 (s); \(^{31}P\) NMR (161.97 MHz, CDCl\(_3\)) \(\delta\) 17.34 (s); HRMS (EI): \(m/z\) Calcd. for C\(_{86}H_{78}N_{8}O_{19}P_{2} [M+H]^+: 681.17; Found: 681.1790; \(\delta\): 211.7-212.1°C.

II.8. 4,4'-bis(diphenylphosphinoxy)-1,1'-bis(benzyloxymethyl)-5,5'-bis-1,2,3-triazole dioxide, 8.7

The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); Yield : 12%; \(^{1}H\) NMR (400.13 MHz, CDCl\(_3\)) \(\delta\) 8.04-7.97 (m, 4H), 7.64 - 7.40 (m, 10H), 7.37 - 7.11 (m, 16H), 5.87 (d, \(J = -11.2\) Hz, 2H), 5.75 (d, \(J = -11.2\) Hz, 2H), 4.42 (s, 4H); \(^{13}C\) NMR (100.61 MHz, CDCl\(_3\)) \(\delta\) 141.51 (d, \(J = 129.5\) Hz), 135.72 (s), 132.43 (d, \(J = 2.6\) Hz), 132.07 (d, \(J = 2.7\) Hz), 131.84 (dd, \(J = 31.1\) Hz, \(J = 111\) Hz), 131.78 (d, \(J = 10.2\) Hz), 131.22 (d, \(J = 10.9\) Hz), 130.84 (dd, \(J = 21.3\) Hz, \(J = 12.8\) Hz), 128.50 (s), 128.42 (d, \(J = 12.9\) Hz), 128.36 (s), 128.26 (s), 76.79 (s), 71.29 (s); \(^{31}P\) NMR (161.97 MHz, CDCl\(_3\)) \(\delta\) 17.34 (s); HRMS (EI): \(m/z\) Calcd. for C\(_{90}H_{88}N_{8}O_{19}P_{2} [M+H]^+: 777.24; Found: 777.25183; \(\delta\): 154.0-154.8 °C.
III. Reduction of bistriazolylphosphane oxides 8 into bisphosphanes 11

III.1. General procedure

To a mixture of bistriazole (1eq) and triethylamine (12 eq) in anhydrous toluene (0.15 mol.ml⁻¹) was added dropwise trichlorosilane (10 eq) at room temperature under a nitrogen atmosphere. The mixture was stirred at reflux for 12 h. After complete reduction, observed by ³¹P RMN, the reaction mixture was quenched with 2M NaOH aq and diluted with dichloromethane and water. The organic layer was separated, washed with water and dried over Na₂SO₄. After concentration under vacuum, the diphosphanes were obtained.

![Scheme 1. Reduction of the bis(triazolylphosphane) oxides 8.1-8.3 to diphosphanes 11.1-11.3.](image)

III.2. 4,4'-bis(diphenylphosphino)-1,1'-dibenyl-5,5'-bis-1,2,3-triazole, 11-Bn

The compound was isolated as a white solid after precipitation with diethylether and pentane; Yield : 99%; ¹H NMR (400,13 MHz, CDCl₃) δ 7.68 - 7.65 (m, 4H), 7.40 - 7.16 (m, 22H), 6.84 - 6.82 (m, 4H), 4.98 (d, J = 14.9 Hz, 2H), 4.55 (d, J = 14.9 Hz, 2H); ¹³C NMR (100,61 MHz, CDCl₃) δ 145.74 - 145.72 (m (ABX)), 145.57 - 145.56 (m (ABX)), 134.92 - 134.87 (m (ABX)), 134.48 (d, J = 21.7 Hz), 133.38 (s), 133.30 (d, J = 20.7 Hz), 130.56 (d, J = 44.4 Hz), 129.14 (d, J = 65 Hz), 128.93 (s), 128.67 - 128.59 (m (ABX)), 128.41-128.32 (m (ABX)), 128.22 (s), 52.49 - 52.45 (m (ABX)); ³¹P NMR (161.97 MHz, CDCl₃) δ - 37.97 (s); HRMS (EI): m/z Calcd. for C₄₂H₃₄N₆P₂ [M+H⁺]: 685.23; Found: 685.2398; mp : 205.4-206.5 °C.

III.3. 4,4'-bis(diphenylphosphino)-1,1'-dibutyl-5,5'-bis-1,2,3-triazole, 11-Bu

The compound was isolated as a white solid after precipitation with diethylether and pentane; Yield : 98%; ¹H NMR (400,13 MHz, CDCl₃) δ 7.48 - 7.58 (m, 4H), 7.30 - 7.22 (m, 6H), 7.21 - 7.06 (m, 10H), 3.96 - 3.78 (m, 4H), 1.63 - 1.50 (m, 4H), 1.08 - 0.89 (m, 4H), 0.63 (t, J = 7.6 Hz, 6H); ¹³C NMR (100,61 MHz, CDCl₃) δ 144.02 - 145.96 (m (ABX)), 144.88 - 144.82 (m (ABX)), 135.51 - 135.46 (m (ABX)), 135.08 - 135.04 (m (ABX)), 134.37 - 134.14 (m (ABX)), 133.48 - 133.24 (m (ABX)), 130.64 (d, J = 44.9 Hz), 129.11 (d, J = 53.3 Hz), 128.71 - 128.59 (m (ABX)), 128.44 - 128.32 (m (ABX)), 49.07 (m (ABX)), 31.72 (m (ABX)), 19.81 (s), 13.30 (s); ³¹P NMR (161.97 MHz, CDCl₃) δ - 37.75 (s); HRMS (EI): m/z Calcd. for C₃₆H₃₈N₆P₂ [M+H⁺]: 617.26; Found: 617.2715; mp : 154.1-155.0 °C.

III.4. 4,4'-bis(diphenylphosphino)-1,1'-diisobutyl-5,5'-bis-1,2,3-triazole, 11-iBu

The compound was isolated as a white solid after precipitation with diethylether and pentane; Yield : 98%; ¹H NMR (400,13 MHz, CDCl₃) δ 7.99 - 7.49 (m, 4H), 7.28 - 7.23 (m, 6H), 7.22 - 7.16 (m, 4H), 7.16 - 7.07 (m, 6H), 3.79 (dd, J = 7.6 Hz, J = 13.6 Hz, 2H), 3.67 (dd, J = 7.6 Hz, J = 13.6 Hz, 2H), 1.99 - 1.75 (m, 2H), 0.61 (d, J = 6.7 Hz, 6H), 0.58 (d, J = 6.7 Hz, 6H); ¹³C NMR (100,61 MHz, CDCl₃) δ 145.15 - 145.06 (m (ABX)), 144.96 - 144.91 (m (ABX)), 135.71 - 135.67 (m (ABX)), 135.05 - 135.00 (m (ABX)), 133.56 - 133.29 (m (ABX)).
(ABX)), 133.13 - 133.14 (m (ABX)), 131.20 (d, J = 1.20 Hz), 130.74 (d, J = 1.37 Hz), 129.06 (d, J = 66.8 Hz), 128.68 - 128.50 (m (ABX)), 128.42 - 128.24 (m (ABX)), 56.45 - 56.6 (m (ABX)), 45.85 (s), 28.68 (s), 19.88 (s); 31P NMR (161.97 MHz, CDCl3) δ - 38.08 (s); HRMS (EI): m/z Calcd. for C36H38N6P2 [M+H]+: 617.26; Found: 617.2714; mp: 154.2-154.8 °C.

IV. Synthesis of complexes 12-17

IV.1. Synthesis of the palladium complex 13

In a Schlenk tube under argon, a mixture of compound 11.1 (20 mg, 0.029 mmol) and bis(acetonitrile)dibromopalladium (10.1 mg, 0.029 mmol) was dissolved in dry chloroform (2 ml). The reaction was carried out at room temperature for 2 hours. The solvent was evaporated and the resulting orange solid was washed by dry pentane. After evaporation of the solvent, 22.1 mg of 12.1 were obtained (yield = 80%).

1H(31P) NMR (500 MHz, CDCl3) δ (ppm) : 7.98 (4H, m, PPh2), 7.63 (4H, m, PPh2), 7.52 (2H, m, PPh2), 7.49 (2H, m, PPh2), 7.46 (4H, m, PPh2), 7.36 (4H, m, PPh2), 7.32 (2H, m, Ph/Bn), 7.25 (4H, m, Ph/Bn), 6.77 (4H, m, Ph/Bn), 4.69 (2H, d, J = 15.7 Hz, NCH2), 4.49 (2H, d, J = 15.7 Hz, NCH2).

13C{1H} NMR (500 MHz, CDCl3) δ (ppm): 141.7 (JCP = 61.1 Hz, quat, PCN), 135.8 (JCP = 6.5 Hz, PPh2), 133.9 (JCP = 5.0 Hz, PPh2), 132.9 (PPh2), 132.1 (quat, Ph/Bn), 131.2 (PPh2), 129.2 (JCP = 6.3 Hz, PPh2), 129.2 (Ph/Bn), 129.0 (Ph/Bn), 128.2 (quat, JCP = 19.9 Hz, PPh2), 127.7 (JCP = 6.0 Hz, PPh2), 127.6 (quat, PCCN)127.1 (Ph/Bn), 125.8 (quat, JCP = 40.8 Hz, PPh2), 52.5 (NCPh).

31P{1H} NMR (500 MHz, CDCl3) δ (ppm): 8.4.

HR/MS (ES+) m/e: 871.0541 (M-Br, 100%) (calc. M: 871.0311).

IV.2. Synthesis of the platinum complex 14

In a Schlenk tube, under argon, a mixture of ligand 11.1 (20 mg, 0.029 mmol) and bis(benzonitrile)dichloroplatinum (13.7 mg, 0.029 mmol) was dissolved in dry chloroform (2 ml). The reaction was carried out at reflux for 2 hours. The solvent was evaporated and the resulting white solid was washed by dry pentane. After evaporation of the solvent, 19.3 mg of 14.1 were obtained (yield = 70%).

1H(31P) NMR (500 MHz, CDCl3) δ (ppm) : 7.93 (4H, m, PPh2), 7.63 (4H, m, PPh2), 7.50 (2H, m, PPh2), 7.49 (2H, m, PPh2), 7.46 (4H, m, PPh2), 7.36 (4H, m, PPh2), 7.34 (4H, m.), 7.33 (2H, m, Ph/Bn), 7.25 (4H, m, Ph/Bn), 6.77 (4H, m, Ph/Bn), 4.74 (2H, d, J = 15.3 Hz, NCH2), 4.60 (2H, d, J = 15.3 Hz, NCH2).

13C{1H} NMR (500 MHz, CDCl3) δ (ppm): 140.4 (JCP = 82 Hz, quat, PCN), 135.4 (JCP = 6.5 Hz, PPh2), 134.2 (JCP = 4.9 Hz, PPh2), 132.8 (PPh2), 132.2 (quat, Ph/Bn), 131.4 (PPh2), 129.2 (Ph/Bn), 129.0 (PPh2), 129.0 (Ph/Bn), 127.7 (JCP = 6.0 Hz, PPh2), 127.6 (quat, PCCN)127.1 (Ph/Bn), 125.8 (quat, JCP = 40.8 Hz, PPh2), 52.5 (NCPh).

31P{1H} NMR (500 MHz, CDCl3) δ (ppm): -5.1. HR/MS (ES+) m/e: 915.1645 (M-Cl, 100%) (calc. M: 915.0311).

A single crystal of 14 suitable for X-ray diffraction analysis was obtained by slow diffusion of pentane in a dichloromethane solution.
IV.3. Synthesis of the iridium complex 16

In a Schlenk tube under argon, a mixture of compound 11.1 (20 mg, 0.029 mmol) and [Ir(cod)Cl]₂ (9.8 mg, 0.015 mmol) was dissolved in dry dichloromethane (2 ml). The reaction was carried out at room temperature for 45 minutes. The solvent was evaporated and the resulting yellow solid was washed by dry pentane. After evaporation of the solvent, 29.3 mg of 16 were obtained (yield = 99%).

\[
\begin{align*}
\text{1H}^{31\text{P}} \text{ NMR (500 MHz, CDCl}_3 \text{) } & \delta \text{ (ppm)} : 7.75 \text{ (4H, m, PPh}_2 \text{), 7.57 \text{ (4H, m, PPh}_2 \text{),} \\
& 7.44 \text{ (6H, m, PPh}_2 \text{), 7.33 \text{ (2H, m, PPh}_2 \text{), 7.25 \text{ (4H, m, PPh}_2 \text{), 7.17 \text{ (2H, m, Ph/Bn), 7.07 \text{ (4H, m, Ph/Bn),} } \\
& 6.77 \text{ (4H, m, PPh}_2 \text{), 4.65 \text{ (2H, d, J = 15.3 Hz, NCH}_2 \text{), 4.58 \text{ (2H, d, J = 15.3 Hz, NCH}_2 \text{), 3.67 \text{ (2H, m, COD), 3.13 \text{ (2H, m, COD), 2.00 \text{ (2H, m, COD),} } } \\
& 1.74 \text{ (2H, m, COD), 1.69 \text{ (2H, m, COD), 1.53 \text{ (2H, m, COD).} }}
\end{align*}
\]

HR/MS (ES+) m/e: 985.2919 (M-Cl, 80%) (calc. M: 985.2888).

A single crystal of 16 suitable for X-ray diffraction analysis has been obtained by slow diffusion of pentane in a dichloromethane solution.

IV.4. Synthesis of the iridium complex 17

In a Schlenk tube under argon, a mixture of compound 11.1 (20 mg, 0.029 mmol) and Ir(COD)Cl₂ (19.6 mg, 0.029 mmol) was dissolved in dry dichloromethane (4 ml). The mixture was stirred at room temperature for 45 minutes. The solvent was then evaporated and the resulting yellow solid was washed by dry pentane. After evaporation of the solvent, 35.4 mg of 17.1 were obtained (yield = 90%).

\[
\begin{align*}
\text{1H}^{31\text{P}} \text{ NMR (500 MHz, CDCl}_3 \text{) } & \delta \text{ (ppm)} : 7.67 \text{ (4H, m, PPh}_2 \text{), 7.50 \text{ (4H, m, PPh}_2 \text{), 7.50 \text{ (2H, m, PPh}_2 \text{), 7.31 \text{ (2H, m, PPh}_2 \text{), 7.30 \text{ (4H, m, PPh}_2 \text{), 7.24 \text{ (4H, m, PPh}_2 \text{), 6.97 \text{ (2H, m, Ph/Bn), 6.91 \text{ (4H, m, Ph/Bn), 6.63 \text{ (4H, m, Ph/Bn),} } } \\
& 5.26 \text{ (2H, m, COD), 5.17 \text{ (2H, m, COD), 4.92 \text{ (2H, d, J = 15.6 Hz, NCH}_2 \text{), 4.26 \text{ (2H, d, J = 15.6 Hz, NCH}_2 \text{,} } \\
& 2.68 \text{ (2H, m, COD), 2.48 \text{ (2H, m, COD), 2.37 \text{ (2H, m, COD), 2.15 \text{ (4H, m, COD), 2.14 \text{ (2H, m, COD), 1.98 \text{ (2H, m, COD), 1.76 \text{ (2H, m, COD), 1.67 \text{ (2H, m, COD), 1.45 \text{ (2H, m, COD).} }}
\end{align*}
\]

HR/MS (ES+) m/e: 985.2916 (M+Cl, 100%) (calc. M: 985.2888).
V. Copies of spectra for phosphane oxides 8.1-8.7

V.1. 4,4'-bis(diphenylphosphinoxy)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole 8.1
V.2. 4,4′-bis(diphenylphosphinoxy)-1,1-dibutyl-5,5′-bis-1,2,3-triazole 8.2
### Elemental Composition Report

#### Single Mass Analysis

**Tolerance = 3.0 mDa / DBE: min = -10.0, max = 100.0**  
Isotope cluster parameters: Separation = 1.0  
Abundance = 1.0%

Monoisotopic Mass, Even Electron Ions  
767 formula(e) evaluated with 3 results within limits (all results up to 1000) for each mass

<table>
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<tr>
<th>Q-TOF Y-JP12041711 17 (9.315) Sm (Mn, 10x1.00); Cm (10:18)</th>
<th>CL-Bistriazole-nButyl / Mmono = 648.25</th>
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</thead>
<tbody>
<tr>
<td>17-APR-2012 TOF MS ES+ 2.69e3</td>
<td>648.2607</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum:</td>
<td>Maximum:</td>
</tr>
<tr>
<td>649.2607</td>
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<tr>
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</table>

Page 1
Sep10-2012
CL-bis-iBu
P31 CPD CDCl3 /opt/topspin am2n1 S7

Q-TOF
CL-Bistriazole-isobutyl / Mono = 648.25 17-APR-2012
TOF MS ESI+ 3.17e6
V.4. 4,4’-bis(diphenylphosphinoxy)-1,1’-dicyclohexyl-5,5’-bis-1,2,3-triazole 8.4
Clemental Composition Report

Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -10.0, max = 100.0
Isotope cluster parameters: Separation = 1.0, Abundance = 1.0%

Monoisotopic Mass, Even Electron Ions
531 formula(e) evaluated with 3 results within limits (all results up to 1000) for each mass

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</table>
V.5. 4,4′-bis(diphenylphosphinoxy)-1,1′-bis(benzyloxyacetyl)-5,5′-bis-1,2,3-triazole 8.5

Feb07-2012
CL109-118 sec
PROTON CDCl3 opt/topspin am2n1 10

Feb07-2012
CL109-118 sec, cdd3, 13c
C13APT CDCl3 opt/topspin am2n1 58

S-19
V.6. 4,4’-bis(diphenylphosphinoxy)-1,1’-bis(methoxyacetyl) -5,5’-bis-1,2,3-triazole dioxide 8.6
### Jemental Composition Report

**Single Mass Analysis**

Tolerance = 3.0 mDa  
DBE: min = -10.0, max = 100.0

Isotope cluster parameters: Separation = 1.0  
Abundance = 1.0%

Monoisotopic Mass, Even Electron Ions

902 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

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<tr>
<th>Q-TOF</th>
<th>CL-Bistiazole-methylacete / Mmono = 680.17</th>
<th>17-APR-2012</th>
<th>TOF MS ES+</th>
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<td>75 (1.430) Cn (Cn4, 80.00, Ar); Sm (SG, 101.01); Cn (71-76)</td>
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<td>682.1913</td>
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<table>
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<th>Minimum:</th>
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<td>-10.0</td>
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<table>
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<td>C33 H35 N2 O10 P2</td>
</tr>
</tbody>
</table>
V.7. 4,4’bis(diphenylphosphino)-1,1’-(dibenzylxyloxy)dimethyl-5,5’-bis-1,2,3-triazole dioxide 8.7

Feb10-2012
CL159 P, cdcl3, 1h
PROTON CDCl₃ opt/topspin am2n1 48

Feb10-2012
CL159 P, cdcl3, 13c
C13APT CDCl₃ opt/topspin am2n1 48
Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -10.0, max = 100.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Even Electron Ions
317 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

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<td>777.2508</td>
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<td>2</td>
<td>C44 H39 N6 O4 P2</td>
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</table>
VI. Copies of spectra for phosphanes 11.1 – 11.3

VI.1. 4,4'-bis(diphenylphosphino)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole 11.1

![Spectrum Image]

Jun03-2014
CLBiBi-P
PROTON CDCl3 [opt/topspin am2n1 5]

C13APT CDCl3 [opt/topspin am2n1 5]

52.45 52.47 52.49 128.22 128.33 128.37 128.41 128.60 128.67 128.82 128.92 129.46 130.32 130.76 133.19 133.36 133.39 134.37 134.59 134.84 134.89 135.42 135.46 145.57 145.72
VI.2. 4,4’bis(diphenylphosphino)-1,1’-dibutyl-5,5’-bis-1,2,3-triazole 11.2
### Elemental Composition Report

**Single Mass Analysis**

Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0  
Element prediction: Off  
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions  
003 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)  
Elements Used:  
C: 0-100  H: 0-150  N: 0-30  P: 0-3

---

**SYNAPT G2-SiNetSet**  
Y-JLP14030503 49 (0.992) Cm (49:1:3)  
BsnBuP  
05 Mar 2014  
1. TOF MS ES+  
3.56e+008

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<th>PPM</th>
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<td>1329.7</td>
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<td>C36 H39 N6 P2</td>
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</tbody>
</table>
VI.3. 4,4'bis(diphenylphosphino)-1,1'-diisobutyl-5,5'-bis-1,2,3-triazole 11.3
**Single Mass Analysis**

Tolerance = 2.0 PPM  /  DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
565 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100  H: 0-150  N: 1-30  P: 1-3

<table>
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<th>Mass</th>
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<th>PPM</th>
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<th>i-FIT</th>
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<td>11.955</td>
<td>0.00</td>
<td>C15 H36 N22 P3</td>
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</tr>
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</table>
VII. X-ray crystallography.

A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a cryoloop and cooled in the cryostream of either an Oxford-Diffraction XCALIBUR SAPHIRE-I CCD diffractometer or an Agilent Technologies GEMINI EOS CCD diffractometer. Data were collected using the monochromatic MoKα radiation (λ = 0.71073).

The structures were solved by direct methods (SIR97) [1] and refined by least-squares procedures on F2 using SHELXL-97 [2]. All H atoms attached to carbon were introduced in idealised positions and treated as riding on their parent atoms in the calculations. The drawing of the molecules was realised with the help of ORTEP3. [3]

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1031965-1031970. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

VII.1. 4,4'-bis(diphenylphosphinoxy)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole 8.1

Crystal data

<table>
<thead>
<tr>
<th>2(C_{22}H_{34}N_{6}O_{2}P_{2})·C_{2}H_{3}N</th>
<th>V = 3756.64 (11) Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_r = 1474.44</td>
<td>Z = 2</td>
</tr>
<tr>
<td>Monoclinic, P2_1/n</td>
<td>Mo Kα radiation</td>
</tr>
<tr>
<td>a = 12.8008 (2) Å</td>
<td>μ = 0.16 mm⁻¹</td>
</tr>
<tr>
<td>b = 16.6628 (3) Å</td>
<td>T = 175 K</td>
</tr>
<tr>
<td>c = 17.8668 (3) Å</td>
<td>0.43 × 0.35 × 0.25 mm</td>
</tr>
<tr>
<td>β = 99.6830 (17)°</td>
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</table>

Data collection

<table>
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<tr>
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<th>9225 independent reflections</th>
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</thead>
<tbody>
<tr>
<td>T_min = 0.955, T_max = 1.000</td>
<td>R_int = 0.023</td>
</tr>
<tr>
<td>64742 measured reflections</td>
<td>θ_max = 29.1°</td>
</tr>
</tbody>
</table>

Refinement

| R(F²) > 2σ(F²) = 0.045                                 | 2 restraints                |
| wR(F²) = 0.143                                        | H-atom parameters constrained|
| S = 0.85                                              | Δρ_max = 0.49 e Å⁻³         |
9225 reflections

$\Delta \rho_{\text{min}} = -0.67 \text{ e Å}^{-3}$

476 parameters
VII.2. 4,4′-bis(diphenylphosphinoxy)-1,1′-diisobutyl-5,5′-bis-1,2,3-triazole 8.3

Crystal data

\[ V = 6752.5 \text{ (2) \, \AA}^3 \]
\[ M_r = 848.66 \]
\[ Z = 8 \]

Monoclinic, \textit{C}2/c

\[ \alpha = 23.4908 \text{ (5) \, \AA} \]
\[ \mu = 0.17 \text{ mm}^{-1} \]
\[ b = 11.0856 \text{ (2) \, \AA} \]
\[ T = 175 \text{ K} \]
\[ c = 25.9333 \text{ (5) Å} \]
\[ 0.30 \times 0.25 \times 0.15 \text{ mm} \]
\[ \theta = 90.8818 \text{ (18)°} \]

Data collection

Xcalibur, Sapphire3, Gemini diffractometer

Absorption correction: multi-scan

8090 independent reflections

6655 reflections with \( I > 2.0 \sigma (I) \)

\( T_{\text{min}} = 0.877, T_{\text{max}} = 1.000 \)

\( 27328 \) measured reflections

\( R_{\text{int}} \) = 0.047

\( \theta_{\text{max}} = 29.3° \)

Refinement

\( R[F^2 > 2\sigma(F^2)] = 0.049 \)

\( wR(F^2) = 0.055 \)

\( S = 1.09 \)

\( 6655 \) reflections

\( \Delta \rho_{\text{max}} = 0.40 \text{ e Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.27 \text{ e Å}^{-3} \)

415 parameters

0 restraints
VII.3. dichloro(4,4'-bis(diphenylphosphinoxy)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole)palladium 12.1

Crystal data

$\text{C}_{42}\text{H}_{34}\text{Cl}_{2}\text{N}_{6}\text{P}_{2}\text{Pd·CHCl}_{3}$  \quad V = 8524.8 (3) Å$^3$

$M_r = 981.36$  \quad Z = 8

Monoclinic, $P2_1/c$  \quad Mo Kα radiation

$a = 20.0222$ (3) Å  \quad $\mu = 0.86$ mm$^{-1}$

$b = 18.8861$ (4) Å  \quad $T = 175$ K

$c = 22.6056$ (4) Å  \quad $0.25 \times 0.20 \times 0.15$ mm

$\beta = 94.2374$ (16)$^\circ$

Data collection

Xcalibur, Sapphire3, Gemini  \quad 1449 independent reflections

diffractometer
Absorption correction: multi-scan

10170 reflections with $I > 2.0 \sigma(I)$

$T_{\text{min}} = 0.990$, $T_{\text{max}} = 1.000$  
$R_{\text{int}} = 0.032$

32286 measured reflections  
$\theta_{\text{max}} = 26.5^\circ$

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.044$  
0 restraints

$wR(F^2) = 0.025$  
H-atom parameters constrained

$S = 1.12$  
$\Delta \rho_{\text{max}} = 1.64$ e Å$^{-3}$

10170 reflections  
$\Delta \rho_{\text{min}} = -1.63$ e Å$^{-3}$

1027 parameters
VII.4. dichloro(4,4’-bis(diphenylphosphinoxy)-1,1’-dibenzyl-5,5’-bis-1,2,3-triazole)platinum 14

Crystal data

\[ \text{C}_{84}\text{H}_{68}\text{Cl}_{4}\text{N}_{12}\text{P}_{4}\text{Pt}_{2} \]

\[ M_r = 1901.36 \]

Monoclinic, \( P2_1/c \)

\[ a = 25.778 \pm 5 \] Å

\[ \mu = 3.47 \text{ mm}^{-1} \]

\[ b = 17.954 \pm 5 \] Å

\[ c = 19.364 \pm 5 \] Å

\[ T = 180 \text{ K} \]

\[ \beta = 104.467 \pm 5 ^\circ \]

\[ V = 8678 \pm (4) \] Å³

\[ Z = 4 \]

Data collection

Bruker APEX-II CCD 7804 independent reflections
Absorption correction: multi-scan SADABS (Sheldrick, 2008)

6507 reflections with $I > 2\sigma(I)$

$T_{\text{min}} = 0.540$, $T_{\text{max}} = 0.744$

$R_{\text{int}} = 0.073$

70384 measured reflections

$\theta_{\text{max}} = 19.8^\circ$

Refinement

$R(F^2 > 2\sigma(F^2)) = 0.032$

$wR(F^2) = 0.075$

$S = 1.04$

7804 reflections

955 parameters

$\Delta\rho_{\text{max}} = 0.72$ e Å$^{-3}$

$\Delta\rho_{\text{min}} = -0.46$ e Å$^{-3}$

$w = 1/\left[\sigma^2(F_o^2) + (0.0405P)^2 + 11.5437P\right]$

where $P = (F_o^2 + 2F_c^2)/3$
VII.5. \((4,4',\text{bis(diphenylphosphinoxy)}\)-1,1'-dibenzyl-5,5'-\text{bis-1,2,3-triazole})\text{iridium(cyclooctadiene)}\text{chloride 16}

Crystal data

\[
\begin{align*}
\text{C}_{50}\text{H}_{46}\text{ClIrN}_{6}\text{P}_{2}\text{(CHCl}_{3}\text{)}_{3} & \quad \gamma = 111.798 (2)^\circ \\
M_r = 1378.62 & \quad V = 2767.68 (10) \text{ Å}^3 \\
\text{Triclinic, } P & \quad Z = 2 \\
a = 14.3765 (3) \text{ Å} & \quad \text{Mo } K\alpha \text{ radiation} \\
b = 14.3894 (3) \text{ Å} & \quad \mu = 3.00 \text{ mm}^{-1} \\
c = 16.3672 (3) \text{ Å} & \quad T = 180 \text{ K} \\
\alpha = 113.044 (2)^\circ & \quad 0.37 \times 0.27 \times 0.06 \text{ mm} \\
\beta = 95.930 (2)^\circ & 
\end{align*}
\]

Data collection

\[
\begin{align*}
\text{Xcalibur, Eos, Gemini ultra diffractometer} & \quad 15709 \text{ independent reflections} \\
\text{Absorption correction: multi-scan} & \quad 14139 \text{ reflections with } I > 2\sigma(I) \\
T_{\text{min}} = 0.825, T_{\text{max}} = 1.000 & \quad R_{\text{int}} = 0.033 \\
73416 \text{ measured reflections} & \quad \theta_{\text{max}} = 30.0^\circ \\
\end{align*}
\]

Refinement

\[
\begin{align*}
R[F^2 > 2\sigma(F^2)] = 0.026 & \quad 0 \text{ restraints} \\
wR(F^2) = 0.063 & \quad \text{H-atom parameters constrained} \\
S = 1.04 & \quad \Delta\rho_{\text{max}} = 1.27 \text{ e Å}^{-3} \\
15709 \text{ reflections} & \quad \Delta\rho_{\text{min}} = -1.21 \text{ e Å}^{-3} \\
649 \text{ parameters} & 
\end{align*}
\]
VIII. References

