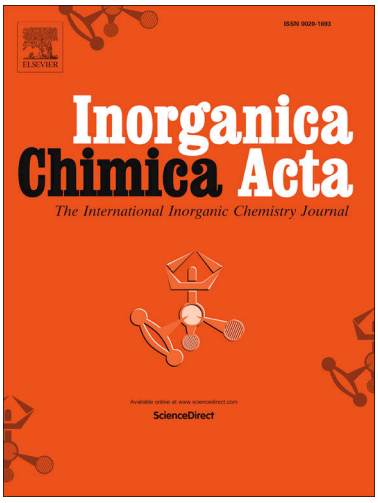
Journal Pre-proofs



Research paper

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

Matthew. J. G. Sinclair, Adrian B. Chaplin

PII: S0020-1693(20)31148-8
DOI: https://doi.org/10.1016/j.ica.2020.119948
Reference: ICA 119948

To appear in: *Inorganica Chimica Acta*

Received Date: 15 June 2020
Revised Date: 27 July 2020
Accepted Date: 5 August 2020

Please cite this article as: Matthew. J. G. Sinclair, A.B. Chaplin, Oxidative ring expansion of a low-coordinate palladacycle:synthesis of a robust T-shaped alkylpalladium(II) complex, *Inorganica Chimica Acta* (2020), doi: https://doi.org/10.1016/j.ica.2020.119948

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

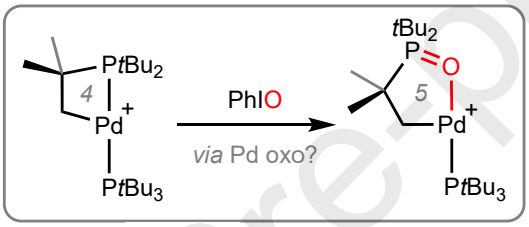
Matthew. J. G. Sinclair and Adrian B. Chaplin*

Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, UK

Email: a.b.chaplin@warwick.ac.uk

Submitted to the special issue of Inorganica Chimica Acta in honour of Maurizio Peruzzini, a protagonist in Transition Metal Chemistry

TOC



Abstract

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).

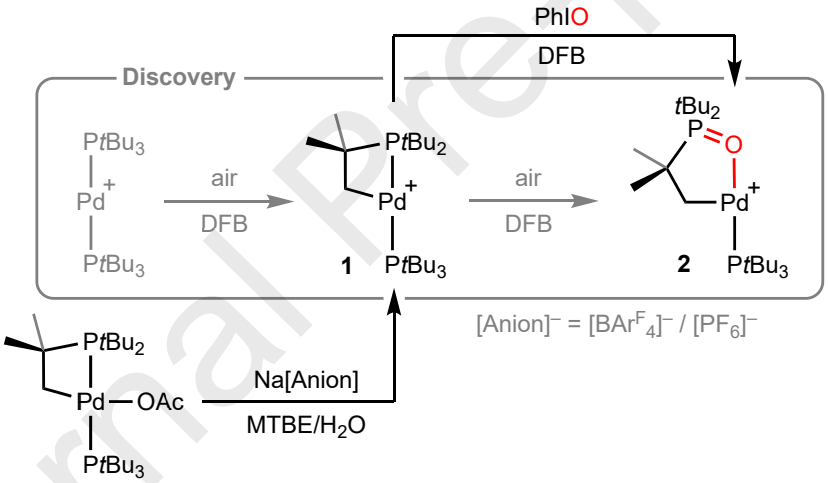
Keywords

Palladium; cyclometallation reactions; terminal oxo complexes; low-coordinate complexes; agostic interactions.

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_3)(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(P*t*Bu_3)$_2$(Me)]$^+$ (**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(P*t*Bu_3)$_2$][PF_6] in the weakly coordinating solvent 1,2-difluorobenzene (DFB)[5] resulted in the consecutive formation of novel cyclometalated Pd(II) complexes [Pd($\kappa^2_{P,C}$-P*t*Bu_2CMe_2CH_2)(P*t*Bu_3)]$^+$ (**1**) and [Pd($\kappa^2_{O,C}$-O=P*t*Bu_2CMe_2CH_2)(P*t*Bu_3)]$^+$ (**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.

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



Results and discussion

The identity of **1** was verified by independent synthesis as the [BAr^F_4]$^-$ salt (**1**.BAr^F_4; Ar^F = 3,5-(CF_3)$_2$$C_6H_3$), by metathesis of the previously reported four-coordinate acetate derivative [Pd($\kappa^2_{P,C}$-P*t*Bu_2CMe_2CH_2)(P*t*Bu_3)(OAc)]·HOAc [7] with Na[BAr^F_4] under biphasic conditions (Scheme 1). This method subsequently proved to be the most expedient method for obtaining analytically pure materials of **1** on a practically useful scale. Isolated **1**.BAr^F_4 is characterised by NMR spectroscopy in DFB solution by ^{31}P resonances at δ 57.8 (P*t*Bu_3) and -0.6 (P*t*Bu_2), which display diagnostically large *trans*-phosphine $^2J_{PP}$ coupling of 317 Hz,[8] and a metal alkyl ^{13}C resonance at δ 26.2 (dd, $^2J_{PC}$ = 23, 3 Hz). The easily handled reagent PhIO was identified as an effective oxidant[9] and enabled quantitative oxidation of **1**.BAr^F_4 to **2**.BAr^F_4 within 1 hour 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 ^{31}P resonances to δ 90.0 (O–P*t*Bu$_2$) and 72.6 (P*t*Bu$_3$), with no appreciable $^3J_{PP}$ coupling (< 2 Hz), and a metal alkyl ^{13}C resonance at δ 38.6 (app. t, $^2J_{PP}$ = 3 Hz) in DFB solution.

Structural elucidation of **1**.BAr$^F_4$ and **2**.BAr$^F_4$ using X-ray diffraction was frustrated by whole molecule structural disorder of both the palladium-based cations and counteranions in the high symmetry $P2_13$ space group. Consequently, single crystalline samples of the corresponding $[PF_6]^-$ salts, which can be prepared in a similar manner and do not suffer from such crystallographic problems, where analysed (Figure 1). The solid-state structures of **1**.PF$_6$ and **2**.PF$_6$ are notable for the adoption of distorted T-shaped geometries (P2/O1–Pd1–P3 angles > 170°; *cf.* 173.40(5)° in **A**) and an agostic interaction with the P*t*Bu$_3$ ligand, with that in **2**.PF$_6$ significantly more pronounced than in **1**.PF$_6$ (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) 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**).

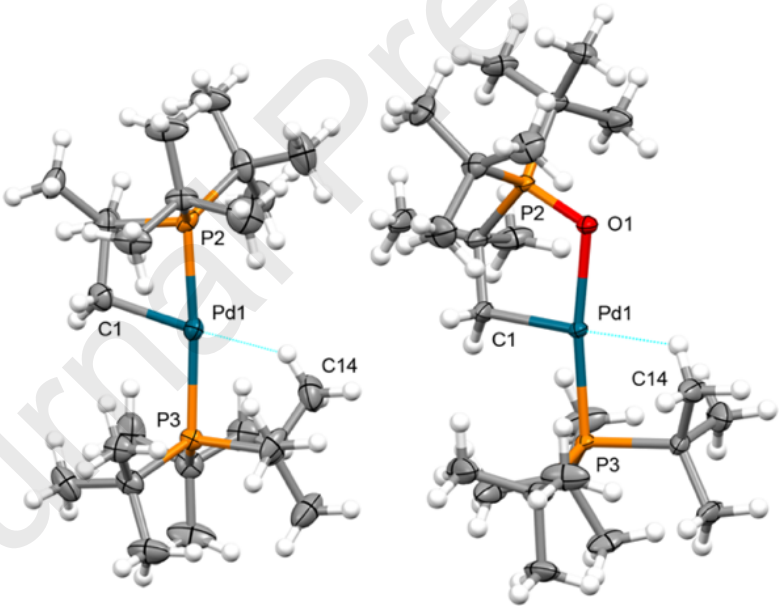
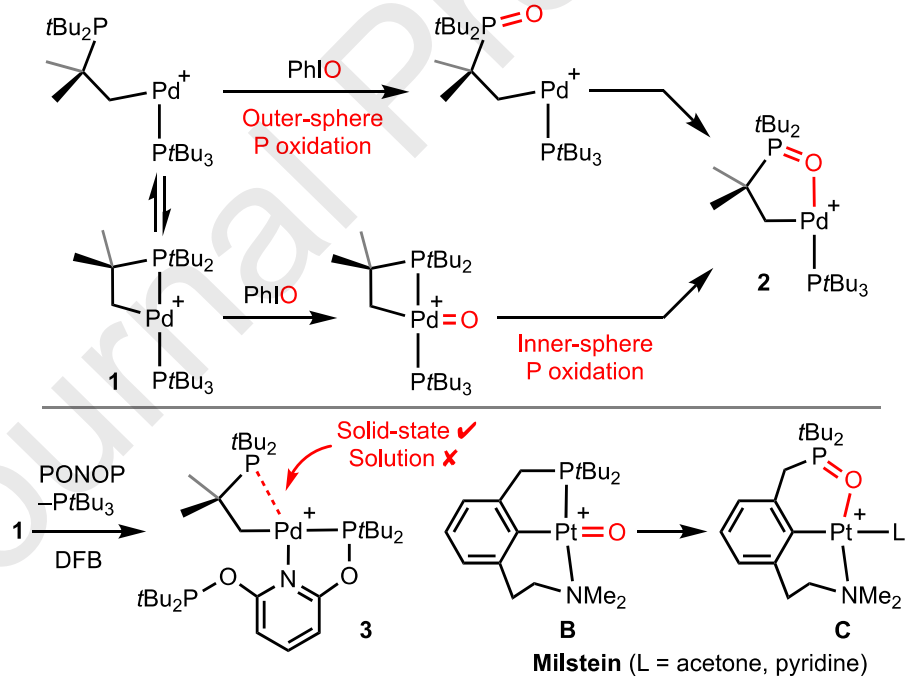


Figure 1. Solid-state structures of **1**.PF$_6$ and **2**.PF$_6$. Thermal ellipsoids drawn at 30% and 50% probability, respectively; minor disordered components and anions omitted for clarity. Selected bond lengths (Å) and angles (deg): **1**.PF$_6$; Pd1-P2, 2.2976(11); Pd1-P3, 2.3250(11); Pd1-C1, 2.075(6); Pd1-C14, 2.825(7); P2-Pd1-P3, 175.38(4); P2-Pd1-C1, 68.2(2); **2**.PF$_6$; 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).

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**.$BAr^F{}_4$ was reacted with 2,6-($tBu_2PO)_2C_5H_3N$ (PONOP) at RT in DFB leading to the formation of **3**.$BAr^F{}_4$ by substitution of P*t*Bu_3, dissociation of the tethered phosphine donor, and the (unusual) partial chelation of the pincer ligand; as evidenced by singlet ^{31}P resonances at δ 182.6, 180.0, and -12.0 (P*t*Bu_2) in an integral 1:1:1 ratio, and a doublet of doublets metal alkyl ^{13}C resonance at δ 24.2 ($^2J_{PC}$ = 70, 34 Hz). Whilst the X-ray structure of isolated **3** indicates the palladacycle is retained in the solid state (Figure 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 P*t*Bu_3 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),[11] On this basis, whilst we currently cannot definitively distinguish between the two possibilities, we postulate a discrete terminal oxo derivative is involved.

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



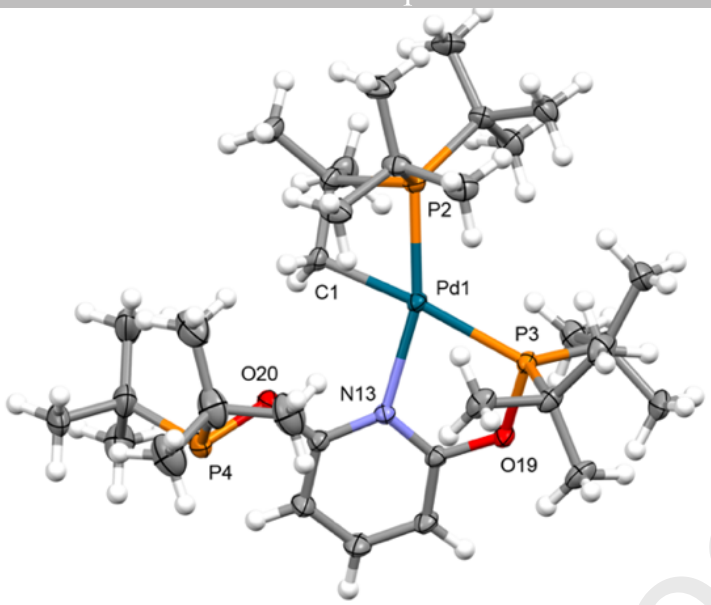


Figure 2. Solid-state structure of **3**.BAr^F_4. Thermal ellipsoids drawn at 30% probability; anion omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1-P2, 2.2837(7); Pd1-P3, 2.3831(7); Pd1-N13, 2.229(2); Pd1-C1, 2.082(3); P2-Pd1-N13, 162.56(6); P2-Pd1-C1, 67.40(8); C1-Pd1-P3, 171.23(9).

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(P*t*Bu$_3$)$_2$], P*t*Bu$_3$ and palladium black was observed on placing under H_2 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.

Conclusions

In summary, we report 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. We speculate that this reaction may include transient formation of a palladium oxo intermediate, however, further work is needed to substantiate this claim.

Experimental

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_2Cl_2 was dried over activated molecular sieves (3 Å) and stored under an argon atmosphere. 1,2-$F_2C_6H_4$ (DFB) was pre-dried over Al_2O_3, 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-pump-thaw

degassed, and stored over 3 Å molecular sieves under argon. [Pd(P*t*Bu$_3$)$_2$][PF$_6$],[4a] [Pd($\kappa_{P,C}$-P*t*Bu$_2$CMe$_2$CH$_2$)(P*t*Bu$_3$)(OAc)]·HOAc,[7] Na[BAr$^F_4$],[13] PhIO,[14] 2,6-(*t*Bu$_2$PO)$_2$C$_5$H$_3$N (PONOP)[15] were prepared using literature procedures. All other reagents are commercially available and were used as received. NMR spectra were recorded on Bruker spectrometers at 298 K. Chemical shifts are quoted in ppm and coupling constants in Hz. NMR spectra in DFB were recorded using an internal capillary of C_6D_6. ^{31}P NMR spectra are referenced to a solution of O=P(OMe)$_3$ in C_6D_6 (0.025 mmol L^{-1}, δ 3.80 relative to 85% H_3PO_4). High resolution (HR) ESI-MS were recorded on a Bruker Maxis Plus spectrometer. Microanalyses were performed at the London Metropolitan University by Stephen Boyer.

2. NMR scale reaction of [Pd(P*t*Bu$_3$)$_2$][PF$_6$] with air

A solution of [Pd(P*t*Bu$_3$)$_2$][PF$_6$] (6.6 mg, 10 μmol) in DFB (0.5 mL) within an open NMR tube containing an internal sealed capillary of O=P(OMe)$_3$ in C_6D_6 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($\kappa^2_{P,C}$–P*t*Bu$_2$CMe$_2$CH$_2$)(P*t*Bu$_3$)]$^+$ (δ 57.8 and -0.6) and [Pd($\kappa^2_{O,C}$–O=P*t*Bu$_2$CMe$_2$CH$_2$)(P*t*Bu$_3$)]$^+$ (δ 90.0 and 72.6) was observed as the major organometallic products along with other unidentified species.

2.1. Preparation of [Pd($\kappa^2_{P,C}$–P*t*Bu$_2$CMe$_2$CH$_2$)(P*t*Bu$_3$)][BAr$^F_4$] 1.BAr$^F_4$

To a solution of [Pd($\kappa^2_{P,C}$-P*t*Bu$_2$CMe$_2$CH$_2$)(P*t*Bu$_3$)(OAc)]·HOAc (56.6 mg, 90.1 μmol) in MTBE (5 mL) was added a solution of P*t*Bu$_3$ 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$^F_4$] (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.

^{1}H NMR (500 MHz, DFB/C_6D_6): δ 8.17 – 8.12 (m, 8H, Ar^F), 7.50 (br, 4H, Ar^F), 2.33 (app. t, $^3J_{PH}$ = 5.7, 2H, PdCH$_2$), 1.38 (d, $^3J_{PH}$ = 13.4, 6H, Me), 1.35 (d, $^3J_{PH}$ = 14.3, 18H, P*t*Bu$_2$), 1.23 (d, $^3J_{PH}$ = 12.7, 27H, P*t*Bu$_3$).

^{13}C{^{1}H} NMR (126 MHz, DFB/C_6D_6, selected data only): δ 51.9 (HMBC, PdCH$_2$C), 39.8 (dd, $^1J_{PC}$ = 7, $^3J_{PC}$ = 2, P*t*Bu$_3${C}), 38.7 (app. t, J_{PC} = 5, P*t*Bu$_2${C}), 31.7 (d, $^2J_{PC}$ = 4, P*t*Bu$_2${Me}), 31.1 (d, $^2J_{PC}$ = 4, $^4J_{PC}$ = 1, P*t*Bu$_3${Me}), 29.0 (s, Me), 26.2 (dd, $^2J_{PC}$ = 23, 3, PdCH$_2$).

^{31}P{^{1}H} NMR (162 MHz, DFB/C_6D_6): δ 57.8 (d, $^2J_{PP}$ = 317, 1P, P*t*Bu$_3$), -0.6 (d, $^2J_{PP}$ = 317, 1P, P*t*Bu$_2$).

Anal. Calcd for $C_{56}H_{65}BF_{24}P_2Pd$ (1373.28 gmol^{-1}): C, 48.98; H, 4.77; N, 0.00. Found: C, 48.91; H, 4.65; N, 0.00.

2.2. Preparation of [Pd($\kappa^2_{P,C}$–P*t*Bu$_2$CMe$_2$CH$_2$)(P*t*Bu$_3$)][PF$_6$] 1.PF$_6$

To a solution of [Pd($\kappa^2_{P,C}$-P*t*Bu$_2$CMe$_2$CH$_2$)(P*t*Bu$_3$)(OAc)]·HOAc (130.6 mg, 207.9 μmol) in MTBE (5 mL) was added a solution of P*t*Bu$_3$ in pentane (0.27 mL of a 0.78 M solution, 210 μmol) and the resulting solution was stirred for 5 min before being transferred onto a 5 mL degassed aqueous suspension of Na[PF$_6$] (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 x 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.

^{1}H NMR (300 MHz, DFB/C$_6$D$_6$): *δ* 2.32 (app. t, $^3J_{PH}$ = 5.7, 2H, PdCH$_2$), 1.38 (d, $^3J_{PH}$ = 13.3, 6H, Me), 1.35 (d, $^3J_{PH}$ = 14.4, 18H, P*t*Bu$_2$) 1.23 (d, $^3J_{PH}$ = 12.7, 27H, P*t*Bu$_3$).
^{31}P{^{1}H} NMR (122 MHz, DFB/C$_6$D$_6$): *δ* 57.6 (d, $^2J_{PP}$ = 317, 1P, P*t*Bu$_3$), -0.6 (d, $^2J_{PP}$ = 317, 1P, P*t*Bu$_2$), -142.4 (septet, $^1J_{PF}$ = 710, 1P, PF$_6$).

2.3. NMR scale reactions of 1.BAr$^F_4$ and P*t*Bu$_3$ with PhIO

A suspension of PhIO (22.1 mg, 100 μmol) in a solution of **1**.BAr$^F_4$ (13.9 mg, 10.0 μmol) in DFB (0.5 mL) within a J. Young's valve NMR tube was monitored by ^{31}P NMR spectroscopy, with constant mixing at room temperature when not in the spectrometer. Quantitative conversion to **2**.BAr$^F_4$ was observed within 1 h.

A suspension of PhIO (22.1 mg, 100 μmol) in a solution of P*t*Bu$_3$ (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 ^{31}P NMR spectroscopy, with constant mixing at room temperature when not in the spectrometer. Quantitative conversion to O=P*t*Bu$_3$ (*δ* 64.4 ppm)[16] was observed within 24 h.

2.4. Preparation of [Pd($\kappa^2_{O,C}$-O=P*t*Bu$_2$CMe$_2$CH$_2$)(P*t*Bu$_3$)][BAr$^F_4$] 2.BAr$^F_4$

A suspension of Pd($\kappa^2_{P,C}$–P*t*Bu$_2$CMe$_2$CH$_2$)(P*t*Bu$_3$)][BAr$^F_4$] (73.1 mg, 53.2 μmol) and PhIO (119.6 mg, 543.4 μmol) in DFB (5 mL) was stirred for 30 min. The solution was filtered into hexane (20 mL) affording a yellow precipitate that was isolated by filtration, washed with hexane (3 x 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.

^{1}H NMR (500 MHz, DFB/C$_6$D$_6$): *δ* 8.17 – 8.12 (m, 8H, Ar^F), 7.50 (br, 4H, Ar^F), 2.77 (d, $^3J_{PH}$ = 10.0, 2H, PdCH$_2$), 1.44 (d, $^3J_{PH}$ = 13.0, 6H, Me), 1.27 (d, $^3J_{PH}$ = 13.5, 18H, O=P*t*Bu$_2$), 1.25 (d, $^3J_{PH}$ = 13.1, 27H, P*t*Bu$_3$).
^{1}H NMR (300 MHz, CD$_2$Cl$_2$): *δ* 7.76 – 7.68 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 2.83 (d, $^3J_{PH}$ = 10.1, 2H, PdCH$_2$), 1.61 (d, $^3J_{PH}$ = 13.0, 6H, Me), 1.48 (app. d, $^3J_{PH}$ = 13.3, 45H, O=P*t*Bu$_2$ + P*t*Bu$_3$).

$^{13}C\{^1H\}$ NMR (126 MHz, DFB/C_6D_6, selected data only): δ 53.9 (d, $^2J_{PC}$ = 53, $PdCH_2\underline{C}$), 39.9 (d, $^1J_{PC}$ = 14, P*t*Bu_3{C}), 38.7 (d, $^1J_{PC}$ = 47, O=P*t*Bu_2{C}), 38.6 (app. t, $^2J_{PC}$ = 3, $PdCH_2$), 30.7 (d, $^2J_{PC}$ = 3, P*t*Bu_3{Me}), 27.8 (s, Me), 27.5 (s, $^2J_{PC}$ = 22, O=P*t*Bu_2{Me}).

$^{31}P\{^1H\}$ NMR (162 MHz, DFB/C_6D_6): δ 90.0 (s, 1P, O=P*t*Bu_2), 72.6 (s, 1P, P*t*Bu_3).

$^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 91.0 (s, 1P, O=P*t*Bu_2), 73.8 (s, 1P, P*t*Bu_3).

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

Anal. Calcd for $C_{56}H_{65}BF_{24}OP_2Pd$ (1389.33 gmol^{-1}): C, 48.41; H, 4.72; N, 0.00. Found: C, 48.29; H, 4.87; N, 0.00.

2.5. Preparation of [Pd($\kappa^2_{O,C}$-O=P*t*Bu_2CMe_2CH_2)(P*t*Bu_3)][PF_6] 2.PF_6

A suspension of [Pd($\kappa^2_{P,C}$–P*t*Bu_2CMe_2CH_2)(P*t*Bu_3)][PF_6] (61.2 mg, 93.4 µmol) and PhIO (620.0 mg, 2.814 mmol) in DFB (5 mL) was stirred vigorously for 15 min. The solution was filtered into hexane (20 mL), affording a yellow precipitate which was isolated by filtration, washed with hexane (3 x 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.

^1H NMR (500 MHz, DFB/C_6D_6): δ 2.76 (d, $^3J_{PH}$ = 10.1, 2H, $PdCH_2$), 1.44 (d, $^3J_{PH}$ = 13.0, 6H, Me), 1.31 – 1.18 (m, 45H, O=P*t*Bu_2 + P*t*Bu_3).

^1H NMR (500 MHz, CD_2Cl_2): δ 2.84 (d, $^3J_{PH}$ = 10.0, 2H, $PdCH_2$), 1.62 (d, $^3J_{PH}$ = 13.1, 6H, Me), 1.49 (app. d, $^3J_{PH}$ = 13.3, 45H, O=P*t*Bu_2 + P*t*Bu_3).

$^{31}P\{^1H\}$ NMR (162 MHz, DFB/C_6D_6): δ 90.0 (s, 1P, O=P*t*Bu_2), 72.7 (s, 1P, P*t*Bu_3), -142.4 (septet, $^1J_{PF}$ = 710, 1P, PF_6).

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 89.2 (s, 1P, O=P*t*Bu_2), 72.0 (s, 1P, P*t*Bu_3), -144.5 (septet, $^1J_{PF}$ = 710, 1P, PF_6).

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

2.6. NMR scale reaction of 1.BAr^F_4 with PONOP

A solution of **1**.BAr^F_4 (13.8 mg, 10.1 µmol) and PONOP (3.9 mg, 11 µmol; δ 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)$_3$ in C_6D_6. Analysis by ^{31}P NMR spectroscopy after 30 min at room temperature indicated complete conversion to [Pd(PONOP)(P*t*Bu_2CMe_2CH_2)][BAr^F_4] (δ 182.6, 180.0 and -12.0) and P*t*Bu_3 (δ 62.8).

2.7. Preparation of [Pd(PONOP)(P*t*Bu_2CMe_2CH_2)][BAr^F_4] 3.BAr^F_4

A solution of [Pd($\kappa^2_{P,C}$–P*t*Bu_2CMe_2CH_2)(P*t*Bu_3)][BAr^F_4] (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}H NMR (500 MHz, DFB/C_6D_6, selected data only): δ 8.17 – 8.12 (m, 8H, Ar^F), 7.50 (br, 4H, Ar^F), 1.82 (d, $^{3}J_{PH}$ = 7.0, 2H, $PdCH_2$), 1.41 (d, $^{3}J_{PH}$ = 14.2, 18H, P*t*Bu_2), 1.31 (d, $^{3}J_{PH}$ = 14.6, 6H, Me), 1.20 (d, $^{3}J_{PH}$ = 14.1, 18H, P*t*Bu_2O), 1.06 (d, $^{3}J_{PH}$ = 12.4, 18H, P*t*Bu_2O).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.79 (t, $^{3}J_{HH}$ = 7.8, 1H, py), 7.76 – 7.68 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 7.35 (app. t, *J* = 6, 1H, py), 6.72 (d, $^{3}J_{HH}$ = 7.9, 1H, py), 1.92 (d, $^{3}J_{PH}$ = 7.0, 2H, $PdCH_2$), 1.60 (d, $^{3}J_{PH}$ = 14.3, 18H, P*t*Bu_2), 1.51 (d, $^{3}J_{PH}$ = 14.5, 6H, Me), 1.36 (d, $^{3}J_{PH}$ = 14.2, 18H, P*t*Bu_2O), 1.20 (d, $^{3}J_{PH}$ = 12.4, 18H, P*t*Bu_2O).

^{13}C{^{1}H} NMR (126 MHz, DFB/C_6D_6, selected data only): δ 46.0 (d, $^{1}J_{PC}$ = 25, $PdCH_2\underline{C}$), 38.7 (d, $^{1}J_{PC}$ = 9, P*t*Bu_2{C}), 38.4 (s, P*t*Bu_2O{C}), 35.9 (d, $^{1}J_{PC}$ = 33, P*t*Bu_2O{C}), 32.0 (d, $^{2}J_{PC}$ = 3, P*t*Bu_2{Me}), 30.8 (d, $^{2}J_{PC}$ = 5, Me), 27.0 (d, $^{2}J_{PC}$ = 3, P*t*Bu_2O{Me}), 27.1 (d, $^{2}J_{PC}$ = 3, P*t*Bu_2O{Me}), 24.2 (dd, $^{2}J_{PC}$ = 70, 34, $PdCH_2$).

^{31}P{^{1}H} NMR (162 MHz, DFB/C_6D_6): δ 182.6 (s, 1P, P*t*Bu_2O), 180.0 (s, 1P, P*t*Bu_2O), -12.0 (s, 1P, P*t*Bu_2).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 182.1 (s, 1P, P*t*Bu_2O), 178.9 (s, 1P, P*t*Bu_2O), -12.6 (s, 1P, P*t*Bu_2).

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

Anal. Calcd for $C_{56}H_{78}BF_{24}NO_2P_3Pd$ (1570.40 $gmol^{-1}$): C, 49.68; H, 5.00; N, 0.89. Found: C, 49.77; H, 5.01; N, 0.86.

2.8. NMR scale reaction of 2.BAr$^F_4$ with air

A solution of **2**.BAr^F_4 (13.9 mg, 10.0 μmol) in DFB (0.5 mL) within an open NMR tube containing an internal sealed capillary of $O=P(OMe)_3$ in C_6D_6 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}P NMR spectroscopy.

2.9. NMR scale reactions of 1.BAr$^F_4$ and 2.BAr$^F_4$ with H_2.

Solutions of **1**.BAr^F_4 (13.8 mg, 10.1 μmol) and **2.**BAr^F_4 (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 $O=P(OMe)_3$ in C_6D_6) were freeze-pump-thaw degassed and placed under an atmosphere of H_2 (1 bar). Reactions were monitored by NMR spectroscopy, with constant mixing at room temperature when not in the spectrometer. The reaction of **1.**BAr^F_4 with H_2 generated P*t*Bu_3 (δ 62.9), [Pd(P*t*$Bu_3)_2$] (δ 84.4) and palladium black aver 40 h. No reaction of **2.**BAr^F_4 with H_2 was observed after 72 h at room temperature. Subsequent heating at 50 °C, however, resulted in complete decomposition of **2.**BAr^F_4 to a palladium mirror within 18 h.

Conflicts of interest

There are no conflicts to declare.

Supporting information

- NMR and ESI-MS spectra of new compounds, and selected reactions (PDF)
- Primary NMR data (MNOVA)
- Accession Codes: CCDC 1961743-1961745 contain the supplementary crystallographic data for this paper.

Acknowledgements

We gratefully acknowledge the EPSRC (DTP studentship; M.J.G.S), University of Warwick, and Royal Society (UF100592, UF150675; A.B.C.) for financial support. Crystallographic data were collected using an instrument that received funding from the ERC under the European Union's Horizon 2020 research and innovation programme (grant agreement No 637313).

Notes and References

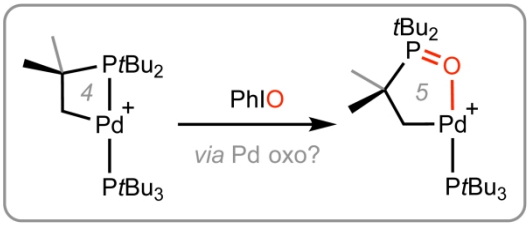
Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

- Novel low-coordinate palladacycles have been isolated and full characterised
- Oxidation of cyclometalated tri-*tert*-butylphosphine using PhIO
- Oxygen-atom transfer is proposed to proceed by formation of a palladium oxo species

- Hemi-labile coordination of cyclometalated tri-*tert*-butylphosphine



1 (a) J.F. Hartwig, Organotransition Metal Chemistry-From Bonding to Catalysis, University Science Books, 2010; (b) U. Christmann, R. Vilar, Angew. Chem. Int. Ed. 44 (2005) 366–374.

2 (a) J.P. Stambuli, M. Bühl, J.F. Hartwig, J. Am. Chem. Soc. 124 (2002) 9346–9347; (b) M. Yamashita, J.F. Hartwig, J. Am. Chem. Soc. 126 (2004) 5344–5345; (c) J.P. Stambuli, C.D. Incarvito, M. Bühl, J.F. Hartwig, J. Am. Chem. Soc. 126 (2004) 1184–1194; (d) M. Yamashita, I. Takamiya, K. Jin, K. Nozaki, Organometallics. 25 (2006) 4588–4595; (e) J.P. Stambuli, Z. Weng, C.D. Incarvito, J.F. Hartwig, Angew. Chem. Int. Ed. 46 (2007) 7674–7677; (f) F. Barrios-Landeros, B.P. Carrow, J.F. Hartwig J. Am. Chem. Soc. 131 (2009) 8141–8154; (g) P.S. Hanley, D. Marković, J.F. Hartwig, J. Am. Chem. Soc. 132 (2010) 6302–6303; (h) P.S. Hanley, J.F. Hartwig, J. Am. Chem. Soc. 133 (2011) 15661–15673; (i) P.S. Hanley, S.L. Marquard, T.R. Cundari, J.F. Hartwig, J. Am. Chem. Soc. 134 (2012) 15281–15284; (j) S. Sugawara, M. Abe, Y. Fujiwara, M. Wakioka, F. Ozawa, Y. Yamamoto, Eur. J. Inorg. Chem. (2015) 534–541; (k) D.M. Peacock, Q. Jiang, P.S. Hanley, T.R. Cundari, J.F. Hartwig, J. Am. Chem. Soc. 140 (2018) 4893–4904;

3 M.D. Walter, P.S. White, M. Brookhart, New. J. Chem. 37 (2013) 1128–1133.

4 (a) T. Troadec, S.-Y. Tan, C.J. Wedge, J.P. Rourke, P.R. Unwin, A.B. Chaplin, Angew. Chem. Int. Ed. 55 (2016) 3754–375; (b) Q. Simpson, M.J.G. Sinclair, D.W. Lupton, A.B. Chaplin, J.F. Hooper, Org. Lett. 20 (2018) 5537–5540.

5 S.D. Pike, M.R. Crimmin, A.B. Chaplin, Chem. Commun. 53 (2017) 3615–3633.

6 For a related oxidation reaction involving a palladium(I) dimer see: V. Durà-Vilà, D.M.P. Mingos, R. Vilar, A.J.P. White, D.J. Williams, Chem. Commun. (2000) 1525–1526.

7 W.H. Henderson, J.M. Alvarez, C.C. Eichman, J.P. Stambuli, Organometallics 30 (2011) 5038–5044.

8 P.S. Pregosin, NMR in Organometallic Chemistry, Wiley-VCH, 2012.

9 N.R. Deprez, M.S. Sanford, Inorg. Chem. 46 (2007) 1924–1935.

10 For an illustrative example of concerted insertion into a M–P bond see: E.A. LaPierre, M.L. Clapson, W.E. Piers, L. Maron, D.M. Spasyuk, C. Gendy, Inorg. Chem. 57 (2017) 495–506.

11 E. Poverenov, I. Efremenko, A.I. Frenkel, Y. Ben-David, L.J.W. Shimon, G. Leitus, L. Konstantinovski, J.M.L. Martin, D. Milstein, Nature 455 (2008) 1093–1096.

[12] (a) D. Delony, M. Kinauer, M. Diefenbach, S. Demeshko, C. Würtele, M.C. Holthausen, S. Schneider, Angew. Chem. Int. Ed. 58 (2019) 10971–10974; (b) D. Munz, Chem. Sci. 9 (2018) 1155–1167; (c) K. Ray, F. Heims, F.F. Pfaff, Eur. J. Inorg. Chem. 2013 (2013) 3784–3807; (d) R.S. Hay-Motherwell, G. Wilkinson, B. Hussain-Bates, M.B. Hursthouse, Polyhedron 12 (1993) 2009–2012.

[13] (a) W.E. Buschmann, J.S. Miller, K. Bowman-James, C.N. Miller, Inorg. Synth. 33 (2002) 83–91; (b) A.J. Martínez-Martínez, A.S. Weller, Dalton Trans. 48 (2019) 3551–3554.

[14] K. Li, A.E. Weber, L. Tseng, S.J. Malcolmson, Org. Lett. 19 (2017) 4239–4242.

[15] S. Kundu, W.W. Brennessel, W.D. Jones, Inorg. Chem. 50 (2011) 9443–9453.

[16] O=P*t*Bu$_3$ prepared independently using an adapted literature (C.R. Hilliard, N. Bhuvanesh, J.A. Gladysz, J. Blümel, Dalton Trans. 41 (2012) 1742–1754.) was characterised by ^{31}P NMR spectroscopy by a signal at δ 64.4.