

## Supporting Information

# Synthesis and reactivity of the methylene arenium form of a benzyl cation, stabilized by complexation

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## General Procedures

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with an MO 40-2 inert gas purifier, or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. Commercially available reagents were used as received. The precursor (tmeda)Pd(BHT-OSiMe<sub>3</sub>)Br was prepared according to a literature procedure. NMR spectra were recorded at 400 (<sup>1</sup>H), 100 (<sup>13</sup>C) and 162 (<sup>31</sup>P) MHz using a Bruker AMX-400 NMR spectrometer and at 500 (<sup>1</sup>H), 126 (<sup>13</sup>C), 202 (<sup>31</sup>P) using Bruker DPX 500 spectrometer. All spectra were recorded at 23 °C unless otherwise specified. <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. <sup>1</sup>H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents (2.09 ppm, toluene; 5.32 CH<sub>2</sub>Cl<sub>2</sub> and 7.24 ppm, CDCl<sub>3</sub>). In <sup>13</sup>C{<sup>1</sup>H} NMR measurements the signals of d<sup>8</sup>-toluene (20.09 ppm), CD<sub>2</sub>Cl<sub>2</sub> (53.80 ppm) and CDCl<sub>3</sub> (77.00 ppm) were used as a reference. <sup>31</sup>P NMR chemical shifts are reported in ppm downfield from H<sub>3</sub>PO<sub>4</sub> and referenced to an external 85% solution of phosphoric acid in D<sub>2</sub>O. Screw-cap 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet.

## Preparation of (dtp)Pd(QM) (2)

To a THF solution (1 mL) of complex **1** (40 mg, 0.07 mmol), pre-cooled to -30 °C, was added a THF solution (1 mL) of the dtp ligand (25 mg, 0.08 mmol) pre-cooled to -30 °C and the reaction mixture was kept at -30 °C for 30 min. The solvent was evaporated and the resulting yellow solid was washed with pentane and dissolved in ether. Evaporation of the solvent yielded 36 mg (0.06 mmol, 79 % yield) of **2**.

<sup>31</sup>P{<sup>1</sup>H} NMR (d<sup>8</sup>-toluene): 50.48 (d, J<sub>P-P</sub> = 7 Hz), 40.75 (d, J<sub>P-P</sub> = 7 Hz). <sup>1</sup>H NMR (d<sup>8</sup>-toluene): 6.72 (s, 2H, QM-ring), 2.97 (t, J<sub>P-H</sub> = 6 Hz, 2H, exocyclic), 1.68 (s, 18 H, tBu-QM), 1.38 (d, J<sub>H-H</sub> = 4 Hz, 2H, dtp), 1.26 (m, 2H, dtp), 1.14 (m, 2H, dtp), 1.00 (d, J<sub>P-H</sub> = 12 Hz, 18 H, tBu-dtp), 0.90 (d, J<sub>P-H</sub> = 12 Hz, 18 H, tBu-dtp). <sup>13</sup>C{<sup>1</sup>H} NMR (d<sup>8</sup>-toluene): 184.09 (d, J<sub>P-C</sub> = 4 Hz, C=O), 141.92 (d, J<sub>P-C</sub> = 3 Hz, QM-ring), 139.14 (dd, J<sub>P-C</sub> = 3 Hz, 1 Hz, QM-ring), 77.65 (dd, J<sub>P-C</sub> = 2 Hz,

2 Hz, C=CH<sub>2</sub>), 49.01 (dd, J<sub>P-C</sub> = 31 Hz, 1 Hz, exocyclic), 36.17 (dd, J<sub>P-C</sub> = 5 Hz, 3 Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 35.38 (d, J<sub>P-C</sub> = 1 Hz, C(CH<sub>3</sub>)<sub>3</sub>-QM), 35.12 (dd, J<sub>P-C</sub> = 6 Hz, 1 Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 30.14 (d, J<sub>P-C</sub> = 9 Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 29.94 (d, J<sub>P-C</sub> = 5 Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 29.93 (s, C(CH<sub>3</sub>)<sub>3</sub>-QM), 24.02 (t, J<sub>P-C</sub> = 5 Hz, dtp), 21.96 (dd, J<sub>P-C</sub> = 7 Hz, 3 Hz, dtp), 21.48 (dd, J<sub>P-C</sub> = 10 Hz, 2 Hz, dtp). (Assignment of <sup>13</sup>C{<sup>1</sup>H} NMR signals was confirmed by <sup>13</sup>C DEPT). **ES-MS**: m/z<sup>+</sup> 657.81 (M-1) [calc. 658.20].

Characterization of **2** in CD<sub>2</sub>Cl<sub>2</sub> (for comparison with the methylene arenium complex **3**):

**<sup>31</sup>P{<sup>1</sup>H} NMR** (CD<sub>2</sub>Cl<sub>2</sub>): 51.75 (d, J<sub>P-P</sub> = 14 Hz), 40.55 (d, J<sub>P-P</sub> = 14 Hz). **<sup>1</sup>H NMR** (CD<sub>2</sub>Cl<sub>2</sub>): 6.57 (s, 2H, QM-ring), 2.90 (dd, J<sub>P-H</sub> = 6 Hz, 5 Hz, 2H, exocyclic), 1.45 (m, 2H, dtp), 1.38 (m, 2H, dtp), 1.35 (m, 2H, dtp), 1.29 (d, J<sub>P-H</sub> = 12 Hz, 18 H, tBu-dtp), 1.28 (s, 18 H, tBu-QM), 0.99 (d, J<sub>P-H</sub> = 12 Hz, 18 H, tBu-dtp). **<sup>13</sup>C{<sup>1</sup>H} NMR** (CD<sub>2</sub>Cl<sub>2</sub>): 183.57 (d, J<sub>P-C</sub> = 3 Hz, C=O), 141.19 (d, J<sub>P-C</sub> = 2 Hz, QM-ring), 139.35 (dd, J<sub>P-C</sub> = 3 Hz, 1 Hz, QM-ring), 78.12 (dd, J<sub>P-C</sub> = 12 Hz, 5 Hz, C=CH<sub>2</sub>), 47.67 (d, J<sub>P-C</sub> = 33 Hz, exocyclic), 36.90 (dd, J<sub>P-C</sub> = 7 Hz, 4 Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 35.27 (d, J<sub>P-C</sub> = 6 Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 34.94 (s, C(CH<sub>3</sub>)<sub>3</sub>-QM), 30.30 (d, J<sub>P-C</sub> = 12 Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 30.27 (d, J<sub>P-C</sub> = 15 Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 29.46 (s, C(CH<sub>3</sub>)<sub>3</sub>-QM), 27.02 (d, J<sub>P-C</sub> = 5 Hz, dtp), 23.10 (dd, J<sub>P-C</sub> = 10 Hz, 2 Hz, dtp), 21.99 (dd, J<sub>P-C</sub> = 7 Hz, 3 Hz, dtp).

**IR** (film): 1600.5 cm<sup>-1</sup>.

### Preparation of (dtp)Pd(methylene arenium) (**3**)

To a CD<sub>2</sub>Cl<sub>2</sub> solution (1 mL) of (dtp)Pd(QM) **2** (30 mg, 0.05 mmol) pre-cooled to -30 °C, was added 5 μL of MeOTf (0.05 mmol). The reaction mixture was kept at -30 °C for 10 min and then warmed up to room temperature. After 1 h the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum revealed quantitative formation of complex **3**. Yellow X-ray quality crystals of **3** were obtained by slow diffusion of pentane into a solution of **3** in toluene at -20 °C.

Slow conversion of **3** to **4** takes place at room temperature. Complex **3** was characterized at -30 °C.

**<sup>31</sup>P{<sup>1</sup>H} NMR** (CD<sub>2</sub>Cl<sub>2</sub>): 52.91 (d, J<sub>P-P</sub> = 20 Hz), 39.05 (d, J<sub>P-P</sub> = 20 Hz). **<sup>1</sup>H NMR** (CD<sub>2</sub>Cl<sub>2</sub>): 6.59 (bs, 2H, MA-ring), 4.22 (s, 3H, O-CH<sub>3</sub>), 2.97 (dd, J<sub>P-H</sub> = 6 Hz, J<sub>P-H</sub> = 1 Hz, 2H, exocyclic), 1.89 (m, 2H, dtp), 1.65 (m, 2H, dtp), 1.53 (m, 2H, dtp), 1.26 (s, 18 H, tBu), 1.24 (d, J<sub>P-H</sub> = 12 Hz, 18 H, tBu-dtp), 0.92 (d, J<sub>P-H</sub> = 12 Hz, 18 H, tBu-dtp). **<sup>13</sup>C{<sup>1</sup>H} NMR** (CD<sub>2</sub>Cl<sub>2</sub>): 166.08 (dd, J<sub>P-C</sub> = 7 Hz, 1 Hz, C-O-CH<sub>3</sub> of MA-ring), 139.88 (s, *ortho* of MA-ring), 129.14 (s, *meta* of MA-

ring), 107.51 (bd,  $J_{P-C} = 6$  Hz, C=CH<sub>2</sub>), 62.89 (s, C-O-CH<sub>3</sub>), 45.89 (d,  $J_{P-C} = 34$  Hz, exocyclic), 36.70 (d,  $J_{P-C} = 10$  Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 34.55 (d,  $J_{P-C} = 10$  Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 34.48 (s, C(CH<sub>3</sub>)<sub>3</sub>-MA), 29.77 (d,  $J_{P-C} = 5$  Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 29.60 (d,  $J_{P-C} = 5$  Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 28.96 (s, C(CH<sub>3</sub>)<sub>3</sub>-MA), 23.39 (m, dtp), 21.40 (t,  $J_{P-C} = 8$  Hz, dtp), 20.64 (d,  $J_{P-C} = 11$  Hz, dtp). (Assignment of <sup>13</sup>C{<sup>1</sup>H} NMR signals was confirmed by <sup>13</sup>C DEPT and C-H correlation measurements).

#### Formation of (dtp)Pd(benzyl)(triflate) (**4**)

When complex **3** was allowed to stand at room temperature (in CD<sub>2</sub>Cl<sub>2</sub>), the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum revealed formation of the new complex **4**. Complex **4** continued to grow and after 7 h 70 % of **4** (with 30 % of complex **3**) were observed. The relative amounts of complexes **3** and **4** remained unchanged after 3 h.

<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 69.10 (d,  $J_{P-P} = 42$  Hz), 42.92 (d,  $J_{P-P} = 42$  Hz). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 6.79 (s, 2H, Ar), 3.80 (s, 3H, O-CH<sub>3</sub>), 2.95 (dd,  $J_{P-H} = 8$  Hz, 1Hz, 2 H, Pd-CH<sub>2</sub>), 2.07 (m, 2 H, dtp), 2.08 (m, 2 H, dtp), 1.70 (m, 2 H, dtp), 1.43 (s, 18 H, tBu), 1.42 (d,  $J_{P-H} = 12$  Hz, 18 H, tBu-dtp), 0.99 (d,  $J_{P-H} = 12$  Hz, 18 H, tBu-dtp). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 147.98 (d,  $J_{P-C} = 6$  Hz, C-O-CH<sub>3</sub> of benzylic ring), 136.12 (s, benzylic ring), 128.32 (d,  $J_{P-C} = 18$  Hz, benzylic ring), 125.45 (d,  $J_{P-C} = 17$  Hz, benzylic ring), 64.60 (d,  $J_{P-C} = 5$  Hz, C-O-CH<sub>3</sub>), 40.70 (dd,  $J_{P-C} = 42$  Hz, 9 Hz, Pd-CH<sub>2</sub>), 39.50 (d,  $J_{P-C} = 15$  Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 36.08 (s, C(CH<sub>3</sub>)<sub>3</sub>), 34.95 (d,  $J_{P-C} = 12$  Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 31.55 (s, C(CH<sub>3</sub>)<sub>3</sub>), 30.76 (d,  $J_{P-C} = 4$  Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 29.95 (d,  $J_{P-C} = 6$  Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtp), 22.78 (d,  $J_{P-C} = 5$  Hz, dtp), 21.82 (t,  $J_{P-C} = 8$  Hz, dtp), 20.52 (d,  $J_{P-C} = 15$  Hz, dtp). (Assignment of <sup>13</sup>C{<sup>1</sup>H} NMR signals was confirmed by <sup>13</sup>C DEPT and C-H correlation measurements). ES-MS:  $m/z^+$  671.81 (M-OTf) [calc. 671.81],  $m/z^-$  148.94 (OTf) [calc. 149.07].

Note: It is not clear if **3** and **4** are in equilibrium. Spin Saturation Transfer studies did not show any evidence of it, and upon prolonged standing at room temperature side reactions of the remaining **3** to give other (different from **4**) compounds took place.

### Reaction of complex **3** with water and Et<sub>3</sub>N

To a CD<sub>2</sub>Cl<sub>2</sub> solution (1.5 mL) of complex **2** (60 mg., 0.092 mmol) was added 10.4 μL (0.092 mmol) of MeOTf at -30 °C. After keeping the reaction mixture at room temperature for 1.5 h, <sup>31</sup>P and <sup>13</sup>C NMR spectra revealed formation of complex **3** as a major product with minor signals of the benzyl complex **4**. 80 μL (4.6 mmol, 50 equiv) of H<sub>2</sub>O were added at room temperature followed after 5 min by addition of Et<sub>3</sub>N (12 μL, 0.092 mmol). <sup>31</sup>P and <sup>13</sup>C NMR revealed formation of the initial complex **2** as a major product, while the benzyl complex **4** remained unchanged.

### Methylene arenium release

To a CD<sub>2</sub>Cl<sub>2</sub> solution (1.5 mL) of complex **2** (30 mg, 0.046 mmol) was added 5.2 μL (0.046 mmol) of MeOTf at -30 °C. After keeping the reaction mixture at room temperature for 1.5 h, <sup>31</sup>P and <sup>13</sup>C NMR revealed formation of complex **3** as a major product, together with minor signals of the benzyl complex **4**. 100 equiv of H<sub>2</sub>O (4.6 mmol, 80 μL) were added, followed by addition after 5 min of a CD<sub>2</sub>Cl<sub>2</sub> solution of diphenyl acetylene (0.046 mmol, 8.2 mg). The released methylene arenium reacted with water to give 3, 5-di-*tert*-butyl-4-hydroxybenzyl alcohol, which was detected by GC/MS, giving an identical fragmentation pattern to that of an authentic sample. <sup>31</sup>P NMR spectrum of the solution revealed formation of (dtpp)Pd(diphenylacetylene), **5** in 30 % yield. (Rearrangement to the benzyl complex competes with the release of the methylene arenium moiety, whereas the benzyl complex **4** remained unchanged).

Characterization of complex **5**:

<sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 46.55 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.62 – 7.00 (10 H, Ar), 2.19 (m, 2 H, dtpp), 2.04 (m, 4 H, dtpp), 1.17 (d, J<sub>P-H</sub> = 12 Hz, 36 H, tBu-dtpp). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 141.55 (t, J<sub>P-C</sub> = 2 Hz, C<sub>ipso</sub>), 128.88 (s, C<sub>ortho</sub>), 126.91 (s, C<sub>meta</sub>), 124.07 (s, C<sub>para</sub>), 122.64 (dd, J<sub>P-C trans</sub> = 67 Hz, J<sub>P-C cis</sub> = 2 Hz, C≡), 34.57 (d, J<sub>P-C</sub> = 11 Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtpp), 30.95 (d, J<sub>P-C</sub> = 8 Hz, C(CH<sub>3</sub>)<sub>3</sub>-dtpp), 23.59 (dd, J<sub>P-C</sub> = 13 Hz, J<sub>P-C</sub> = 4 Hz, dtpp), 21.79 (dd, J<sub>P-C</sub> = 7 Hz, J<sub>P-C</sub> = 3 Hz, dtpp). (Assignment of the <sup>13</sup>C{<sup>1</sup>H} NMR signals was confirmed by <sup>13</sup>C DEPT). IR (film): 1818.14 cm<sup>-1</sup>. ES-MS: m/z<sup>+</sup> 617.88 (M+1) [calc. 617.75].

### X ray structure determination and refinement of complexes 2 and 3.

The crystals were mounted in a nylon loop and flash frozen in a cold nitrogen stream (120 K) on a Nonius Kappa CCD with Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ). Accurate unit cell dimensions were obtained from 20° of data. The data were processed with the Denzo-Scalepack package. The structure was solved by direct methods, (Shelxs-97) and refined by full-matrix least-squares based on F<sup>2</sup> with Shelxl-97.

Complex No.	Complex 3	Complex 2
Empirical formula	C <sub>36</sub> H <sub>67</sub> F <sub>3</sub> O <sub>4</sub> P <sub>2</sub> S <sub>1</sub> Pd <sub>1</sub> (C <sub>35</sub> H <sub>67</sub> O <sub>1</sub> P <sub>2</sub> Pd <sub>1</sub> + S <sub>1</sub> F <sub>3</sub> C <sub>1</sub> O <sub>3</sub> )	C <sub>34</sub> H <sub>64</sub> O <sub>1</sub> P <sub>2</sub> Pd <sub>1</sub>
Fw	821.30	657.19
Z	2	2
Crystal system	monoclinic	triclinic
Space group	P2(1)	P-1
Unit cell		
a/Å	10.963(2)	9.338(2)
b/Å	13.760(3)	11.847(2)
c/Å	13.558(3)	17.238(2)
$\alpha$ /deg		79.13 (3)
$\beta$ /deg	103.21(1)	76.00(3)°
$\gamma$ /deg		73.19 (3)
D <sub>c</sub> (Mg/m <sup>3</sup> )	1.370	1.242
$\mu$ (MoK $\alpha$ ) /mm <sup>-1</sup>	0.648	0.642
Crystal size /mm <sup>3</sup>	0.7 x 0.3 x 0.3	0.8 x 0.2 x 0.2
Total/ independent reflections	16370/ 4725	38188/ 8033
Parameters/restraints	444/ 1	361 / 0
Final R1 (based on F <sup>2</sup> ) for	0.0339	0.0340

data with $I > 2\sigma(I)$		
$R_{\text{int}}$	0.039	0.039
$R_1, wR_2$	0.0385, 0.0823	0.0389, 0.0787
Goodness-of-fit on $F^2$	1.079	1.138
Largest electron density peak ( $e/\text{\AA}^3$ )	1.294	1.248