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

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

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

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ABSTRACT

The synthesis of an unusual T-shaped alkylpalladium(II) complex featuring a cyclometalated tri-tert-butylphosphinoxo 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(PR3)(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(PtBu3)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(PtBu3)2][PF6] in the weakly coordinating solvent 1,2-difluorobenzene (DFB) [5] resulted in the consecutive formation of novel cyclometalated Pd(II) complexes [Pd(κ2,P,C-PtBu2CMe2CH2)(PtBu3)]⁺ (1) and [Pd(κ2,O,C-O-PtBu2CMe2CH2)(PtBu3)]⁺ (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]+ salt (1-BAR4; ArR = 3,5-(CF3)2C6H3), by metathesis of the previously reported four-coordinate acetate derivative [Pd(κ2,C-PtBu2CMe2CH2)(PtBu3)(OAc)]·HOAc [7] with Na[BAR4] under biphasic conditions (Scheme 1). This method subsequently proved to be the most expedient method for obtaining analytically pure samples of 1 on a practically useful scale. Isolated 1-BAR4 is characterised by NMR spectroscopy in DFB solution by 31P resonances at δ 57.8 (PtBu3) and −0.6 (PtBu2), which display diagnostically large trans-phosphine 2JPP coupling of 317 Hz [8], and a metal alkyl 13C resonance at δ 26.2 (app. t, 2JPP = 23, 3 Hz). The easily handled reagent PhIO was identified as an effective oxidant [9] and enabled quantitative oxidation of 1-BAR4 to 2-BAR4 within 1 h at RT in DFB (10 eqv PhIO). The product was subsequently obtained in 55% isolated yield and fully characterised.

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

* Corresponding author.
E-mail address: a.b.chaplin@warwick.ac.uk (A.B. Chaplin).

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Structural elucidation of 1·BArF and 2·BArF using X-ray diffraction was frustrated by whole molecule structural disorder of both the palladium-based cations and counteranions in the high symmetry P2₁3 space group. Consequently, single crystalline samples of the corresponding [PF₆]⁻ salts, which can be prepared in a similar manner and do not suffer from such crystallographic problems, where analysed (Fig. 1). The solid-state structures of 1·PF₆ and 2·PF₆ are notable for the adoption of distorted T-shaped geometries (P₂/P₂–Pd₁–P₃ angles > 170°; cf. 173.40(5)° in A) and an agostic interaction with the PtBu₃ ligand, with that in 2·PF₆ significantly more pronounced than in 1·PF₆ (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/P₂–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·BArF was reacted with 2,6-(rBu₂PO)₂C₅H₃N (PONOP) at RT in DFB leading to the formation of 3·BArF by substitution of PtBu₃, dissociation of the tethered phosphine donor, and the (unusual) partial chelation of the pincer ligand; as evidenced by singlet ⁴⁰P resonances at δ 182.6, 180.0, and −12.0 (PtBu₃) in an integral 1:1:1 ratio, and a doublet of doublets metal alkyl¹³C resonance at δ 24.2 (JₚC = 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 PtBu₃ 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(PtBu₃)₂]₂, PtBu₃ and palladium black was observed on placing under H₂ 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. 1. Solid-state structures of 1·PF₆ and 2·PF₆. 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·PF₆; 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·PF₆; 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.

Fig. 2. Solid-state structure of 3·BArF. 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-C₁, 1.525(2); P₂-Pd₁-O₁, 1.525(2); P₂-Pd₁-C₁₄, 2.770(3); P₂-Pd₁-C₁₄, 171.55(5); O₁-Pd₁-C₁, 87.91(9); Pd₁-O₁-P₂, 114.79(10).
3. Conclusions

In summary, we report the synthesis of an unusual T-shaped alkyl-
palladium(II) complex featuring a cyclometalated tri-tert-butylphosphineoxido ligand by oxidation of the corresponding cyclometalated tri-tetra-tert-butyliophosphate 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. CD₂Cl₂ was dried over activated molecular sieves (3 Å) and stored using Schlenk and glovebox techniques unless otherwise stated. Glassware was purged 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(Ph₃P)₂][PF₆] [4a], [Pd₂κ₄-Cu⁵-Me₄C₆H₆] (PdBu₃)(OAc)]·HOAc [7], Na[BArF₂] [13], PhIO [14], 2,6-(BuPO₂)₃C₆H₃N (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 within an open NMR tube containing an internal sealed capillary of O₂ (P(Bu₃)₂ 1H NMR (500 MHz, DFB/C₆D₆): δ 7.77-7.68 (m, 8H, Ar F), 7.56 (br, 4H, Ar²), 2.83 (d, 3JPH = 10.1, 2H, PhCH₂), 1.61 (d, 3JPH = 13.0, 6H, Me), 1.48 (app. d, 3JPH = 13.3, 45H, O=PPh₃ + PPh₃). 

31P{¹H} NMR (126 MHz, DFB/C₆D₆, selected data only): δ 51.9

To a solution of [Pd₂κ₄-Cu⁵-Me₄C₆H₆](PdBu₃)(OAc)]·HOAc (130.6 mg, 207.9 µmol) in MTBE (5 mL) was added a solution of PdBu₃ 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[P₄F₁₀] (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.

1H NMR (500 MHz, DFB/C₆D₆): δ 8.17-8.12 (m, 8H, Ar²), 7.50 (br, 4H, Ar²), 2.33 (app. t, 3JPH = 5.7, 2H, PdCH₂), 1.38 (d, 3JPH = 13.4, 6H, Me), 1.35 (d, 3JPH = 14.3, 18H, PdBu₂), 1.23 (d, 3JPH = 12.7, 27H, PhBu₃).

13C{¹H} NMR (126 MHz, DFB/C₆D₆, selected data only): δ 53.9 (d, 1JPC = 53, PdCH₂), 39.9 (d, 1JPC = 14, PdBu₂(C)), 38.7 (app. t, 1JPC = 5, PdBu₂(C)), 31.7 (d, 2JPC = 4, PdBu₂(Me)), 31.1 (d, 2JPC = 4, 3JPC = 1, PdBu₂(Me)), 26.2 (dd, 2JPC = 23, 3, PdCH₂).

13P{¹H} NMR (162 MHz, DFB/C₆D₆): δ 57.6 (d, 2Jpp = 317, 1P, PdBu₃), −0.6 (d, 2Jpp = 317, 1P, PdBu₂), −142.2 (septet, 1Jpp = 710, 1P, Pf₂).

4.5. NMR scale reactions of 1BAr₄ and PdBu₃ with PhIO

A suspension of PhIO (22.1 mg, 100 µmol) in a solution of 1BAr₄ (13.9 mg, 10.0 µmol) in DFB (0.5 mL) with a J. Young’s valve NMR tube was monitored by 31P NMR spectroscopy, with constant mixing at room temperature when not in the spectrometer. Quantitative conversion to 2BAr₄ was observed within 1 h.

A suspension of PhIO (22.1 mg, 100 µmol) in a solution of PdBu₃ (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 31P NMR spectroscopy, with constant mixing at room temperature when not in the spectrometer. Quantitative conversion to O=PPh₃ (δ 64.4 ppm) [16] was observed within 24 h.

4.6. Preparation of [Pd(κ₄-Cu⁵-Me₄C₆H₆)](PdBu₃)² 2BAr₄

A suspension of [Pd₂κ₄-Cu⁵-Me₄C₆H₆](PdBu₃)(OAc)]·HOAc (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.
(d, JPC = 3, PrBu3(Me)), 27.8 (s, Me), 27.5 (s, JPC = 22, O=PrBu2(Me)).

$^{31}P(\text{H})$ NMR (162 MHz, DFB/C6D6): δ 90.0 (s, 1P, O=PrBu2), 72.6 (s, 1P, PrBu2).

$^{31}P(\text{H})$ NMR (121 MHz, CD2Cl2): δ 91.0 (s, 1P, O=PrBu2), 73.8 (s, 1P, PrBu2).

HR ESI-MS (MeCN, 180 °C, 4 kV) positive ion: 525.2611 ($[\text{M}+\text{H}]^+$, calcld 525.2611) m/z.

Anal. Calcd for C62H56BF24NO2P3Pd (1570.40 g mol$^{-1}$): C, 49.68; H, 4.87; N, 0.00. Found: C, 49.66; H, 4.87; N, 0.00.

4.7. Preparation of [Pd(PONOP)(PtBu2CMe2CH2)][BArF4]

A suspension of [Pd($\text{C}_8$-$\text{C}_5$-$\text{C}_6$-$\text{C}_7$)(PtBu2)][BPF6] ($61.2$ 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 ($3 \times 5$ 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.

$^1$H NMR (500 MHz, DFB/C6D6): δ 2.76 (d, JPH = 10.1, 2H, PdCH2), 1.44 (d, $^3$JPC = 13.0, 6H, Me), 1.31–1.18 (m, 45H, O=PrBu2 + PrBu2).

$^1$H NMR (500 MHz, CD2Cl2): δ 2.84 (d, JPH = 10.0, 2H, PdCH2), 1.62 (d, $^3$JPC = 13.1, 6H, Me), 1.49 (app. d, $^3$JPH = 13.3, 45H, O=PrBu2 + PrBu2).

$^{31}P(\text{H})$ NMR (162 MHz, DFB/C6D6): δ 90.0 (s, 1P, O=PrBu2), 72.7 (s, 1P, PrBu2), −142.4 (septet, $^{1}$JPF = 710, 1P, PF6).

$^{31}P(\text{H})$ NMR (126 MHz, DFB/C6D6): δ 182.6 (s, 1P, PrBu2). HR ESI-MS (MeCN, 180 °C, 4 kV) positive ion: 706.3263 ($[\text{M}+\text{H}]^+$, calcld 706.3270) m/z.

Anal. Calcd for C30H24BF33NO2P3Pd (1570.40 g mol$^{-1}$): C, 48.29; H, 4.87; N, 0.00. Found: C, 48.29; H, 4.87; N, 0.00.

4.8. NMR scale reaction of 1-Bar4 with PONOP

A solution of 1-Bar4 ($13.8$ 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 tube and monitored periodically for 2 months, topping up with solvent as necessary to maintain a constant volume. No reaction was apparent from analysis by $^{31}$P NMR spectroscopy.

4.11. NMR scale reactions of 1-Bar4 and 2-Bar4 with H2

Solutions of 1-Bar4 ($13.8$ mg, 10.1 μmol) and 2-Bar4 ($13.8$ mg, 10.0 μmol) in DFB (0.5 mL) within an open NMR tube containing an internal sealed capillary of O=P(O)Me3 in C6D6 was held at room temperature and monitored periodically for 2 months, topping up with solvent as necessary to maintain a constant volume. No reaction was apparent from analysis by $^{31}$P NMR spectroscopy, with constant mixing at room temperature when not in the spectrometer. The reaction of 1-Bar4 with H2 generated PrBu3 (δ 62.9, [Pd(PrBu3)2] (δ 84.4) and palladium black over 40 h. No reaction of 2-Bar4 with H2 was observed after 72 h at room temperature. Subsequent heating at 50 °C, however, resulted in complete decomposition of 2-Bar4 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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