Supplementary Material (ESI) for Chemical Communications

Modifiable Bidentate Systems via N-C Rearrangement in Triazoles

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Experimental Section

General Methods. Oxygen- and moisture-sensitive reactions were carried out under an atmosphere of purified nitrogen in a glovebox equipped with an inert gas purifier or by using standard Schlenk techniques. Solvents were purified by passing through a column of activated alumina under inert atmosphere. All commercially available reagents were used as received, unless otherwise indicated. NMR spectra were recorded at 300 MHz/75 MHz/121 MHz ($^{1}H/^{13}C/^{31}P$ NMR) on a Bruker AVANCE 300 MHz spectrometer or at 200 MHz/50 MHz/81 MHz on a Bruker DPX 200 MHz spectrometer at 23 °C. Chemical shifts (δ) are reported in parts per million, and the residual solvent peak was used as an internal standard ($CDCl_3$: δ 7.261/77.0; CD_3OD: δ 3.30/49.0; THF-d8: δ 1.73/25.3; CD_2Cl_2: δ 5.32/53.8 $^{1}H/^{13}C$ NMR). ^{31}P NMR signals are in ppm and referenced to external 85% H_3PO_4. Data are reported as follows: chemical shift, multiplicity (s=singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad), integration, and coupling constant(s) (Hz). Compounds Ph_2PCCH, $Ph_2P(O)CCH$, $(COD)PtCl_2$, and $(COD)PtMe_2$ were prepared according to established literature procedures.[1,2,3]

General Procedure for the Preparation of Dialkyl Azidophosphine-Borane complexes. Diisopropylazidophosphine-borane complex 5a: Borane dimethylsulfide (1.0 g, 13.15 mmol) was added to a solution of diisopropyl chlorophosphine (1.0 g, 6.58 mmol) in dry THF (1 ml) and the mixture was stirred at rt for 1 h. Excess borane and dimethylsulfide were removed under reduced pressure. The resulting colorless oil was dissolved in a mixture of toluene (16 ml) and acetonitrile (8 ml). Sodium azide (0.489 g, 7.52 mmol) and 15-crown-5 (0.331 g, 1.5 mmol) were added and the mixture was stirred overnight at rt. The mixture was then diluted with EtOAc and washed several times with brine. The organic portion was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude mixture was separated by chromatography, hexane/EtOAc (8:2), to afford **5a** as a colorless oil (0.614 g, 60%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: -0.10-1.05 (br m, 3H), 1.15 (dd, J_{HP} = 7.1 Hz, J_{HH} = 4.5 Hz, 3H), 1.21 (dd, J_{HP} = 7.1 Hz, J_{HH} = 1.9 Hz, 3H) 2.00-2.12 (m, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$**,** 50 MHz) δ: 15.4 (d, J_{CP} = 3 Hz), 15.8 (d, J_{CP} = 3 Hz), 24.8 (d, J_{CP} = 35 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) δ: 112.9-114.1 (m). IR ($CHCl_3$, cm^{-1}) 2388, 2143.

Diethylazidophosphine-borane complex 5b: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.11-1.12 (br m, 3H), 1.20 (dt, J_{HP} = 17.5 Hz, J_{HH} = 7.6 Hz, 6H), 1.72-1.90 (m, 4H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) δ: 102.4-103.6 (m).

Dicyclohexylazidophosphine-borane complex 5c: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: -0.22-1.10 (br m, 3H), 1.12-1.55 (m, 10H), 1.60-1.98 (m, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ: 25.1 (d, J_{CP} = 4 Hz), 25.6 (d, J_{CP} = 1 Hz), 25.7 (d, J_{CP} = 1

[1]For and Ph_2PCCH, $Ph_2P(O)CCH$ see Charrier, C., et al. *Mémoires Présentés a la Société Chimique*. **1965**, 1002-1011.
[2] For $(COD)PtCl_2$ see: Peters, T. B., et al. *Organometallics*. **1999**, *18*, 3261-3263.
[3] For $(COD)PtMe_2$ see: *Inorganic Synthesis*. **1995**, *31*, 284-286.

Hz), 26.1 (d, J_{CP} = 4 Hz), 26.2 (d, J_{CP} = 7 Hz), 34.2 (d, J_{CP} = 34 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) δ: 102.7-104.6 (m).

Preparation of Diphenylethynylphosphine-Borane Complex 8b. Diphenylethynylphosphine (0.097 g, 0.461 mmol) was dissolved in THF (2 ml) and cooled to 0ºC. Borane-N-N-diisopropyl ethyl amine complex (0.066 g, 0.461 mmol) was added and the reaction was allowed to warm to rt and then stirred for 4 h. Solvent and volatile byproducts were removed *in vacuo* and the residue was immediately separated by flash chromatography, hexane/$CHCl_3$ (4:3), to afford the product as a colorless oil (0.065 g, 63%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.28-2.30 (br m, 3H), 3.35 (d, J_{HP} = 7.8 Hz), 7.39-7.57 (m, 6H), 7.76-7.92 (m, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50 MHz) δ: 75.0 (d, J_{CP} = 101 Hz), 97.5 (d, J_{CP} = 15 Hz), 127.9 (d, J_{CP} = 64 Hz), 128.9 (J_{CP} = 11 Hz). 131.7, 131.9. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) δ: 6.0-6.6 (m).

General Procedure for the Preparation of 6. Preparation of 6b: To a 1M solution of EtMgBr in THF (0.800 ml, 0.800 mmol) a solution of diphenylethynylphosphine oxide (0.181 g, 0.800 mmol) in THF (10 ml) was added dropwise at rt. The mixture was heated to 50°C for 15 minutes in a closed vessel and then cooled to rt. A solution of diethylazidophosphine-borane complex (0.091 g, 0.628 mmol) in THF was added. The mixture was stirred in a closed vessel overnight. The reaction was quenched with a saturated solution of ammonium chloride and the product was extracted three times with $CHCl_3$, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude mixture was separated by chromatography, hexane/EtOAc (1:1), to afford product **6b** as an off-white solid (0.199 g, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.81 (dt, J_{HP} = 18.6 Hz, J_{HH} = 7.5 Hz, 6H), 1.97-2.14 (m, 2H), 2.37-2.57 (m, 2H), 7.33-7.55 (m, 6H), 7.58-7.80 (m, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ: 1.0, 17.7 (d, J_{CP} = 39 Hz), 128.7 (d, J_{CP} = 13 Hz), 131.5 (d, J_{CP} = 10 Hz), 132.5 (d, J_{CP} = 3 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: 15.0 (br), 18.1. MS (MALDI TOF): *m/z* = 355.66 (M-1).

6a: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.79 (dd, J_{HP} = 16.7 Hz, J_{HH} = 7.0 Hz, 6H), 1.27 (dd, J_{HP} = 17.9 Hz, J_{HH} = 7.1 Hz, 6H), 3.17-3.41 (m, 2H), 7.41-7.62 (m, 6H), 7.78-7.95 (m, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50 MHz) δ: 17.5 (d, J_{CP} = 4 Hz), 18.3, 23.6 (d, J_{CP} = 34 Hz), 128.6 (d, J_{CP} = 13 Hz), 131.5 (d, J_{CP} = 10 Hz), 131.9 (d, J_{CP} = 111 Hz), 132.4 (d, J_{CP} = 3 Hz), 144.0 (d, J_{CP} = 133 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 81 MHz) δ: 30.9 (br), 17.9. HRMS-ESI: $(M-H)^+$ = 398.1720, $C_{20}H_{27}BN_3OP_2$ calc mass 398.1722.

Selected bond lengths [Å] of compound **6a**: P1—C1 1.798(4), P2—C2 1.802(4), N1—N2 1.325(5), N2—N3 1.318(4).

6c: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.69-2.11 (m, 23H), 2.87-3.17 (m, 2H), 7.37-7.63 (m, 6H), 7.78-7.97 (m, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50 MHz) δ: 25.4 (d, J_{CP} = 1 Hz), 26.0 (d, J_{CP} = 3 Hz), 26.1 (d, J_{CP} = 22.6 Hz), 27.5-27.8 (m), 33.0 (d, J_{CP} = 33 Hz), 128.6 (d, J_{CP} = 13 Hz), 131.4 (d, J_{CP} = 10 Hz), 132.0 (d, J_{CP} = 110 Hz), 132.4 (d, J_{CP} = 3 Hz), 144.2 (d, J_{CP} = 131 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 81 MHz) δ: 22.4 (br), 18.

Preparation of 15. **6a** (0.160 g, 0.401 mmol) was dissolved in MeOH. To the solution was added NaOMe 30% in MeOH (0.072 g, 0.401 mmol) and the mixture was stirred at rt for 1 h. MeOH was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (7 ml) and MeI (0.319 g, 2.246 mmol) was added under low-light conditions and stirred at rt. The reaction was quenched by addition of water (5 ml) and the organic product was extracted with CH_2Cl_2 (3 x 5 ml) and washed with brine (1 x 5

ml). The organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude mixture was separated by flash chromatography hexanes/EtOAc (4:1), R_f = 0.4 (hexanes/EtOAc 3:2), to afford **15** (0.067 g, 40%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.79 (dd, J_{HP} = 15.9 Hz, J_{HH} = 7.1 Hz, 6H), 1.25 (dd, J_{HP} = 16.4 Hz, J_{HH} = 7.0 Hz, 6H), 4.31 (s, 3H), 7.43-7.59 (m, 6H), 7.70-7.80 (m, 4H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz) δ: 18.6, 34.4 (br).

General Procedure for Removal of Borane Protecting Group.[4] **Preparation of 12**: A slurry of the protected ligand **6a** (0.046 g, 0.115 mmol) in MeOH (0.9 ml) and dioxane (1.75 ml) was heated to 100°C overnight in a closed vessel. Solvents and volatile side-products were removed *in vacuo* to afford **12** as an off-white solid (0.044 g, 99%). ^{1}H NMR (CD_3OD, 200 MHz) δ: 0.49 (dd, J_{HP} = 12.2 Hz, J_{HH} = 6.9 Hz, 6H), 0.68 (dd, J_{HP} = 15.6 Hz, J_{HH} = 7.0 Hz, 6H), 1.82-2.06 (m, 2H), 7.08-7.31 (m, 6H), 7.33-7.50 (m, 4 H). ^{13}C{^{1}H} NMR (CD_3OD, 50 MHz) δ: 20.3 (d, J_{CP} =10 Hz), 20.9 (d, J_{CP} = 19 Hz), 25.0 (d, J_{CP} = 11 Hz), 129.6 (d, J_{CP} = 13 Hz), 132.9 (d, J_{CP} = 10 Hz), 133.5 (d, J_{CP} = 3 Hz), 133.4 (d, J_{CP} = 111 Hz), 144.6 (dd, $^1J_{CP}$ = 47, Hz $^2J_{CP}$ = 26 Hz), 146.8 (dd, $^1J_{CP}$ = 138 Hz, $^2J_{CP}$ = 22 Hz). ^{31}P{^{1}H} NMR (CD_3OD,) δ: -19.6, 21.0.

Deboranated product of 6b: ^{1}H NMR (CD_3OD, 200 MHz) δ: 0.88 (dt, J_{HP} = 15.5 Hz, J_{HH} = 7.7 Hz, 6H), 1.61-1.97 (m, 4H), 7.44-7.65 (m, 6H), 7.67-7.82 (m, 4H). ^{13}C{^{1}H} NMR (CD_3OD, 75 MHz) δ: 10.1 (d, J_{CP} = 13 Hz), 19.3 (d, J_{CP} = 10 Hz), 129.7 (d, J_{CP} = 13 Hz), 130.3 (d, J_{CP} = 112 Hz), 132.9 (d, J_{CP} = 10 Hz), 133.6 (d, J_{CP} = 3 Hz), 133.9 (d, J_{CP} = 11 Hz). ^{31}P{^{1}H} NMR (CD_3OD, 121 MHz) δ: -38.8, 21.9.

Deboranated product of 6c: ^{1}H NMR (CD_3OD, 200 MHz) δ: 0.77-1.92 (m, 20H), 2.00-2.22 (m, 2H), 7.43-7.66 (m, 6H), 7.67-7.84 (m, 4H). ^{13}C{^{1}H} NMR (CD_3OD, 50 MHz) δ: 27.5 (d, J_{CP} = 21 Hz), 27.9 (d, J_{CP} = 6 Hz), 31.0 (d, J_{CP} = 9 Hz), 31.6 (d, J_{CP} = 18 Hz), 34.7 (d, J_{CP} = 11 Hz), 129.7 (d, J_{CP} = 13 Hz), 133.0 (d, J_{CP} = 10 Hz), 133.5 (d, J_{CP} = 111 Hz), 133.8 (d, J_{CP} = 3 Hz), 146,7 (dd, $^1J_{CP}$ = 138 Hz, $^2J_{CP}$ = 20 Hz). ^{31}P{^{1}H} NMR (CD_3OD, 81 MHz) δ: -26.0, 20.5.

General Procedure for Reduction of Phosphine Oxide Protecting Group.[5] **Preparation of 13**: $PhSiH_3$ (2.5 g, 23.1 mmol) was added to a slurry of bisphosphine monoxide **12** (0.237 g, 0.771 mmol) in toluene (5 ml). The mixture was stirred in a closed vessel for 3 d at 100ºC. The reaction mixture was concentrated *in vacuo* and then filtered through silica. Impurities were eluted with toluene and the pure product was eluted with THF. The THF fraction was concentrated *in vacuo*, affording the viscous product (0.280 g, 98%). ^{1}H NMR (THF-d8, 200 MHz) δ: 1.04 (dd, J_{HP} = 11.5 Hz, J_{HH} = 6.9 Hz, 6H) 1.17 (dd, J_{HP} = 15.4 Hz, J_{HH} = 7.1 Hz, 6H), 7.15-7.65 (m, 10H). ^{13}C{^{1}H} NMR (THF-d8, 50 MHz) δ: 19.9 (d, J_{CP} = 9 Hz), 20.5 (J_{CP} = 19 Hz), 129.1 (d, J_{CP} = 11 Hz), 130.7, 134.4 (d, J_{CP} = 20 Hz), 136.5, 138.1 (d, J_{CP} = 9 Hz). ^{31}P{^{1}H} NMR (THF-d8, 81 MHz) δ: -36.9 (d, J_{PP} = 47 Hz), -19.3 (d, J_{PP} = 47 Hz).

Fully deprotected product of 6b: ^{1}H NMR (THF-d8, 300 MHz) δ: 1.06 (dt, J_{HP} = 15.3 Hz, J_{HH} = 7.7 Hz, 6H), 1.77-1.93 (m, 2H), 1.93-2.11 (m, 2H), 7.38-7.46 (m, 6H), 7.51-7.62 (m, 4H), 14.4 (br s). ^{13}C{^{1}H} NMR (THF-d8, 50 MHz) δ: 10.3 (d, J_{CP} = 14 Hz), 19.8 Hz (dd, $^1J_{CP}$ = 9, Hz $^4J_{CP}$ = 3 Hz), 129.0 (d, J_{CP} = 7 Hz), 129.2 (d,

[4] For BH_3 deprotection with methanol, see: Schroder, M.; Nozaki, K.; Hiyama, T. *Bull. Chem. Soc. Jpn*. **2004**, *77*, 1931.
[5] For phosphine oxide reduction with phenylsilane, see: Obora, Y.; Liu, Y. K; Tokunaga, M.; Tsuji, Y. *Eur J. Inorg. Chem*. **2006**, *1*, 222.

J_{CP} = 16 Hz), 131.8 (d, J_{CP} = 116 Hz), 134.5 (d, J_{CP} = 20 Hz), 138.0. $^{31}P\{^{1}H\}$ NMR (THF-d8, 121 MHz) δ: -41.1 (br), -36.9 (br).

Fully deprotected product of 6c: ^{1}H NMR (THF-d8, 200 MHz) δ: 0.62-1.84 (m, 20H), 1.89-2.17 (m, 2H), 7.08-7.21 (m, 6H), 7.23-7.41 (m, 4H) 14.2 (br s). $^{13}C\{^{1}H\}$ NMR (THF-d8, 50 MHz) δ: 27.5 (d, J_{CP} = 26 Hz), 27.8 (d, J_{CP} = 19 Hz), 30.4 (d, J_{CP} = 8 Hz), 31.4 (d, J_{CP} = 17 Hz), 34.0 (d, J_{CP} = 3 Hz), 34.2 (d, J_{CP} = 3 Hz), 129.0 (d, J_{CP} = 7 Hz), 129.3, 130.6, 134.5 (d, J_{CP} = 20 Hz), 138.2. $^{31}P\{^{1}H\}$ NMR (THF-d8, 81 MHz) δ: -35.9 (br), -27.0 (d, J_{PP} = 39 Hz).

16: ^{1}H NMR (THF-d8, 200 MHz) δ: 0.90 (dd, J_{HP} = 11.6 Hz, J_{HH} = 6.9 Hz, 6H), 1.02 (dd, J_{HP} = 14.9 Hz, J_{HH} = 7.1 Hz, 6H), 2.11-2.35 (m, 2H), 4.18 (s, 3H), 7.19-7.34 (m, 6H), 7.45-7.54 (m, 4H). $^{13}C\{^{1}H\}$ NMR (THF-d8, 50 MHz) δ: 19.9 (d, J_{CP} = 9 Hz), 20.6 (d, J_{CP} = 18 Hz), 42.2, 129.0 (d, J_{CP} = 7 Hz),129.3, 132.8 (d, J_{CP} = 10 Hz), 134.9 (d, J_{CP} = 21 Hz), 138.6 (d, J_{CP} = 9 Hz), 150.8 ($^{1}J_{CP}$ = 35 Hz, $^{2}J_{CP}$ = 29 Hz), 152.7 (dd, $^{1}J_{CP}$ = 29 Hz, $^{2}J_{CP}$ = 18 Hz). $^{31}P\{^{1}H\}$ NMR (THF-d8, 81 MHz) δ: -35.8 (d, J_{PP} = 48 Hz), -19.2 (d, J_{PP} = 48 Hz).

Preparation of 14: To a solution of **13** (0.045 g, 0.122 mmol) in THF (1 ml), sodium disilazane (0.022 g, 0.122 mmol) was added. The mixture was stirred at rt for 1 h. Solvent and volatile byproducts were removed *in vacuo* to afford the viscous product **14**. ^{1}H NMR (THF-d8, 200 MHz) δ: 0.85 (dd, J_{HP} = 11.4 Hz, J_{HH} = 6.9 Hz, 6H), 1.02 (dd, J_{HP} = 14.6 Hz, J_{HH} = 7.0 Hz, 6H), 2.26-2.50 (m, 2H), 7.08-7.21 (m, 6H), 7.38-7.53 (m, 4H). $^{13}C\{^{1}H\}$ NMR (THF-d8, 50 MHz) δ: 20.6 (d, J_{CP} = 10 Hz), 21.2 (d, J_{CP} = 20 Hz), 127.8, 128.1 (d, J_{CP} = 7 Hz), 134.5 (d, J_{CP} = 20 Hz), 142.0 (d, J_{CP} = 10 Hz), 144.9 (dd, $^{1}J_{CP}$ = 24 Hz, $^{2}J_{CP}$ = 5 Hz), 146.3 (dd, $^{1}J_{CP}$ = 39 Hz, $^{2}J_{CP}$ = 20 Hz). $^{31}P\{^{1}H\}$ NMR (THF-d8, 81 MHz) δ: -36.0 (d, J_{PP} = 40 Hz), -17.7 (d, J_{PP} = 40 Hz).

Preparation of Complex 17. Ligand **16** (0.009 g, 0.023 mmol) was dissolved in THF (0.25 ml) and added to a slurry of (cod)PtCl2 (0.008 g, 0.023 mmol) in THF (0.25 ml) and stirred for 0.5 h at rt. THF was removed in vacuo and the residue was washed with hexanes (3 x 1 ml), ether (3 x 1 ml), and toluene (3 x 1 ml), and extracted in CH_2Cl_2 (3 x 1 ml). The combined fractions were evaporated yielding the pure complex **17** as a white solid (0.012 g, 80%). ^{1}H NMR (CD_2Cl_2, 200 MHz) δ: 1.16 (dd, J_{HP} = 17.5 Hz, J_{HH} = 7.0 Hz, 6H), 1.33 (dd, J_{HP} = 19.0 Hz, J_{HH} = 7.1 Hz, 6H), 2.76-3.03 (m, 2H), 4.28 (s, 3H), 7.35-7.60 (m, 6H), 7.74-7.96 (m, 4H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 50 MHz) δ: 18.1 (d, J_{CP} = 18 Hz), 25.0 (d, J_{CP} = 37 Hz, J_{CPt} = 27 Hz), 44.2, 128.7 (d, J_{CP} = 12 Hz), 132.0 (d, J_{CP} = 3 Hz), 134.0 (d, J_{CP} = 12 Hz, J_{CPt} = 18 Hz). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 81 MHz) δ: 1.76 (d, J_{PPt} = 3741 Hz, J_{PP} = 6.9 Hz), 35.1 (J_{Pt} = 3542 Hz, J_{PP} = 6.9 Hz). MS (ES-TOF): *m/z* = 648.11 (M-1).

Selected bond lengths [Å] and angles [deg] of complex **17**: Pt1—P1 2.223(3), Pt1—P2 2.236(3), Pt1—Cl1 2.351(2), Pt—Cl2 2.340(4), P1—Pt1—P2 89.81(12), P1—Pt1—Cl2 178.60(14), P2—Pt1—Cl2 90.19(13), P1—Pt1—Cl1 89.83(12), P2—Pt1—Cl1 79.42(12), Cl2—Pt1—Cl1 90.18(13).

Preparation of Complex 18. Ligand **14** (0.015 mg, 0.038 mmol) was dissolved in THF (0.25 ml) and added to a slurry of (cod)$PtCl_2$ (0.007 g, 0.019 mmol) in THF (0.25 ml) at rt and stirred for 0.5 h. THF was removed in vacuo and the residue was washed with toluene (3 x 1 ml) and extracted in CH_2Cl_2 (3 x 1 ml). The combined extracts were filtered and evaporated to yield the complex **18** as a white solid. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.82 (dd, J_{HP} = 19.4 Hz, J_{HH} = 7.2 Hz, 12H), 1.10 (dd, J_{HP} = 16.1 Hz, J_{HH} = 7.1 Hz, 12H), 1.64-1.77 (m, 4H), 7.52-7.71 (m, 12H), 7.78-7.98

(m, 8H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz) δ: 19.1, 20.7, 27.3 (t, J_{CP} = 17 Hz), 129.5 (t, J_{CP} = 6 Hz), 133.3 (d, J_{CP} = 1 Hz), 134.3 (t, J_{CP} = 7 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81 MHz) δ: -6.3 (t, J_{PPt} = 2360, J_{PP} = 21 Hz), 19.3 (t, J_{PPt} = 2107, J_{PP} = 21 Hz). MS (ES-TOF): *m/z* = 932.45 (M+1). HRMS-ESI: $(M-H)^+$ = 932.2622, $C_{40}H_{49}N_6P_4Pt$ calc mass 932.2617. Anal. Calcd: C, 51.56; H, 5.19. Found: C, 51.37; H, 5.10.

Selected bond lengths [Å] and angles [deg] of complex **18**: Pt1—P1 2.3410(13), Pt1—P1^i 2.3411(13), Pt1—P2 2.3587(13), Pt1—P2^i 2.3588(13), P1—Pt1—P1^i 180.0, P1—Pt1—P2 85.85(5), P1^i —Pt1—P2 94.16(5), P1—Pt1—P2^i 94.16(5), P1^i —Pt1—P2^i 85.84(5), P2—Pt1—P2^i 179.999(2).

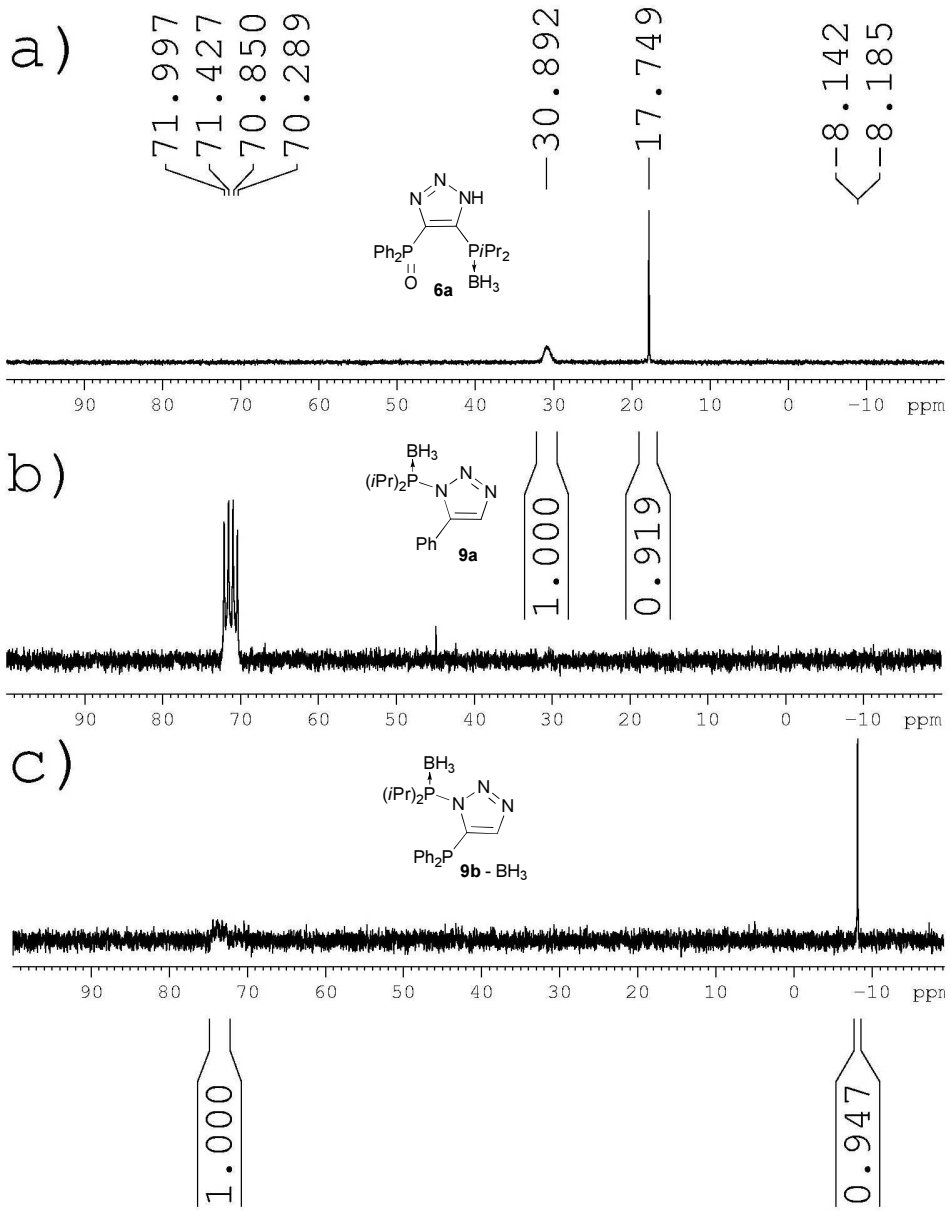
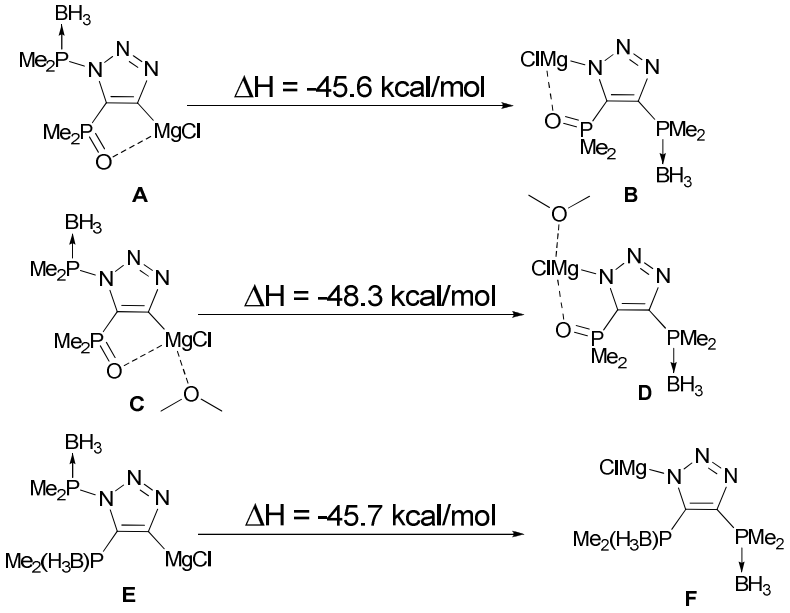


Fig. ^{31}P NMR spectra of compounds **6a**, **9a**, **9b** (after spontaneous removal of BH_3 from Ph_2P group of **9b**).

Calculation details

Full reference 13: Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

Calculated compounds (b3lyp/6-31+g(d,p))



Structures (cartesian coordinates) of the calculated compounds:

A

Mg	-2.91238800	-0.48652700	0.01258700
Cl	-5.09931500	-0.91278000	0.12176900
N	-0.20543900	-2.39778800	-0.20659500
P	-0.57924500	1.47904800	-0.05489400
P	3.00336300	-0.43723100	0.04234300
C	0.06225200	2.43030400	1.35846200
H	1.14112400	2.59263800	1.30254600
H	-0.44510700	3.39928300	1.37741900
H	-0.17750300	1.89138600	2.27874600

C	-0.15695200	2.38500300	-1.57527200
H	-0.51728200	1.80823600	-2.43101000
H	-0.67558500	3.34805200	-1.55502500
H	0.91626300	2.55196300	-1.67962500
H	4.11343500	-1.69148400	-1.87130900
H	5.28045400	-1.02932800	-0.35587100
H	4.19098100	-2.72072700	-0.10417000
C	3.13788400	-0.16938900	1.85070700
H	4.16693100	0.12368200	2.07815400
H	2.44945300	0.59607200	2.21666700
H	2.92898000	-1.11745600	2.35283900
C	3.20459400	1.21823500	-0.71448900
H	2.63119600	2.00709300	-0.22526100
H	4.26782000	1.46339200	-0.63848300
H	2.95003100	1.16124700	-1.77561700
B	4.29340100	-1.67111700	-0.67833300
O	-2.11031900	1.35396000	0.06339100
C	0.05835600	-0.20087500	-0.08774400
C	-0.90920700	-1.20539800	-0.12028100
N	1.06587100	-2.18683100	-0.23844600
N	1.29500200	-0.82667900	-0.18161900

B

Mg	-2.90063100	-0.34027700	-0.01028500
Cl	-4.99175000	-1.06954900	-0.01777600
N	-0.39973900	-2.25458800	0.00893700
P	-0.57343700	1.59732100	0.00632800
P	3.00562200	-0.36260500	-0.02069200
C	-0.02587300	2.46430800	1.50067300
H	1.06292100	2.55960400	1.50424100
H	-0.48478400	3.45732300	1.51646500
H	-0.35517200	1.90431200	2.37955200
C	0.01212100	2.52017600	-1.43477700
H	-0.31371200	2.00597700	-2.34256800
H	-0.42881500	3.52116300	-1.41164100
H	1.10326400	2.58781200	-1.42194000
H	2.89492400	2.15823100	0.52725200
H	4.64787400	1.52342100	-0.22408400
H	3.07417000	1.75533800	-1.45742500
C	3.73548400	-1.47808700	-1.27965400
H	4.82398000	-1.37736700	-1.24682300
H	3.44323800	-2.51328200	-1.09183200
H	3.38668800	-1.17531800	-2.27007700
C	3.63212000	-1.00064800	1.58407300
H	3.36682200	-2.05315800	1.70955600
H	4.71904500	-0.88189400	1.60912100
H	3.20028200	-0.41679500	2.40096800
B	3.44172600	1.49970900	-0.33151800
O	-2.11961900	1.45814000	-0.00830700
C	0.04856800	-0.09623900	-0.00810900

N	0.91047900	-2.14209800	-0.00135600
C	1.24415200	-0.81857800	-0.01423400
N	-0.95178000	-1.03470400	0.00620800

C

Cl	3.83086500	0.67313400	-2.06867300
N	-0.23439200	-2.10262700	-0.83081200
P	-0.13720300	1.52518900	0.58703600
P	-3.57796900	-0.53077800	-0.16967300
C	-0.85905400	2.88776700	-0.38408900
H	-1.95067600	2.90819900	-0.34017300
H	-0.46548900	3.83420400	-0.00195500
H	-0.53913200	2.77109800	-1.42294800
C	-0.63136800	1.76420800	2.32478900
H	-0.26091100	0.91823600	2.90930200
H	-0.15078700	2.67850500	2.68544000
H	-1.71121600	1.84853500	2.45390900
H	-4.43556300	-2.40558400	1.31237000
H	-5.77593000	-1.44448900	0.14073600
H	-4.57457600	-2.85908200	-0.67658900
C	-3.85099000	0.26995600	-1.79587700
H	-4.91118300	0.52543300	-1.88167800
H	-3.24381800	1.16959900	-1.92445100
H	-3.60192000	-0.45117200	-2.57844400
C	-3.86938800	0.78625400	1.06780900
H	-3.37159200	1.72979400	0.84045800
H	-4.94972400	0.95662800	1.08224300
H	-3.57558200	0.42456400	2.05587900
B	-4.71425200	-2.04371300	0.19391300
O	1.39326900	1.56307000	0.48010700
C	-0.65596300	-0.07733300	-0.04229600
C	0.37954000	-0.90827200	-0.46983200
N	-1.51034200	-2.04981200	-0.64823900
N	-1.83675600	-0.80735200	-0.14347900
Mg	2.33390000	0.02323000	-0.47588000
O	3.52405100	-1.02495000	0.89141700
C	4.95286900	-0.86922500	0.97172900
H	5.23170000	-0.53143800	1.97651800
H	5.44014300	-1.82469500	0.74829100
H	5.23371100	-0.13040100	0.22140600
C	3.01351800	-2.05266800	1.75276800
H	3.49415100	-3.00891600	1.51762900
H	3.20020300	-1.79044700	2.80098700
H	1.94240800	-2.12875400	1.56458500

D

C	-1.76671800	-0.75109200	-0.28255300
Cl	3.87101600	0.48679000	-2.04234000
N	-0.02592200	-1.93581300	-0.85217800
N	0.43452000	-0.74477300	-0.45347700

P	-0.12495600	1.67300200	0.48691000
P	-3.55313500	-0.46963800	-0.10035300
C	-0.78259900	2.94732800	-0.62498400
H	-1.87541800	2.94352300	-0.60347800
H	-0.41001100	3.92313100	-0.29953800
H	-0.42593200	2.75103800	-1.63931500
C	-0.76085800	2.00305900	2.15018200
H	-0.36689600	1.24934300	2.83654700
H	-0.41238100	2.99094800	2.46594800
H	-1.85325600	1.96983200	2.15522100
H	-3.64447300	2.07560100	0.33120000
H	-5.33134600	1.07200200	0.77053000
H	-3.75778400	0.95218000	2.02120400
C	-4.16501800	-2.02458400	0.65569500
H	-5.25832700	-2.00203200	0.66716800
H	-3.80734100	-2.89045900	0.09479400
H	-3.80648100	-2.08526600	1.68626100
C	-4.18517100	-0.51905500	-1.82556800
H	-3.84489900	-1.42485400	-2.33320000
H	-5.27819500	-0.48909400	-1.80214700
H	-3.82483700	0.35815400	-2.36906800
B	-4.12458400	1.10425800	0.87588600
O	1.41975500	1.65609900	0.46979300
C	-0.62734100	0.03502000	-0.08157300
N	-1.34057500	-1.95672200	-0.75684300
O	3.34816200	-1.02064900	1.01015100
C	4.78189100	-1.17488400	1.02236200
H	5.18184400	-0.80960500	1.97470300
H	5.03688800	-2.23126900	0.88636700
H	5.17092000	-0.58945100	0.18964200
C	2.68492300	-1.80437500	2.01464300
H	1.61263400	-1.65836100	1.88657500
H	2.92482200	-2.86407000	1.87666000
H	2.99824200	-1.47476800	3.01168900
Mg	2.35542400	0.12461200	-0.40308900

E

Cl	4.03511300	0.29294900	-2.12571600
N	0.02332300	-1.99652400	-0.50105400
P	-3.51086300	-0.78347600	-0.19133900
C	-1.44510900	2.89004700	-0.64085600
H	-2.52218100	2.74584300	-0.53783300
H	-1.19906000	3.92408200	-0.38259000
H	-1.15220700	2.71731900	-1.67977000
C	-1.03781700	2.07264100	2.15484400
H	-0.49071800	1.40304800	2.82327400
H	-0.79391800	3.10463400	2.42312600
H	-2.10795200	1.91000100	2.28063100
H	-4.22171100	-2.72787700	1.29015100
H	-5.58243100	-1.96451600	0.00261600

H	-4.16137400	-3.23340800	-0.69083800
C	-3.78543200	-0.08093100	-1.86214000
H	-4.86309400	0.02674900	-2.01581700
H	-3.29641100	0.88625100	-1.99716300
H	-3.39911600	-0.79031900	-2.59843100
C	-4.06395800	0.50895300	0.98100900
H	-3.70314100	1.51090100	0.74867800
H	-5.15681600	0.51050200	0.93565800
H	-3.77238500	0.22271200	1.99431600
B	-4.46134600	-2.42588600	0.14583500
C	-0.67007400	0.05494000	-0.01855800
C	0.47122200	-0.69594200	-0.29462800
N	-1.25760400	-2.07722900	-0.36956900
N	-1.75010400	-0.82946900	-0.05533500
Mg	2.47961100	0.04735700	-0.48383900
O	3.58676000	-0.90326800	1.02323600
C	5.02685300	-0.92515100	1.05910200
H	5.37895000	-0.45527100	1.98454800
H	5.37855400	-1.96126500	1.00651600
H	5.37429600	-0.37321000	0.18637400
C	2.98514200	-1.67537300	2.07361100
H	3.32658500	-2.71456600	2.01316200
H	3.25114500	-1.25144400	3.04907800
H	1.90610500	-1.63984500	1.92494700
P	-0.45023400	1.78390100	0.43787100
H	2.04463900	1.55084200	1.07988500
H	1.75623000	2.10116400	-0.85922300
H	1.51711000	3.41997700	0.61788200
B	1.43429600	2.26118200	0.29968600

F

Cl	4.06909500	0.32288700	-1.99508600
N	0.23799800	-1.75221300	-0.65685600
P	-3.47586900	-0.72633100	-0.15271300
C	-1.31379600	2.96850800	-0.79967400
H	-2.38422500	2.75358900	-0.79738500
H	-1.14948500	4.01696400	-0.53417400
H	-0.89495800	2.78857700	-1.79289100
C	-1.24065800	2.20157200	2.03360300
H	-0.75337400	1.57905900	2.78841200
H	-1.09877800	3.25244200	2.30309200
H	-2.30594200	1.96707500	1.99302200
H	-4.04406000	1.78563900	0.13051000
H	-5.53517100	0.49876700	0.53553300
H	-4.05075700	0.73950100	1.87361700
C	-3.89309400	-2.31866600	0.65654000
H	-4.97624300	-2.46072200	0.60735400
H	-3.37603200	-3.14689000	0.16821300
H	-3.59564800	-2.27208300	1.70717500
C	-3.99095300	-0.95048400	-1.90313400

H	-3.49695200	-1.82135000	-2.34062500
H	-5.07678600	-1.07664100	-1.93726200
H	-3.72674000	-0.05776600	-2.47585700
B	-4.36500400	0.76841500	0.70384600
C	-0.63321300	0.18192500	-0.06017000
N	-1.06455200	-1.93253300	-0.60363700
Mg	2.49542400	0.21157200	-0.37636900
O	3.36345800	-0.97667600	1.09007900
C	4.73485900	-1.42277100	1.03109000
H	5.24595200	-1.14989400	1.96072400
H	4.75983900	-2.50858900	0.89051700
H	5.19448100	-0.92677700	0.17705600
C	2.61813800	-1.60058200	2.14885100
H	2.59567400	-2.68477000	1.99790700
H	3.07710300	-1.36150200	3.11451800
H	1.60191500	-1.21038500	2.10846200
P	-0.43741500	1.91782000	0.41586300
H	1.98385900	1.52223300	1.23821100
H	1.87435300	2.20273600	-0.67990400
H	1.62451400	3.44167900	0.85022200
B	1.46694200	2.31607100	0.46316400
C	-1.65622100	-0.75961900	-0.23722600
N	0.52930900	-0.48375200	-0.33604600