Electronic Supplementary Information for Dalton Transactions

The First Complexes and Cyclodimerisations of Methylphosphaalkyne (P≡CMe)

Cameron Jones*, Christian Schulten and Andreas Stasch

Syntheses of compounds 3 -7.

Compound 3: To a solution of [Pt(dppe)(C_2H_4)] (100 mg, 0.16 mmol) in toluene (10 ml) at 25^0C was added P≡CMe (28 mg, 0.48 mmol) in diethyl ether. The reaction mixture was stirred for 1hr and volatiles subsequently removed *in vacuo*. The residue was recrystallised from diethyl ether to yield **3** as colourless crystals.

Compound 4: To a solution of [Pt(PEt_3)$_2$(C_2H_4)] (80 mg, 0.26 mmol) in THF (30 ml) at 25^0C was added P≡CMe (44 mg, 0.76 mmol) in diethyl ether. The reaction mixture was stirred for 1hr and volatiles subsequently removed *in vacuo*. The residue was recrystallised from toluene to yield **4** as colourless crystals.

Compound 5: To a solution of [Pt(PCy_3)$_2$] (50 mg, 0.067 mmol) in toluene (5 ml) at -78^{o}C was added P≡CMe (8 mg, 0.13mmol). The reaction mixture was stirred for 10 min before warming to 25^{o}C. After a further 1 hr volatiles were removed *in vacuo* and the residue recrystallised from toluene to yield **5** as red crystals.

Compounds 6 and 7: To a solution of [W(CO)$_5$(THF)] (194 mg, 0.55 mmol) in THF (50 ml) at 25^{o}C was added P≡CMe (80 mg, 1.40 mmol). The mixture was stirred for 18 hrs and volatiles removed *in vacuo*. The residue was extracted with hexane and the extract placed at -30^{o}C for 24 hrs to yield **7** as yellow-orange crystals. The remaining solution was

chromatographed (silica gel/hexane) and the orange band collected and concentrated to yield **6** as orange crystals.

$^{31}P\{^{1}H\}$ NMR spectroscopic data for compounds 1 and 2.

Compound 1: $^{31}P\{^{1}H\}$ NMR (121.6 MHz, C_6D_6, 298K): δ 51.0 (dd, $^{2}J_{PP}$ = 23.9 and 58.6 Hz, $^{1}J_{PtP}$ = 3214 Hz, dppe), 54.9 (dd, $^{2}J_{PP}$ = 17.9 and 58.6 Hz, $^{1}J_{PtP}$ = 2977 Hz, dppe), 102.4 (dd, $^{2}J_{PP}$ = 23.9 and 17.9 Hz, $^{1}J_{PtP}$ = 178.0 Hz, PCMe).

Compound 2: $^{31}P\{^{1}H\}$ NMR (121.6 MHz, C_6D_6, 298K): δ 13.4 (v. tr., $^{2}J_{PP}$ = 21.3 Hz, $^{1}J_{PtP}$ = 3141 Hz, PEt_3), 21.3 (v. tr., $^{2}J_{PP}$ = 21.3 Hz, $^{1}J_{PtP}$ = 3476 Hz, PEt_3), 90.4 (v. tr., $^{2}J_{PP}$ = 23.1 Hz, $^{1}J_{PtP}$ = 167.5 Hz, PCMe).

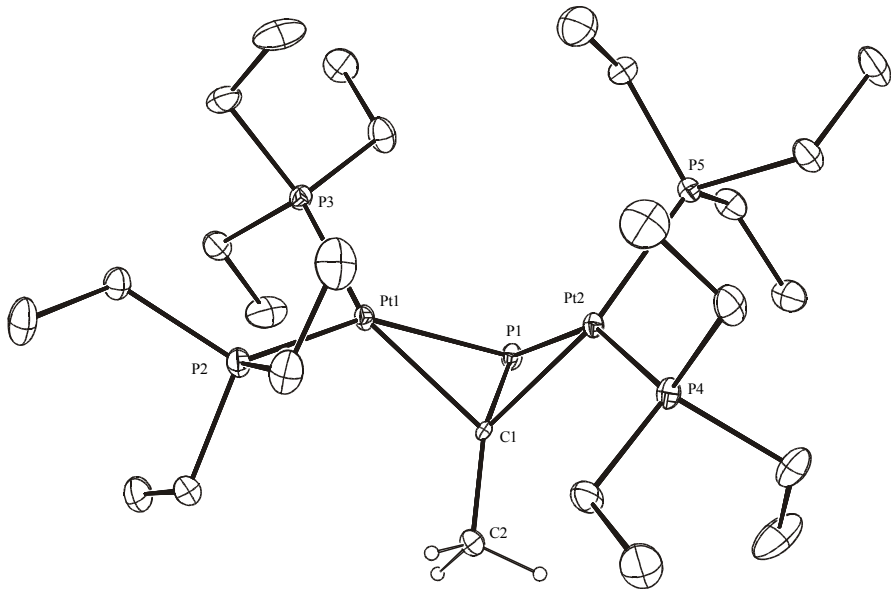

Fig. 1-S Molecular structure of **4** (25% thermal ellipsoids, non-phosphaalkyne hydrogens omitted for sake of clarity). Selected bond lengths (Å) and angles (°) relating to one of the two components of the disordered PCMe ligand: Pt(1)-C(1) 2.21(4), Pt(1)-P(2) 2.269(2), Pt(1)-P(3) 2.270(2), Pt(1)-P(1) 2.394(7), Pt(2)-C(1) 2.13(4), Pt(2)-P(4) 2.265(2), Pt(2)-P(5) 2.275(2), Pt(2)-P(1) 2.376(6), P(1)-C(1) 1.715(17), C(1)-C(2) 1.518(17), C(1)-Pt(1)-P(2) 105.5(6), C(1)-Pt(1)-P(3) 147.7(6), P(2)-Pt(1)-P(3) 105.93(9), C(1)-Pt(1)-P(1) 43.5(5), P(2)-Pt(1)-P(1) 148.66(15), P(3)-Pt(1)-P(1) 104.34(15), C(1)-Pt(2)-P(1) 44.3(6), P(4)-Pt(2)-P(1) 147.74(15), P(5)-Pt(2)-P(1) 101.03(15), C(1)-P(1)-Pt(2) 60.2(13), C(1)-P(1)-Pt(1) 62.4(13), Pt(2)-P(1)-Pt(1) 82.9(2), P(1)-C(1)-Pt(1) 74.1(11), Pt(2)-C(1)-Pt(1) 93.5(12), P(1)-C(1)-Pt(2) 75.5(11).

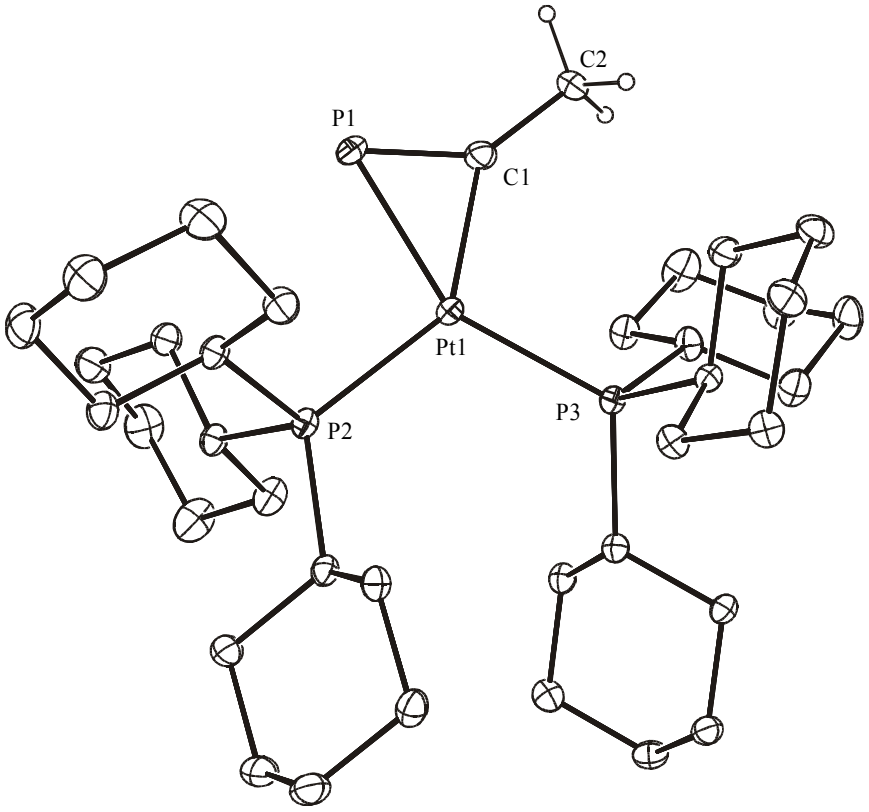

Fig. 2-S Molecular structure of **5** (25% thermal ellipsoids, non-phosphaalkyne hydrogens omitted for sake of clarity). Selected bond lengths (Å) and angles (º) relating to one of the two components of the disordered PCMe ligand: Pt(1)-C(1) 2.034(8), Pt(1)-P(3) 2.3035(11), Pt(1)-P(2) 2.3072(10), Pt(1)-P(1) 2.354(3), P(1)-C(1) 1.623(9), C(1)-C(2) 1.505(11), C(1)-Pt(1)-P(3) 106.7(3), C(1)-Pt(1)-P(2) 140.0(3), P(3)-Pt(1)-P(2) 113.32(3), C(1)-Pt(1)-P(1) 42.6(3), P(3)-Pt(1)-P(1) 149.35(8), P(2)-Pt(1)-P(1) 97.33(8), C(1)-P(1)-Pt(1) 58.1(3), C(2)-C(1)-P(1) 140.9(6), C(2)-C(1)-Pt(1) 139.8(6), P(1)-C(1)-Pt(1) 79.2(4).

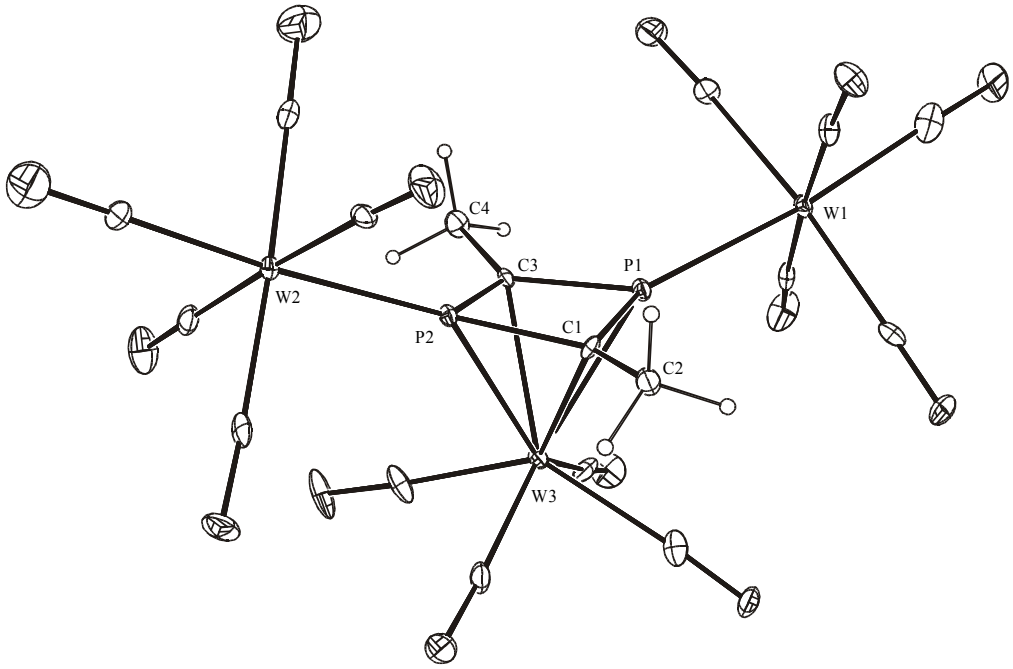

Fig. 3-S Molecular structure of **7** (25% thermal ellipsoids). Selected bond lengths (Å) and angles (º) for one of the crystallographically independent molecules in the asymmetric unit: P(1)-C(3) 1.765(16), P(1)-C(1) 1.797(17), W(1)-P(1) 2.440(5), P(1)-C(3) 1.765(16), P(1)-C(1) 1.797(17), P(1)-W(3) 2.494(5), C(1)-P(2) 1.806(16), C(1)-W(3) 2.356(17), W(2)-P(2) 2.440(4), P(2)-C(3) 1.755(17), P(2)-W(3) 2.492(4), C(3)-P(1)-C(1) 84.2(8), C(2)-C(1)-P(1) 131.8(13), C(2)-C(1)-P(2) 132.2(13), P(1)-C(1)-P(2) 93.8(7), C(3)-P(2)-C(1) 84.3(7).