Electronic Supplementary Material (ESI) for Chemical Communications

Phosphine-alkene ligand-mediated alkyl-alkyl and alkyl-halide elimination processes from palladium(II)

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ELECTRONIC SUPPLEMENTARY INFORMATION

Experimental Details

All operations were conducted under an atmosphere of dry nitrogen using standard Schlenk and cannula techniques, or in a nitrogen-filled glove box (Saffron Scientific), under ambient laboratory lighting, unless stated otherwise. All NMR-scale reactions were conducted using NMR tubes fitted with Young's tap valves. Bulk solvents were purified using an Innovative Technologies SPS facility and degassed prior to use. DME was distilled from Na/benzophenone. NMR solvents (C_6D_6 and toluene-d_8) were dried over CaH_2, distilled and degassed prior to use. $CDCl_3$ was dried over P_2O_5, passed through a column of alumina, and degassed prior to use.

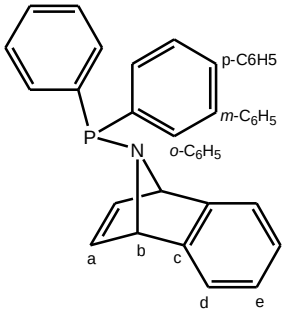
N-BOC-7-*aza*-benzobicyclo[2.2.1]hept-2-ene,[1] 7-*aza*-benzobicyclo-[2.2.1]hept-2-ene (**1**),[2] $PdMe_2$(tmeda),[3] and PdCl(Me)(COD)[4] were prepared according to literature procedures. Toluene-d_8 and C_6D_6 were purchased from Goss Scientific. All other reagents were purchased from Aldrich. Where appropriate, liquid reagents were dried, distilled, and deoxygenated prior to use,[5] while gases were passed through a drying column (silica/$CaCO_3$/P_2O_5) prior to use.

Solution phase NMR spectra were collected on a Varian Mercury 400, a Varian Inova 500, a Varian VNMRS-600, a Varian VNMRS-700, and a Bruker Avance 400 at ambient probe temperatures (~290 K) unless stated otherwise. Chemical shifts were referenced to residual protio impurities in the deuterated solvent (^{1}H), ^{13}C shift of the solvent (^{13}C), or to external aqueous 85% H_3PO_4 (^{31}P). Solvent proton shifts (ppm): $CDCl_3$, 7.26 (s); C_6D_6, 7.15 (s); CD_2Cl_2 5.32 (t); C_7D_8 2.08 (m). Solvent carbon shifts (ppm): $CDCl_3$, 77.4 (t); C_6D_6, 128.6 (t); CD_2Cl_2, 54.0 (quin); C_7D_8 20.4 (m). Where necessary ^{1}H NMR and ^{13}C NMR spectra were assigned with the aid of COSY, DEPT 135, HMBC and HMQC experiments. Where reaction conversions were measured by NMR spectroscopy, spectra were recorded a standard 5 mm NMR tube fitted with a J. Young's valve with a sealed glass capillary tube placed inside containing $CDCl_3$ and an appropriate quantity of PPh_3, acting as a standard.

Mass spectra were recorded by the EPSRC National Mass Spectrometry Service at the University of Wales, Swansea, (nano-ESI: Waters ZQ-4000) or Durham University Mass Spectrometry Service (Waters TQD equipped with Acquity UPLC and an electrospray ion source) and are reported in (*m/z*). The isotope distributions for all parent ion peaks were verified *via* comparison with the theoretical isotope pattern. Elemental analyses were performed by The Analytical Services Department of the Chemistry Department, Durham University.

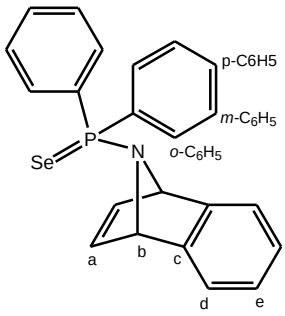
Synthesis of N-PPh$_2$-7-aza-benzobicyclo[2.2.1]hept-2-ene (2)

A solution of Ph_2PCl (1.70, 2.09 g cm^3, 9.47 mmol) in CH_2Cl_2 (20 cm^3) was added drop-wise to a cooled solution (–30 °C) of amine **1** (1.316 g, 9.19 mmol) and NEt_3 (2.60 cm^3, 1.89 g, 18.7 mmol) in CH_2Cl_2 (60 cm^3). The reaction was subsequently stirred for 15 mins before being allowed to warm to RT overnight. All volatile components were removed *in vacuo*. Recrystallation from hot hexane afforded compound **2** as an off-white solid (2.085 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.94 (2H, s, H_b), 6.60-6.62 (2H, m, H_d), 6.77-6.78 (2H, m, H_a), 6.79-6.81 (2H, m, H_e), 7.15-7.21 (10H, m, C_6H_5); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 68.1 (d, $^2J_{PC}$ = 10 Hz, C_b), 118.7 (s, C_d), 122.8 (s, C_e), 126.9 (d, J_{PC} = 7 Hz, *o-/m*-C_6H_5), 127.3 (s, *p*-C_6H_5), 131.2 (d, J_{PC} = 20 Hz, *o-/m*-C_6H_5), 138.2 (d, $^1J_{PC}$ = 11 Hz, *ipso*-C_6H_5), 143.0 (d, $^3J_{PC}$ = 4 Hz, C_a), 150.0 (d, $^3J_{PC}$ = 3 Hz, C_c); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 41.6 (s). Anal. Calcd. for $C_{22}H_{18}NP$: C, 80.72; H, 5.54; N, 4.28. Found C, 80.42; H, 5.60; N, 4.33.



Synthesis of 2.Se

An NMR tube fitted with a J. Young's valve was charged with **2** (40 mg, 0.12 mmol), elemental grey Se (10 mg, 0.13mg), and $CDCl_3$ (0.7 mL). Compound **2.Se** was obtained quantitatively (according to ^{31}P NMR spectroscopy) after 12 h at r.t. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: +50.8 (d, $^1J_{SeP}$ = 764 Hz).

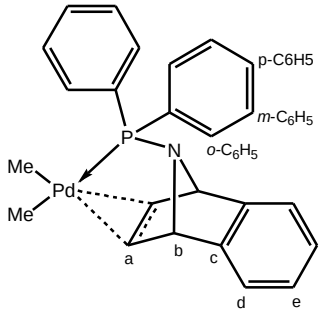


Synthesis of [PdMe$_2$(κ^2-P,C-2)] (3)

A solution of **2** (40 mg, 0.12 mmol) in toluene (5 mL) was added drop-wise to a solution of $PdMe_2$(tmeda) (30 mg, 0.12 mmol) in toluene (5 mL). The mixture was allowed to stir for 1 h at r.t. affording compound **3** quantitatively (according to ^{31}P NMR spectroscopy). Subsequently, crystals of **3** suitable for an X-ray diffraction study were grown by cooling (–30 °C) the concentrated toluene solution of **3**. If left in solution at r.t. complex **3** transformed cleanly into **4** over a period of 5h at r.t.

In a separate experiment, an NMR tube fitted with a J. Young's valve was loaded with **2** (13 mg, 0.12 mmol), $PdMe_2$(tmeda) (10 mg, 0.12 mmol), C_6D_6 (0.7 mL), and a sealed capillary tube containing a solution of PPh_3 as a standard. In less than 10 minutes complete consumption of **2** was evident, something accompanied by a >99% conversion to **3** according to proton coupled ^{31}P NMR spectroscopic analysis. Once conversion to **3** was complete (5 days) >0.9 equivalents of ethane were present in solution according to integration (^{1}H NMR spectroscopy).

^{1}H NMR (700 MHz, C_6D_6) δ: 0.97 (3H, d, $^3J_{PH}$ = 7.7 Hz, CH_3), 1.69 (3H, d, $^3J_{PH}$ = 7.5 Hz, CH_3), 4.25 (2H, d, $^3J_{HH}$ = 2.9 Hz, CH_b), 5.78 (2H, bs, CH_a), 6.69-6.74 (4H, m, CH_d and CH_e), 7.01-7.04 (6H, m, *o*- and *p*-C_6H_5), 7.93-7.98 (4H, m, *m*-C_6H_5); ^{13}C{^{1}H} NMR (176 MHz, C_6D_6) 2.6 (d, $^2J_{PC}$ = 8 Hz, CH_3), 5.8 (d, $^2J_{PC}$ = 120 Hz, CH_3), 71.3 (d, $^2J_{PC}$ = 11 Hz, C_b), 119.2 (s, C_a), 121.4 (s, C_d), 125.6 (s, C_e), 128.4 (s, C_c), 129.2 (d, $^2J_{PC}$ = 10 Hz, *o*-C_6H_5), 131.4 (d, $^4J_{PC}$ = 2 Hz, *p*-C_6H_5), 133.2 (d, $^3J_{PC}$ = 15 Hz, *m*-C_6H_5), 145.7 (d, $^1J_{PC}$ = 10 Hz, *ipso*-C_6H_5); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: +81.3 (s) ppm. Despite repeated attempts, satisfactory elemental analyses and mass spectrometric data for **3** could not be obtained since the complex degrades slowly even in the solid state.

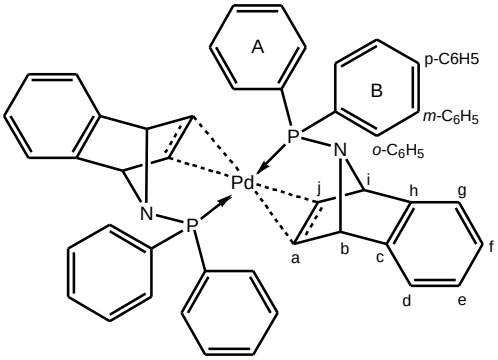


Synthesis of [Pd(κ^2-P,C-2)$_2$] (4)

A solution of **2** (0.15 g, 4.58×10^{-4} mol) in toluene (15 mL) was added dropwise to a suspension of $PdMe_2$(tmeda) (0.057 g, 2.26×10^{-4} mol) in toluene (10 mL). The mixture was allowed to stir for 18 h at r.t., resulting in the quantitative formation of complex **4** (according to proton coupled ^{31}P NMR spectroscopy). Removal of volatile components under reduced pressure afforded **4** as a dark brown solid, which was washed with Et_2O (0.15 g, 87%). Crystals suitable for an X-ray diffraction study were grown by slow diffusion of hexane into a concentrated toluene solution of **4**.

In a separate experiment, an NMR tube fitted with a J. Young's valve was loaded with **2** (26 mg, 0.040 mmol), $PdMe_2$(TMEDA) (10 mg, 0.040 mmol) and d_8-toluene (0.7 mL). The reaction was subsequently monitored by multinuclear NMR spectroscopy until complete formation of **4** was achieved (5 h). A second, identical reaction was undertaken in which the NMR tube was placed in direct sunlight. No appreciable difference in reaction rate was recorded.

Complex **4** presents a coupling pattern consistent with the "X" part of an "ABX" system in its carbon spectrum due to a slight asymmetry about the Pd(0) centre, something consistent with other homoleptic M(0) complexes,[6] and which renders each of the ligands **2** unsymmetrical.
^{1}H NMR (400 MHz, C_6D_6) δ: 4.21 (2H, bs, $CH_{b/i}$), 4.70-4.74 (2H, m, $CH_{a/j}$), 4.76 (2H, bs, $CH_{b/i}$), 4.87-4.92 (2H, m, $CH_{a/j}$), 6.89-6.95 (6H, m, $CH_{d/g}$ and $CH_{e/f}$), 7.06-7.08 (2H, m, $CH_{d/g}$), 7.08-7.19 (12H, m, *o*- and *p*-C_6H_5), 7.94-8.00 (4H, m, *m*-C_6H_5), 8.03-8.09 (4H, m, *m*-C_6H_5); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) 70.7 (m, $C_{b/i}$), 72.1 (m, $C_{b'/i'}$), 75.9 (m, $C_{a/j}$), 80.7 (m, $C_{a'/j'}$), 120.2, 120.4, 125.1 and 125.2 (s, $C_{d/g}$ and $C_{e/f}$), 128.4 (m, *o*-C_6H_5); 129.8 (s, *p*-C_6H_5), 130.0 (s, *p*-C'$_6H_5$), 132.9 (m, *m*-C_6H_5), 133.2 (m, *m*-C'$_6H_5$), 138.3 (m, *ipso*-C_6H_5), 138.5 (m, *ipso*-C'$_6H_5$); 147.3 (m, $C_{c/h}$), 148.4 (m, $C_{c'/h'}$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: +82.2 (s) ppm; MS: despite repeated attempts using a variety of techniques, acquisition of satisfactory mass spectral data proved impossible. Anal. Calcd. for $C_{44}H_{36}N_2P_2Pd$: C, 69.43; H, 4.77; N, 3.68. Found C, 69.22; H, 4.65; N, 3.71.

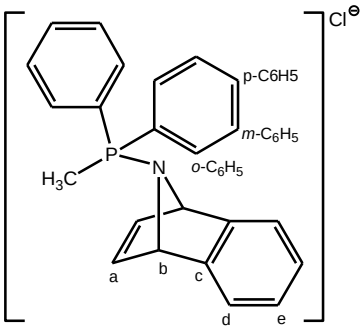


Reaction of PdCl(Me)(COD) with 2 (P:Pd = 3:1) affording 4 and [9]Cl

To an NMR tube fitted with a J. Young's valve containing **2** (35 mg, 0.107 mmol) and $CDCl_3$ (0.8 mL) was added PdCl(Me)(COD) (9 mg, 0.034 mmol). In under 10 minutes complete consumption of **2** was evident by ^{31}P NMR spectroscopic analysis, with the appearance of two new signals in a 2:1 ratio at 82.9 (**4**) and 38.1 ([**9]Cl**) ppm, respectively (by integration of the proton coupled ^{31}P NMR spectrum). By integration of against a standard present in a sealed capillary tube, the conversion of complex **2** to complex **4** was 96% and to [**9]Cl** was 89%. Subsequently, all volatile components were removed from the solution *in vacuo*. Extraction of complex **4** into toluene (3 × 1 mL) afforded phosphonium salt [**9]Cl** as a pale yellow solid (10 mg, 80%).

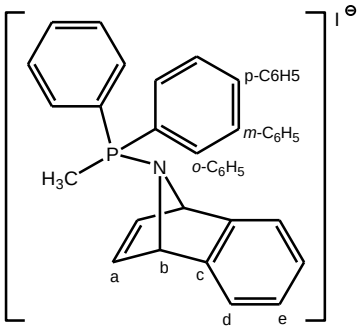
Phosphonium salt [9]Cl:

^1H NMR (400 MHz, $CDCl_3$) δ: 2.82 (3H, d, $^2J_{PH}$ = 13.0 Hz, PCH_3), 5.52 (2H, m, CH_b), 6.92-6.94 (2H, m, CH_d), 7.11 (2H, m, CH_a), 7.23-7.25 (2H, m, CH_e), 7.62-7.65 (4H, m, *m*-C_6H_5), 7.73-7.77 (2H, m, *p*-C_6H_5), 7.84-7.89 (4H, m, *o*-C_6H_5); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ: 38.1 ppm; MS (ES+) 342 $(M–Cl)^+$.



To verify the identity of **[9]Cl**, an authentic sample of the corresponding methyl phosphonium iodide salt **[9]I** was prepared by treating a $CDCl_3$ (0.7 mL) solution of **2** (25 mg, 0.076 mmol) with MeI (5.0 μL, 0.080 mmol). Standing at r.t. for 12 h followed by removal of all volatile components *in vacuo* afforded **[9]I**, (31 mg, 87%).

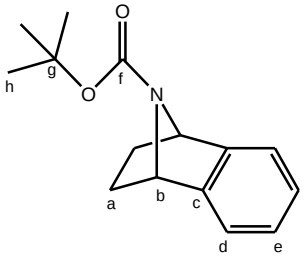
^{1}H NMR (700 MHz, $CDCl_3$) δ: 2.70 (3H, d, $^2J_{PH}$ = 13.0 Hz, PCH_3), 5.49 (2H, m, CH_b), 6.87-6.90 (2H, m, CH_d), 7.12 (2H, m, CH_a), 7.24-7.26 (2H, m, CH_e), 7.59-7.62 (4H, m, *m*-C_6H_5), 7.70-7.74 (2H, m, *p*-C_6H_5), 7.77-7.81 (4H, m, *o*-C_6H_5); ^{13}C NMR (176 MHz, $CDCl_3$) δ: 11.7 (d, $^2J_{CP}$ = 59 Hz, P*C*H_3), 67.7 (s, C_b), 119.9 (d, $^1J_{CP}$ = 100 Hz, *ipso*-C_6H_5), 121.6 (s, C_e), 125.8 (s, C_d), 130.4 (d, $^3J_{CP}$ = 13 Hz, *m*-C_6H_5), 132.6 (d, $^2J_{CP}$ = 11 Hz, *o*-C_6H_5), 135.4 (d, $^4J_{CP}$ = 3 Hz, *p*-C_6H_5), 143.7 (d, $^3J_{CP}$ = 6 Hz, C_a), 151.2 (d, $^3J_{CP}$ = 5 Hz, C_c); ^{31}P NMR (283 MHz, $CDCl_3$) δ: 37.1 ppm; MS (ES+) 342 $(M–I)^+$.



Synthesis of N-BOC-7-aza-benzobicyclo[2.2.1]heptane

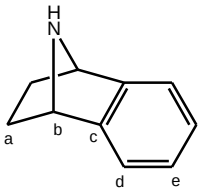
The title compound was prepared according to a slight modification of the literature procedure[7]: *N*-BOC-7-*aza*-benzobicyclo[2.2.1]hept-2-ene (2.41 g, 9.9 mmol) was added to 5% Pd/C (250 mg) in an oven-dried two-necked flask fitted with a reflux condenser and dry absolute MeOH (60 mL) subsequently added under nitrogen. A hydrogen-filled balloon was connected to the apparatus *via* a greased ground glass tap. The ensuing reaction mixture was stirred at r.t. for 24

hours. The mixture was then filtered and passed through Celite. Subsequently, the solvent was removed *in vacuo* to yield *N*-BOC-7-*aza*-benzobicyclo[2.2.1]heptane as a yellow oil (2.15 g, 89%). This oil was subsequently used without further purification. ^{1}H NMR (700 MHz, $CDCl_3$) δ: 1.29 (2H, d, $^{2}J_{HH}$ = 8 Hz, *endo*-H_a), 1.40 (9H, s, BOC), 2.10 (2H, d, $^{2}J_{HH}$ = 8 Hz, *exo*-H_a), 5.11 (2H, s, H_b), 7.12-7.14 (2H, m, H_e), 7.21-7.24 (2H, m, H_d); $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ: 26.8 (s, C_a), 28.3 (s, C_h), 61.2 (s, C_b), 80.1 (s, C_g), 119.5 (s, C_e), 126.4 (s, C_d), 145.0 (s, C_c), 155.4 (s, C_f).



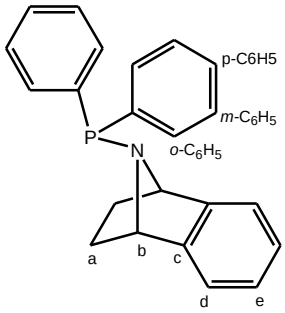
Synthesis of 7-aza-benzobicyclo[2.2.1]heptane

The title compound was prepared according to a slight modification of the literature procedure[7]: Freshly distilled acetyl chloride (5.2 ml, 70.0 mmol) was added drop-wise to absolute MeOH (50 ml) at 0 ^{o}C under a nitrogen atmosphere. The solution was stirred at this temperature for 5 minutes prior to addition of *N*-BOC-7-*aza*-benzobicyclo-[2.2.1]heptane (2.15 g). The reaction mixture was allowed to warm to r.t. and stirred for 2 hours. Distilled water (150 mL) was added and the mixture was extracted with Et_2O (3 × 25 mL). The pH of the aqueous layer was adjusted to pH 10 by addition of potassium carbonate. The amine gradually appeared as a dark organic layer above a pale pink aqueous layer. The aqueous layer was washed with Et_2O (3 × 20 mL). The organic fractions from both extractions were combined, dried over $MgSO_4$, and the solvent removed *in vacuo* overnight. This yielded 7-*aza*-benzobicyclo[2.2.1]heptane as a brown powder (0.978 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.22-1.28 (2H, m, *endo*-H_a), 2.01-2.07 (2H, m, *exo*-H_a), 2.87-3.05 (1H, bs, NH), 4.52-4.54 (2H, m, H_b), 7.05-7.11 (2H, m, H_e), 7.16-7.22 (2H, m, H_d); $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ: 26.3 (s, C_a), 60.9 (s, C_b), 119.1 (s, C_d), 125.9 (s, C_e), 148.0 (s, C_c).



Synthesis of N-PPh$_2$-7-aza-benzobicyclo[2.2.1]heptane (6)

A cooled (–30 °C) solution of 7-*aza*-benzobicyclo[2.2.1]heptane (0.302 g, 2.07 mmol) in dichloromethane (20 mL) was added drop-wise to a simultaneously cooled (–30 °C) solution of $ClPPh_2$ (0.37 mL, 2.07 mmol) and NEt_3 (0.58 mL, 4.20 mmol) in dichloromethane (10 mL). The resulting brown solution was stirred at –30 °C for 10 mins, and then allowed to warm to r.t. and stirred for 18 hours. The solvent was then removed *in vacuo* and the resulting brown solid recrystallised from hexane (80 mL) to yield **6** as a pale yellow solid (0.235 g, 34%). ^{1}H NMR (700 MHz, $CDCl_3$) δ: 1.20-1.26 (2H, m, *endo*-H_a), 1.85-1.89 (2H, m, *exo*-H_a), 4.61-4.63 (2H, m, H_b), 6.86-6.89 (4H, m, H_d and H_e), 7.20-7.26 (10H, m, *o*-C_6H_5, *m*-C_6H_5, *p*-C_6H_5); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ: 28.4 (d, $^3J_{PC}$ = 4 Hz, C_a), 64.6 (d, $^2J_{PC}$ = 10 Hz, C_b), 118.6 (s, $C_{d/e}$), 125.4 (s, $C_{d/e}$), 128.0 (d, $^3J_{PC}$ = 6 Hz, m-C_6H_5), 128.4 (s, *p*-C_6H_5), 132.2 (d, $^2J_{PC}$ = 20 Hz, *o*-C_6H_5), 140.0 (d, $^1J_{PC}$ = 12 Hz, C_f), 147.3 (d, $^3J_{PC}$ = 3 Hz, C_c); ^{31}P{^{1}H} NMR (283 MHz, $CDCl_3$) δ: 38.6 (s). Anal. Calcd. for $C_{22}H_{20}NP$: C, 80.22; H, 6.12; N, 4.25. Found C, 80.03; H, 6.00; N, 4.17.



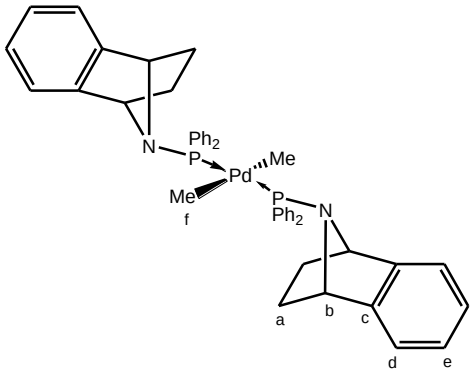
Synthesis of trans-[PdMe$_2$(κ^1-P-6)] (8)

An NMR tube fitted with a J. Young's valve was charged with $PdMe_2$(tmeda) (10 mg, 4 mmol), phosphine **7** (13 mg, 8 mmol) and toluene-d_8 (0.8 mL), and the reaction followed *via* ^{31}P NMR spectroscopy. The rapidly formed *cis*-isomer **7** isomerised completely to afford the *trans* complex **8** (as the only product) with quantitative conversion (by proton coupled ^{31}P NMR spectroscopy) achieved within 24 h at ambient temperature (~20 °C); 40% conversion to 8 occurs within 5

minutes at ambient temperature. Detailed characterisation was only carried out on the stable *trans* isomer due. Attempts were made to definitively confirm the structure of **7** by ^{1}H NMR spectroscopy at low temperature (–20 °C); however, due to overlapping (free tmeda) and broad resonances the characteristic signals of the methyl substituents (and associated coupling to ^{31}P) were obscured. By way of comparison, a related reaction between $PdMe_2$(tmeda) and two equivalents of 1-(diphenylphosphino)pyrrolydine (**DPP**) has been undertaken.[8] This rapidly formed *cis*-$PdMe_2$(**DPP**)$_2$ {^{1}H NMR (400 MHz, C_6D_6) δ: 1.00 (6H, dd, $^{3}J_{PH}$ = 7.3 Hz, $^{3}J_{PH}$ = 4.7 Hz, CH_3, + other resonances); ^{31}P NMR (162 MHz, C_6D_6) δ: 70.1 (s)}, which over a period of 1 day slowly isomerised to *trans*-$PdMe_2$(**DPP**)$_2$ {^{1}H NMR (400 MHz, C_6D_6) δ: –0.20 (6H, t, $^{3}J_{PH}$ = 0.2 Hz, CH_3, + other resonances); ^{31}P NMR (162 MHz, C_6D_6) δ: 67.8 (s)}.

cis-[PdMe$_2$(κ^1-P-6)$_2$] (7): ^{31}P NMR (162 MHz, toluene-d_8) δ: 61.0 (s).

trans-[PdMe$_2$(κ^1-P-6)$_2$] (8): ^{1}H NMR (600 MHz, toluene-d_8) δ: 0.33 (6H, s, H_f), 0.94-0.98 (4H, m, *endo*-H_a), 1.60-a1.63 (4H, m, *exo*-H_a), 4.67 (4H, s, H_b), 6.56-6.60 (4H, m, H_d), 6.76-6.80 (4H, m, H_e), 6.94-7.04 (12H, m, *o*-C_6H_5 and *p*-C_6H_5), 7.29 (8H, bs, *m*-C_6H_5); ^{13}C{^{1}H} NMR (151 MHz, toluene-d_8) δ: –8.5 (s, C_f), 28.6 (s, C_a), 65.0 (s, C_b), 118.5 (s, C_d), 125.4 (s, C_e), 127.5 (s, *o*-C_6H_5 / *p*-C_6H_5), 127.7 (s, *o*-C_6H_5 / *p*-C_6H_5), 132.4 (m, *m*-C_6H_5), 141.7-141.9 (m, *ipso*-C_6H_5), 147.9 (s, C_c); ^{31}P{^{1}H} NMR (162 MHz, toluene-d_8) δ: 59.7 (s).



Computation

All *ab initio* computations were carried out using the Gaussian 03 package.[9] The model and full geometries of **1** and **2** were optimised at the B3LYP/6-31G* level of theory[10,11] with no

symmetry constraints. Frequency calculations on these optimised geometries have no imaginary frequencies. The electronic structures were also computed at the same level of theory.

References

1 M. Lautens, K. Fagnou, and V. Zunic, *Org. Lett.*, 2002, **4**, 3465.

2 A. H. G. P. Prenzel, N. Deppermann, and W. Maison, 2006, **8**, 1681.

3 W. de Graaf, J. Boersma, W. J. J. Smeets, A. L. Spek and G. van Koten, *Organometallics*, 1989, **8**, 2907.

4 C. J. Elsevier, J. M. Ernsting, P. W. N. M. van Leeuwen, R. E. Rulke, A. L. Spek and K. Vrieze, *Inorg.Chem.*, 1993, **32**, 5769-5778.

5 W. L. F. Armarego, D. D. Perrin, *'Purification of Laboratory Chemicals'*, 3rd ed., Pergamon Press, New York, 1988.

6 C. C. Lu, E. Bill, T. Weyhermüller, E. Bothe, and K. Wieghardt, *J. Am. Chem. Soc.*, 2008, **130**, 3181.

7 T. Ohwada, S. Ishikawa, Y. Mine, K. Inami, T. Yanagimoto, F. Karaki, Y. Kabsawa, Y. Otani, M. Mochizuki, *Bioorg. Med. Chem.*, 2011, **19**, 2726

8 A. Phanopoulos, L. Tuxworth, P. W. Dyer, unpublished results.

9 *Gaussian 03*, Revision C.02, 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, 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, USA, 2004.

10 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

11 (*a*) G. A. Petersson and M. A. Al-Laham, *J. Chem. Phys.*, 1991, **94**, 6081; (*b*) G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley and J. Mantzaris, *J. Chem. Phys.*, 1988, **89**, 2193.