



## Research paper

## Oxidative ring expansion of a low-coordinate palladacycle: Synthesis of a robust T-shaped alkylpalladium(II) complex



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## ARTICLE INFO

## ABSTRACT

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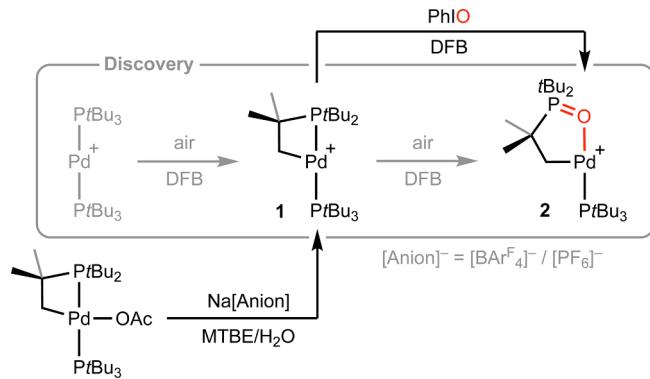
The synthesis of an unusual *T*-shaped alkylpalladium(II) complex featuring a cyclometalated tri-*tert*-butylphosphineoxide ligand by oxidation of the corresponding cyclometalated tri-*tert*-butylphosphine complex with PhIO is reported. We speculate that this reaction proceeds by formation of a transient palladium oxo intermediate and there are structural similarities with a late transition metal exemplar: Milstein's seminal pincer ligated Pt(IV) oxo (*Nature* 2008, 455, 1093–1096).

## 1. Introduction

As intermediates in important palladium catalysed organic transformations, the structure and onward reactivity of low-coordinate Pd(II) organometallics is of fundamental mechanistic interest [1]. With direct relevance to C–C cross coupling reactions, the synthesis of complexes of the form [Pd(PR<sub>3</sub>)(aryl)(halide)] by oxidative addition of aryl halides to palladium(0) precursors is a particularly notable, but not isolated example [2]. Compared to aryl variants, unsaturated Pd(II) alkyls have proven to be more elusive, with cationic [Pd(PtBu<sub>3</sub>)<sub>2</sub>(Me)]<sup>+</sup> (A) the most pertinent exemplar to this work [3]. As part of ongoing work in our laboratories exploring the chemistry of Pd(I) and Pt(I) metalloradicals [4], we serendipitously discovered that aerobic oxidation of [Pd(PtBu<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>]<sup>–</sup> in the weakly coordinating solvent 1,2-difluorobenzene (DFB) [5] resulted in the consecutive formation of novel cyclometalated Pd(II) complexes [Pd(*k*<sub>P,C</sub><sup>2</sup>-PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)]<sup>+</sup> (1) and [Pd(*k*<sub>O,C</sub><sup>2</sup>-O=PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)]<sup>+</sup> (2) as the major organometallic products on prolonged exposure to air (Scheme 1) [6]. We herein disclose our preliminary investigation of the latter step, involving ring expansion of a coordinatively unsaturated palladacycle.

## 2. Results and discussion

The identity of 1 was verified by independent synthesis as the [BAr<sub>4</sub><sup>F</sup>]<sup>–</sup> salt (1-BAr<sub>4</sub><sup>F</sup>; Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), by metathesis of the previously reported four-coordinate acetate derivative [Pd(*k*<sub>P,C</sub><sup>2</sup>-PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)(OAc)]·HOAc [7] with Na[BAr<sub>4</sub><sup>F</sup>] under biphasic conditions (Scheme 1). This method subsequently proved to be the most expedient method for obtaining analytically pure samples of 1



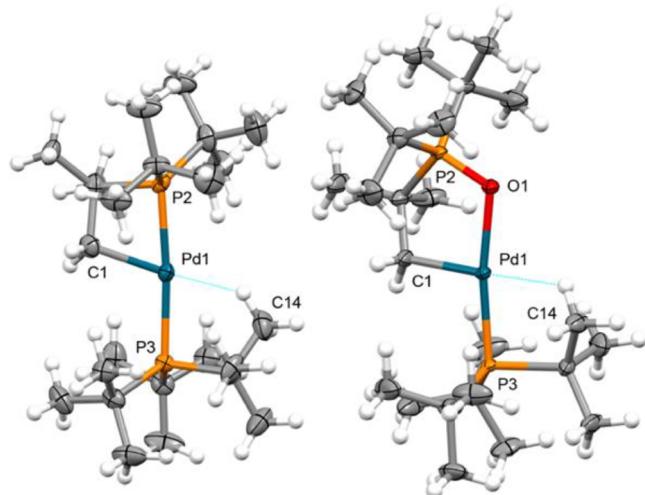
Scheme 1. Discovery and rational synthesis of cyclometalated Pd(II) complexes 1 and 2.

on a practically useful scale. Isolated 1-BAr<sub>4</sub><sup>F</sup> is characterised by NMR spectroscopy in DFB solution by <sup>31</sup>P resonances at  $\delta$  57.8 (PtBu<sub>3</sub>) and –0.6 (PtBu<sub>2</sub>), which display diagnostically large *trans*-phosphine <sup>2</sup>J<sub>PP</sub> coupling of 317 Hz [8], and a metal alkyl <sup>13</sup>C resonance at  $\delta$  26.2 (dd, <sup>2</sup>J<sub>PC</sub> = 23, 3 Hz). The easily handled reagent PhIO was identified as an effective oxidant [9] and enabled quantitative oxidation of 1-BAr<sub>4</sub><sup>F</sup> to 2-BAr<sub>4</sub><sup>F</sup> within 1 h at RT in DFB (10 eqv PhIO). The product was subsequently obtained in 55% isolated yield and fully characterised. The formation of 2 is associated with significant downfield shifts of the <sup>31</sup>P resonances to  $\delta$  90.0 (O=PtBu<sub>2</sub>) and 72.6 (PtBu<sub>3</sub>), with no appreciable <sup>3</sup>J<sub>PP</sub> coupling (< 2 Hz), and a metal alkyl <sup>13</sup>C resonance at  $\delta$  38.6 (app. t, <sup>2</sup>J<sub>PP</sub> = 3 Hz) in DFB solution.

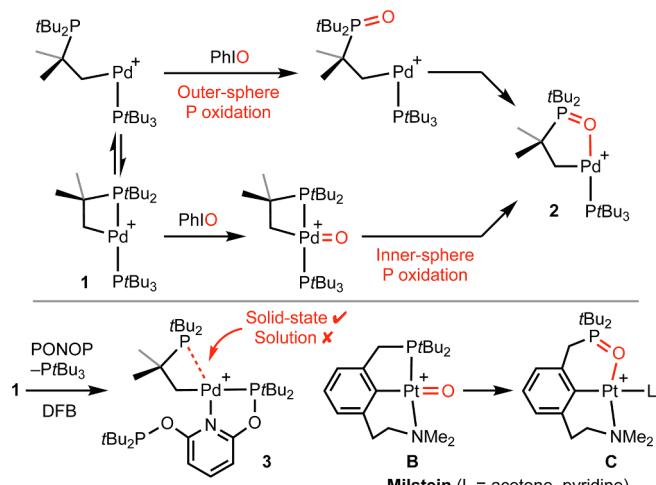
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Structural elucidation of **1·BAr<sub>4</sub><sup>F</sup>** and **2·BAr<sub>4</sub><sup>F</sup>** using X-ray diffraction was frustrated by whole molecule structural disorder of both the palladium-based cations and counteranions in the high symmetry *P*2<sub>1</sub>3 space group. Consequently, single crystalline samples of the corresponding [PF<sub>6</sub>]<sup>-</sup> salts, which can be prepared in a similar manner and do not suffer from such crystallographic problems, were analysed (Fig. 1). The solid-state structures of **1·PF<sub>6</sub>** and **2·PF<sub>6</sub>** are notable for the adoption of distorted *T*-shaped geometries (*P*2/O1-Pd1-P3 angles > 170°; cf. 173.40(5)° in **A**) and an agostic interaction with the PtBu<sub>3</sub> ligand, with that in **2·PF<sub>6</sub>** significantly more pronounced than in **1·PF<sub>6</sub>** (Pd1-C14 = 2.770(3) vs. 2.825(7) Å) and in turn **A** (2.900(2) Å). Transformation from palladacyclobutane to palladacyclopentane is associated with a marked reduction of the Pd1-C1 bond length (2.075(6)



**Fig. 1.** Solid-state structures of **1·PF<sub>6</sub>** and **2·PF<sub>6</sub>**. Thermal ellipsoids drawn at 30% and 50% probability, respectively; minor disordered components and anions omitted for clarity. Selected bond lengths (Å) and angles (deg): **1·PF<sub>6</sub>**; Pd1-P2, 2.2976(11); Pd1-P3, 2.3250(11); Pd1-C1, 2.075(6); Pd1-C14, 2.825(7); P2-Pd1-P3, 175.38(4); P2-Pd1-C1, 68.2(2); **2·PF<sub>6</sub>**; Pd1-O1, 2.093(2); Pd1-P3, 2.2387(6); Pd1-C1, 2.020(3); Pd1-C14, 2.770(3); P2-O1, 1.525(2); O1-Pd1-P3, 171.55(5); O1-Pd1-C1, 87.91(9); Pd1-O1-P2, 114.79(10).

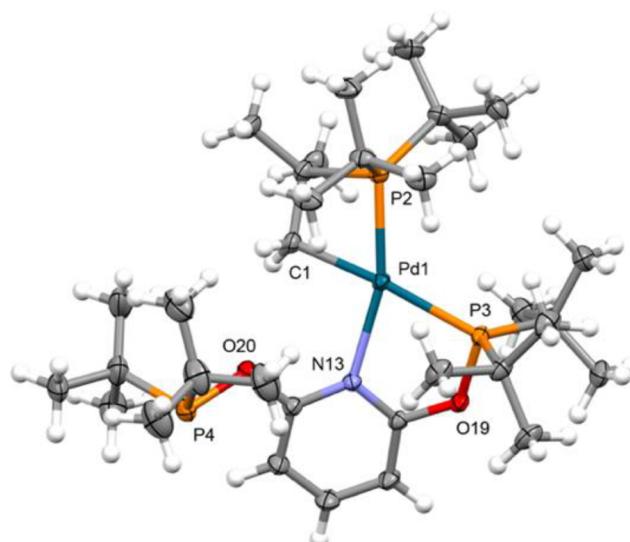


**Scheme 2.** Possible reaction mechanisms and associated evidence/precedents.

vs 2.020(3) Å cf. 2.029(6) Å in **A**) and the expected reduction in ring strain, as gauged by the large increase of the P2/O1-Pd1-C1 angle from 68.2(2) to 87.91(9)° (cf. 91.4(2)/95.1(2)° in **A**).

The formation of **2** can be reconciled by idealised mechanisms involving (a) ring strain promoted hemi-labile coordination of the tethered phosphine or (b) intermediate formation of a palladium oxo derivative (Scheme 2). In order to probe the former, **1·BAr<sub>4</sub><sup>F</sup>** was reacted with 2,6-(tBu<sub>2</sub>PO)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N (PONOP) at RT in DFB leading to the formation of **3·BAr<sub>4</sub><sup>F</sup>** by substitution of PtBu<sub>3</sub>, dissociation of the tethered phosphine donor, and the (unusual) partial chelation of the pincer ligand; as evidenced by singlet <sup>31</sup>P resonances at δ 182.6, 180.0, and -12.0 (PtBu<sub>2</sub>) in an integral 1:1:1 ratio, and a doublet of doublets metal alkyl <sup>13</sup>C resonance at δ 24.2 (<sup>2</sup>J<sub>PC</sub> = 70, 34 Hz). Whilst the X-ray structure of isolated **3** indicates the palladacycle is retained in the solid state (Fig. 2), the solution-phase behaviour suggests outer-sphere phosphine oxidation is a viable option. As a gauge for the timescales associated with such a mechanism, the oxidation of PtBu<sub>3</sub> with PhIO (t > 9 h) was studied, but the corresponding rate is incongruent with the formation of **2** under equivalent conditions (t < 1 h). Correspondingly, we favour an inner-sphere explanation, with the formation of a discrete metal oxo at one extreme and concerted O-atom transfer into the Pd-P bond at the other [10]. Whilst the formation of terminal oxo complexes beyond the “oxo wall” between groups 8 and 9 is rare [11,12], a directly pertinent platinum example supported by an anionic PCN pincer ligand has been reported and, moreover, its onward reactivity involves intramolecular O-atom transfer (**B** → **C**, Scheme 2) [10]. On this basis, whilst we currently cannot definitively distinguish between the two possibilities, we postulate a discrete terminal oxo derivative is involved.

Complex **2** is remarkably stable in solution, with no reaction evident upon exposure to air for 2 months. Moreover, whilst complete decomposition of **1** to [Pd(PtBu<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, PtBu<sub>3</sub> and palladium black was observed on placing under H<sub>2</sub> in DFB at RT (t < 2 days), **2** persists for > 3 days under the same conditions and only upon heating to 50 °C was any evidence of a reaction evident.



**Fig. 2.** Solid-state structure of **3·BAr<sub>4</sub><sup>F</sup>**. Thermal ellipsoids drawn at 30% probability; anion omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1-P2, 2.2837(7); Pd1-P3, 2.3831(7); Pd1-N13, 2.229(2); Pd1-C1, 2.082(3); P2-Pd1-N13, 162.56(6); P2-Pd1-C1, 67.40(8); C1-Pd1-P3, 171.23(9).

### 3. Conclusions

In summary, we report the synthesis of an unusual *T*-shaped alkyl-palladium(II) complex featuring a cyclometalated tri-*tert*-butylphosphineoxide ligand by oxidation of the corresponding cyclometalated tri-*tert*-butylphosphine complex with PhIO. We speculate that this reaction may include transient formation of a palladium oxo intermediate, however, further work is needed to substantiate this claim.

### 4. Experimental

#### 4.1. General experimental methods

All manipulations were performed under an inert atmosphere of argon using Schlenk and glovebox techniques unless otherwise stated. Glassware was oven dried at 150 °C overnight and flame-dried under vacuum prior to use. Molecular sieves were activated by heating at 300 °C *in vacuo* overnight. CD<sub>2</sub>Cl<sub>2</sub> was dried over activated molecular sieves (3 Å) and stored under an argon atmosphere. 1,2-F<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (DFB) was pre-dried over Al<sub>2</sub>O<sub>3</sub>, distilled from calcium hydride and dried over two successive batches of 3 Å molecular sieves under argon. *t*-Butyl methyl ether (MTBE) was sparged with argon prior to use. All other anhydrous solvents were purchased from Aldrich or Acros, freeze-pumpthaw degassed, and stored over 3 Å molecular sieves under argon. [Pd(PtBu<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>] (**4a**), Pd( $\kappa_{P,C}^2$ PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)(OAc) (130.6 mg, 207.9 μmol) in MTBE (5 mL) was added a solution of PtBu<sub>3</sub> in pentane (0.27 mL of a 0.78 M solution, 210 μmol) and the resulting solution was stirred for 5 min at room temperature, before being transferred onto a 5 mL degassed aqueous suspension of Na[PF<sub>6</sub>] (35.4 mg, 211 μmol). The biphasic mixture was stirred vigorously for 5 mins and hexane (5 mL) was added. The yellow precipitate was isolated by filtration and washed with hexane (3 × 5 mL). The product was then extracted into DFB, precipitated by addition of excess hexane, isolated by filtration and dried *in vacuo*. Yield: 78.4 mg (58%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a DFB solution at room temperature.

#### 4.2. NMR scale reaction of [Pd(PtBu<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>] with air

A solution of [Pd(PtBu<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>] (6.6 mg, 10 μmol) in DFB (0.5 mL) within an open NMR tube containing an internal sealed capillary of O=P(OMe)<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> was held at room temperature and monitored periodically over 1 month using NMR spectroscopy, topping up with solvent as necessary to maintain a constant volume. During this time, the consecutive formation of [Pd( $\kappa_{P,C}^2$ PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)]<sup>+</sup> ( $\delta$  57.8 and -0.6) and [Pd( $\kappa_{O,C}^2$ O=PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)]<sup>+</sup> ( $\delta$  90.0 and 72.6) was observed as the major organometallic products along with other unidentified species.

#### 4.3. Preparation of [Pd( $\kappa_{P,C}^2$ PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)][BAr<sub>4</sub><sup>F</sup>] 1·BAr<sub>4</sub><sup>F</sup>

To a solution of [Pd( $\kappa_{P,C}^2$ PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)(OAc)]·HOAc (56.6 mg, 90.1 μmol) in MTBE (5 mL) was added a solution of PtBu<sub>3</sub> in pentane (0.12 mL of a 0.78 M solution, 94 μmol) and the resulting solution was stirred at room temperature for 5 min before being transferred onto a 5 mL degassed aqueous suspension of Na[BAr<sub>4</sub><sup>F</sup>] (79.9 mg, 90.2 μmol). The biphasic mixture was stirred vigorously for 5 min and the organic phase transferred dropwise into excess hexane, affording a yellow precipitate that was isolated by filtration and dried *in vacuo*. Yield: 63.2 mg (51%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a DFB solution at room temperature.

<sup>1</sup>H NMR (500 MHz, DFB/C<sub>6</sub>D<sub>6</sub>): δ 8.17–8.12 (m, 8H, Ar<sup>F</sup>), 7.50 (br, 4H, Ar<sup>F</sup>), 2.33 (app. t,  $^3J_{PH}$  = 5.7, 2H, PdCH<sub>2</sub>), 1.38 (d,  $^3J_{PH}$  = 13.4, 6H, Me), 1.35 (d,  $^3J_{PH}$  = 14.3, 18H, PtBu<sub>2</sub>), 1.23 (d,  $^3J_{PH}$  = 12.7, 27H, PtBu<sub>3</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DFB/C<sub>6</sub>D<sub>6</sub>, selected data only): δ 51.9

(HMBC, PdCH<sub>2</sub>C), 39.8 (dd,  $^1J_{PC}$  = 7,  $^3J_{PC}$  = 2, PtBu<sub>3</sub>{C}), 38.7 (app. t,  $J_{PC}$  = 5, PtBu<sub>2</sub>{C}), 31.7 (d,  $^2J_{PC}$  = 4, PtBu<sub>2</sub>{Me}), 31.1 (d,  $^2J_{PC}$  = 4,  $^4J_{PC}$  = 1, PtBu<sub>3</sub>{Me}), 29.0 (s, Me), 26.2 (dd,  $^2J_{PC}$  = 23, 3, PdCH<sub>2</sub>).

<sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, DFB/C<sub>6</sub>D<sub>6</sub>): δ 57.8 (d,  $^2J_{PP}$  = 317, 1P, PtBu<sub>3</sub>), -0.6 (d,  $^2J_{PP}$  = 317, 1P, PtBu<sub>2</sub>).

Anal. Calcd for C<sub>56</sub>H<sub>65</sub>BF<sub>24</sub>P<sub>2</sub>Pd (1373.28 g mol<sup>-1</sup>): C, 48.98; H, 4.77; N, 0.00. Found: C, 48.91; H, 4.65; N, 0.00.

#### 4.4. Preparation of [Pd( $\kappa_{P,C}^2$ PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)][PF<sub>6</sub>] 1·PF<sub>6</sub>

To a solution of [Pd( $\kappa_{P,C}^2$ PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)(OAc)]·HOAc (130.6 mg, 207.9 μmol) in MTBE (5 mL) was added a solution of PtBu<sub>3</sub> in pentane (0.27 mL of a 0.78 M solution, 210 μmol) and the resulting solution was stirred for 5 min at room temperature, before being transferred onto a 5 mL degassed aqueous suspension of Na[PF<sub>6</sub>] (35.4 mg, 211 μmol). The biphasic mixture was stirred vigorously for 5 mins and hexane (5 mL) was added. The yellow precipitate was isolated by filtration and washed with hexane (3 × 5 mL). The product was then extracted into DFB, precipitated by addition of excess hexane, isolated by filtration and dried *in vacuo*. Yield: 78.4 mg (58%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a DFB solution at room temperature.

<sup>1</sup>H NMR (300 MHz, DFB/C<sub>6</sub>D<sub>6</sub>): δ 2.32 (app. t,  $^3J_{PH}$  = 5.7, 2H, PdCH<sub>2</sub>), 1.38 (d,  $^3J_{PH}$  = 13.3, 6H, Me), 1.35 (d,  $^3J_{PH}$  = 14.4, 18H, PtBu<sub>2</sub>), 1.23 (d,  $^3J_{PH}$  = 12.7, 27H, PtBu<sub>3</sub>).

<sup>31</sup>P{<sup>1</sup>H} NMR (122 MHz, DFB/C<sub>6</sub>D<sub>6</sub>): δ 57.6 (d,  $^2J_{PP}$  = 317, 1P, PtBu<sub>3</sub>), -0.6 (d,  $^2J_{PP}$  = 317, 1P, PtBu<sub>2</sub>), -142.4 (septet,  $^1J_{PF}$  = 710, 1P, PF<sub>6</sub>).

#### 4.5. NMR scale reactions of 1·BAr<sub>4</sub><sup>F</sup> and PtBu<sub>3</sub> with PhIO

A suspension of PhIO (22.1 mg, 100 μmol) in a solution of 1·BAr<sub>4</sub><sup>F</sup> (13.9 mg, 10.0 μmol) in DFB (0.5 mL) within a J. Young's valve NMR tube was monitored by <sup>31</sup>P NMR spectroscopy, with constant mixing at room temperature when not in the spectrometer. Quantitative conversion to 2·BAr<sub>4</sub><sup>F</sup> was observed within 1 h.

A suspension of PhIO (22.1 mg, 100 μmol) in a solution of PtBu<sub>3</sub> (15 μL of a 0.67 M solution in hexane, 10 μmol) in DFB (0.5 mL) within a J. Young's valve NMR tube was monitored by <sup>31</sup>P NMR spectroscopy, with constant mixing at room temperature when not in the spectrometer. Quantitative conversion to O=PtBu<sub>3</sub> ( $\delta$  64.4 ppm) [16] was observed within 24 h.

#### 4.6. Preparation of [Pd( $\kappa_{O,C}^2$ O=PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)][BAr<sub>4</sub><sup>F</sup>] 2·BAr<sub>4</sub><sup>F</sup>

A suspension of [Pd( $\kappa_{P,C}^2$ PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)][BAr<sub>4</sub><sup>F</sup>] (73.1 mg, 53.2 μmol) and PhIO (119.6 mg, 543.4 μmol) in DFB (5 mL) was stirred for 30 min at room temperature. The solution was filtered into hexane (20 mL) affording a yellow precipitate that was isolated by filtration, washed with hexane (3 × 5 mL) and dried *in vacuo*. Yield: 40.7 mg (55%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a DFB solution at room temperature.

<sup>1</sup>H NMR (500 MHz, DFB/C<sub>6</sub>D<sub>6</sub>): δ 8.17–8.12 (m, 8H, Ar<sup>F</sup>), 7.50 (br, 4H, Ar<sup>F</sup>), 2.77 (d,  $^3J_{PH}$  = 10.0, 2H, PdCH<sub>2</sub>), 1.44 (d,  $^3J_{PH}$  = 13.0, 6H, Me), 1.27 (d,  $^3J_{PH}$  = 13.5, 18H, O=PtBu<sub>2</sub>), 1.25 (d,  $^3J_{PH}$  = 13.1, 27H, PtBu<sub>3</sub>).

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.76–7.68 (m, 8H, Ar<sup>F</sup>), 7.56 (br, 4H, Ar<sup>F</sup>), 2.83 (d,  $^3J_{PH}$  = 10.1, 2H, PdCH<sub>2</sub>), 1.61 (d,  $^3J_{PH}$  = 13.0, 6H, Me), 1.48 (app. d,  $^3J_{PH}$  = 13.3, 45H, O=PtBu<sub>2</sub> + PtBu<sub>3</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DFB/C<sub>6</sub>D<sub>6</sub>, selected data only): δ 53.9 (d,  $^1J_{PC}$  = 53, PdCH<sub>2</sub>C), 39.9 (d,  $^1J_{PC}$  = 14, PtBu<sub>3</sub>{C}), 38.7 (d,  $^1J_{PC}$  = 47, O=PtBu<sub>2</sub>{C}), 38.6 (app. t,  $^2J_{PC}$  = 3, PdCH<sub>2</sub>), 30.7

(d,  $^2J_{PC} = 3$ , PtBu<sub>3</sub>{Me}), 27.8 (s, Me), 27.5 (s,  $^2J_{PC} = 22$ , O=PtBu<sub>2</sub>{Me}).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (162 MHz, DFB/C<sub>6</sub>D<sub>6</sub>):  $\delta$  90.0 (s, 1P, O=PtBu<sub>2</sub>), 72.6 (s, 1P, PtBu<sub>3</sub>).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  91.0 (s, 1P, O=PtBu<sub>2</sub>), 73.8 (s, 1P, PtBu<sub>3</sub>).

**HR ESI-MS** (MeCN, 180 °C, 4 kV) positive ion: 525.2611 ([M]<sup>+</sup>, calcd 525.2611) *m/z*.

**Anal.** Calcd for C<sub>56</sub>H<sub>65</sub>BF<sub>24</sub>OP<sub>2</sub>Pd (1389.33 g mol<sup>-1</sup>): C, 48.41; H, 4.72; N, 0.00. Found: C, 48.29; H, 4.87; N, 0.00.

#### 4.7. Preparation of [Pd( $\kappa^2_{\text{P},\text{C}}$ -O=PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)][PF<sub>6</sub>] 2·PF<sub>6</sub>

A suspension of [Pd( $\kappa^2_{\text{P},\text{C}}$ -PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)][PF<sub>6</sub>] (61.2 mg, 93.4 µmol) and PhIO (620.0 mg, 2.814 mmol) in DFB (5 mL) was stirred vigorously for 15 min at room temperature. The solution was filtered into hexane (20 mL), affording a yellow precipitate which was isolated by filtration, washed with hexane (3 × 5 mL) and dried *in vacuo*. Analytically pure material was obtained by recrystallisation from dichloromethane/hexane. Yield: 6.5 mg (10%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a DFB solution at room temperature.

**$^1\text{H}$  NMR** (500 MHz, DFB/C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.76 (d,  $^3J_{\text{PH}} = 10.1$ , 2H, PdCH<sub>2</sub>), 1.44 (d,  $^3J_{\text{PH}} = 13.0$ , 6H, Me), 1.31–1.18 (m, 45H, O=PtBu<sub>2</sub> + PtBu<sub>3</sub>).

**$^1\text{H}$  NMR** (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  2.84 (d,  $^3J_{\text{PH}} = 10.0$ , 2H, PdCH<sub>2</sub>), 1.62 (d,  $^3J_{\text{PH}} = 13.1$ , 6H, Me), 1.49 (app. d,  $^3J_{\text{PH}} = 13.3$ , 45H, O=PtBu<sub>2</sub> + PtBu<sub>3</sub>).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (162 MHz, DFB/C<sub>6</sub>D<sub>6</sub>):  $\delta$  90.0 (s, 1P, O=PtBu<sub>2</sub>), 72.7 (s, 1P, PtBu<sub>3</sub>), -142.4 (septet,  $^1J_{\text{PF}} = 710$ , 1P, PF<sub>6</sub>).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  89.2 (s, 1P, O=PtBu<sub>2</sub>), 72.0 (s, 1P, PtBu<sub>3</sub>), -144.5 (septet,  $^1J_{\text{PF}} = 710$ , 1P, PF<sub>6</sub>).

**HR ESI-MS** (MeCN, 180 °C, 4 kV) positive ion: 525.2605 ([M]<sup>+</sup>, calcd 525.2611) *m/z*.

#### 4.8. NMR scale reaction of 1·BAr<sub>4</sub><sup>F</sup> with PONOP

A solution of 1·BAr<sub>4</sub><sup>F</sup> (13.8 mg, 10.1 µmol) and PONOP (3.9 mg, 11 µmol;  $\delta$  156.0) in DFB (0.5 mL) was prepared in a J. Young's valve NMR tube containing an internal sealed capillary of O=P(OMe)<sub>3</sub> in C<sub>6</sub>D<sub>6</sub>. Analysis by  $^{31}\text{P}$  NMR spectroscopy after 30 min at room temperature indicated complete conversion to [Pd(PONOP)(PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)][BAr<sub>4</sub><sup>F</sup>] ( $\delta$  182.6, 180.0 and -12.0) and PtBu<sub>3</sub> ( $\delta$  62.8).

#### 4.9. Preparation of [Pd(PONOP)(PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)][BAr<sub>4</sub><sup>F</sup>] 3·BAr<sub>4</sub><sup>F</sup>

A solution of [Pd( $\kappa^2_{\text{P},\text{C}}$ -PtBu<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)(PtBu<sub>3</sub>)][BAr<sub>4</sub><sup>F</sup>] (55.1 mg, 40.0 µmol) and PONOP (15.1 mg, 44.0 µmol) in DFB (2 mL) was stirred for 30 min at room temperature. The solution was concentrated *in vacuo* and transferred dropwise into excess hexane, affording a pale blue precipitate that was isolated by filtration and dried *in vacuo*. Yield: 33.1 mg (53%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a DFB solution at room temperature.

**$^1\text{H}$  NMR** (500 MHz, DFB/C<sub>6</sub>D<sub>6</sub>, selected data only):  $\delta$  8.17–8.12 (m, 8H, Ar<sup>F</sup>), 7.50 (br, 4H, Ar<sup>F</sup>), 1.82 (d,  $^3J_{\text{PH}} = 7.0$ , 2H, PdCH<sub>2</sub>), 1.41 (d,  $^3J_{\text{PH}} = 14.2$ , 18H, PtBu<sub>2</sub>), 1.31 (d,  $^3J_{\text{PH}} = 14.6$ , 6H, Me), 1.20 (d,  $^3J_{\text{PH}} = 14.1$ , 18H, PtBu<sub>2</sub>O), 1.06 (d,  $^3J_{\text{PH}} = 12.4$ , 18H, PtBu<sub>2</sub>O).

**$^1\text{H}$  NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.79 (t,  $^3J_{\text{HH}} = 7.8$ , 1H, py), 7.76–7.68 (m, 8H, Ar<sup>F</sup>), 7.56 (br, 4H, Ar<sup>F</sup>), 7.35 (app. t,  $J = 6$ , 1H, py), 6.72 (d,  $^3J_{\text{HH}} = 7.9$ , 1H, py), 1.92 (d,  $^3J_{\text{PH}} = 7.0$ , 2H, PdCH<sub>2</sub>), 1.60 (d,  $^3J_{\text{PH}} = 14.3$ , 18H, PtBu<sub>2</sub>), 1.51 (d,  $^3J_{\text{PH}} = 14.5$ , 6H, Me),

1.36 (d,  $^3J_{\text{PH}} = 14.2$ , 18H, PtBu<sub>2</sub>O), 1.20 (d,  $^3J_{\text{PH}} = 12.4$ , 18H, PtBu<sub>2</sub>O).

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz, DFB/C<sub>6</sub>D<sub>6</sub>, selected data only):  $\delta$  46.0 (d,  $^1J_{\text{PC}} = 25$ , PdCH<sub>2</sub>C), 38.7 (d,  $^1J_{\text{PC}} = 9$ , PtBu<sub>2</sub>C), 38.4 (s, PtBu<sub>2</sub>O{C}), 35.9 (d,  $^1J_{\text{PC}} = 33$ , PtBu<sub>2</sub>O{C}), 32.0 (d,  $^2J_{\text{PC}} = 3$ , PtBu<sub>2</sub>{Me}), 30.8 (d,  $^2J_{\text{PC}} = 5$ , Me), 27.0 (d,  $^2J_{\text{PC}} = 3$ , PtBu<sub>2</sub>O{Me}), 27.1 (d,  $^2J_{\text{PC}} = 3$ , PtBu<sub>2</sub>O{Me}), 24.2 (dd,  $^2J_{\text{PC}} = 70$ , 34, PdCH<sub>2</sub>).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (162 MHz, DFB/C<sub>6</sub>D<sub>6</sub>):  $\delta$  182.6 (s, 1P, PtBu<sub>2</sub>O), 180.0 (s, 1P, PtBu<sub>2</sub>O), -12.0 (s, 1P, PtBu<sub>2</sub>).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  182.1 (s, 1P, PtBu<sub>2</sub>O), 178.9 (s, 1P, PtBu<sub>2</sub>O), -12.6 (s, 1P, PtBu<sub>2</sub>).

**HR ESI-MS** (MeCN, 180 °C, 4 kV) positive ion: 706.3263 ([M]<sup>+</sup> calcd 706.3270) *m/z*.

**Anal.** Calcd for C<sub>56</sub>H<sub>78</sub>BF<sub>24</sub>NO<sub>2</sub>P<sub>3</sub>Pd (1570.40 g mol<sup>-1</sup>): C, 49.68; H, 5.00; N, 0.89. Found: C, 49.77; H, 5.01; N, 0.86.

#### 4.10. NMR scale reaction of 2·BAr<sub>4</sub><sup>F</sup> with air

A solution of 2·BAr<sub>4</sub><sup>F</sup> (13.9 mg, 10.0 µmol) in DFB (0.5 mL) within an open NMR tube containing an internal sealed capillary of O=P(OMe)<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> was held at room temperature and monitored periodically over 2 months, topping up with solvent as necessary to maintain a constant volume. No reaction was apparent from analysis by  $^{31}\text{P}$  NMR spectroscopy.

#### 4.11. NMR scale reactions of 1·BAr<sub>4</sub><sup>F</sup> and 2·BAr<sub>4</sub><sup>F</sup> with H<sub>2</sub>

Solutions of 1·BAr<sub>4</sub><sup>F</sup> (13.8 mg, 10.1 µmol) and 2·BAr<sub>4</sub><sup>F</sup> (13.8 mg, 10.0 µmol) in DFB (0.5 mL) within J. Young's valve NMR tubes (the former containing an internal sealed capillary of O=P(OMe)<sub>3</sub> in C<sub>6</sub>D<sub>6</sub>) were freeze-pump-thaw degassed and placed under an atmosphere of H<sub>2</sub> (1 bar). Reactions were monitored by NMR spectroscopy, with constant mixing at room temperature when not in the spectrometer. The reaction of 1·BAr<sub>4</sub><sup>F</sup> with H<sub>2</sub> generated PtBu<sub>3</sub> ( $\delta$  62.9), [Pd(PtBu<sub>3</sub>)<sub>2</sub>] ( $\delta$  84.4) and palladium black over 40 h. No reaction of 2·BAr<sub>4</sub><sup>F</sup> with H<sub>2</sub> was observed after 72 h at room temperature. Subsequent heating at 50 °C, however, resulted in complete decomposition of 2·BAr<sub>4</sub><sup>F</sup> to a palladium mirror within 18 h.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2020.119948>.

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