



Cite this: *Dalton Trans.*, 2022, **51**, 11617

Received 5th July 2022,  
Accepted 10th July 2022

DOI: 10.1039/d2dt02152h

rsc.li/dalton

The well-defined Pd(*i*) metalloradical  $[\text{Pd}(\text{PtBu}_3)_2]^+$  reacts with aryl and alkyl iodides at room temperature, yielding  $[\text{Pd}(\text{PtBu}_3)(\mu\text{-I})]_2$  and phosphonium salts. Pd(*ii*) aryl/alkyl derivates, reflecting net radical oxidative addition of the substrate to the metalloradical, are generated during the reaction and two examples have been isolated and crystallographically characterised.

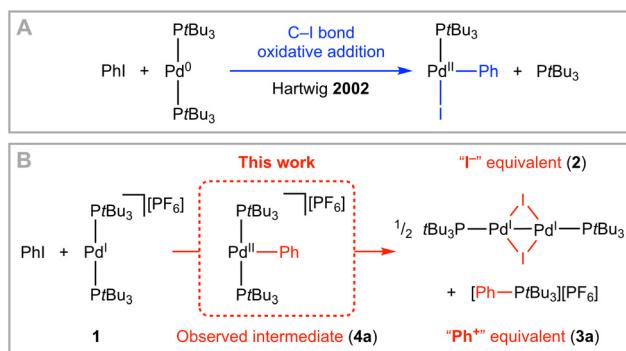
The transition-metal-mediated activation of carbon–halogen bonds is the basis of widely exploited catalytic methods for the construction of organic molecules. Oxidative addition to low-coordinate Pd(0) complexes is a pervading theme, with work by Hartwig and co-workers in 2002 involving isolation of T-shaped aryl Pd(*ii*) halide products a key mechanistic reference point (Scheme 1A).<sup>1,2</sup> Whilst the Pd(0)/Pd(*ii*) redox couple remains the workhorse, processes invoking single electron transfer and Pd(*i*) and Pd(*iii*) intermediates have been attracting growing attention.<sup>3</sup> Well-defined monomeric examples of the former are rare,<sup>4</sup> but as part of work in our group we recently reported the synthesis of  $[\text{Pd}(\text{PtBu}_3)_2]\text{[PF}_6]$  **1** by one-electron oxidation of  $[\text{Pd}(\text{PtBu}_3)_2]$  with  $[\text{Fc}]\text{[PF}_6]$ .<sup>5</sup> Using **1** as an exemplar, we herein present our preliminary findings exploring the activation of aryl and alkyl iodides by palladium metalloradicals.

Treatment of **1** (20 mM) with 1.1 equivalents of phenyl iodide in 1,2-difluorobenzene (DFB) solvent<sup>6</sup> resulted in complete consumption of the metalloradical within 24 h at room temperature and generated a 1 : 2 mixture of the known Pd(*i*) iodide dimer  $[\text{Pd}(\text{PtBu}_3)(\mu\text{-I})]_2$  **2** and phenyl phosphonium salt  $[\text{PtBu}_3\text{Ph}]\text{[PF}_6]$  **3a** with >97% selectivity (Scheme 1B). This outcome can be viewed as heterolytic cleavage of the C–I bond and this interpretation is reinforced by immediate conversion

of **1** into **2** upon addition of excess KI/18-crown-6 in DFB at room temperature. The decisive role of **1** was confirmed by a control experiment involving treatment of  $\text{PtBu}_3$  with excess phenyl iodide which did not lead to formation of **3a**, even under considerably more forcing reaction conditions.

When the reaction was repeated using 1.5 equivalents of phenyl iodide a larger proportion of **3a** was generated and periodic monitoring using UV/vis and NMR spectroscopy indicated complete consumption of **1** within 4 h, sigmoidal reaction kinetics (Fig. 1A), and intermediate formation of a diamagnetic species assigned to three-coordinate Pd(*ii*) aryl  $[\text{Pd}(\text{PtBu}_3)_2\text{Ph}]\text{[PF}_6]$  **4a** ( $\lambda_{\text{max}} = 305$  nm,  $\delta_{31\text{P}} 61.0$ ). Whilst a complex overall mechanism is evident from the reaction profile, observation of **4a** reconciles formation of **3a** by reductive elimination. The resulting Pd(0) is presumably converted into **2** or lost from solution,<sup>7</sup> with the latter pathway evidently more pronounced in the presence of excess phenyl iodide. Addition of 5 equivalents of  $\text{PtBu}_3$  retarded, but did not prevent, reaction of **1** with phenyl iodide.

Intrigued by the generation of **4a**, which corresponds to *net* radical oxidative addition of the substrate to **1**, we explored reactions with aryl iodides bearing electron donating methoxy substituents to facilitate isolation of the corresponding Pd(*ii*)

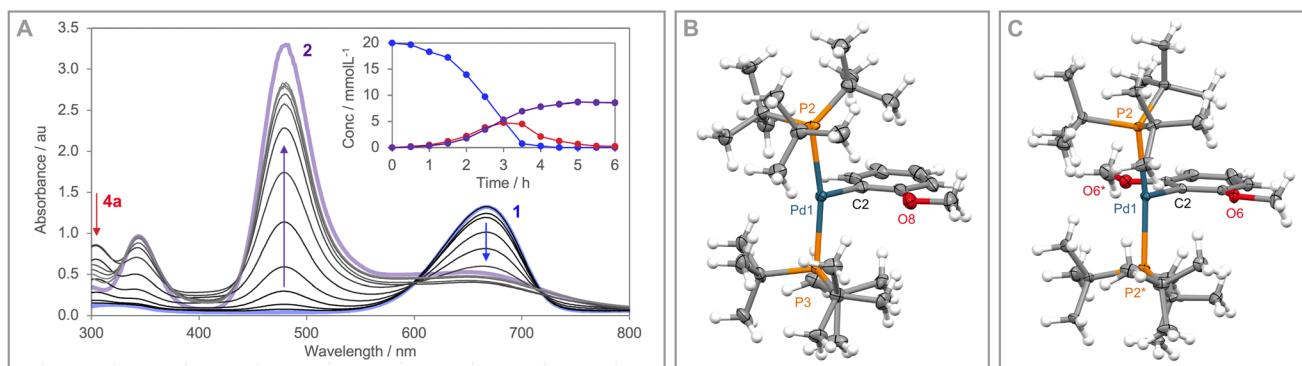


**Scheme 1** Activation of phenyl iodide by (A) Pd(0) and (B) Pd(*i*) complexes.

Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, UK. E-mail: [a.b.chaplin@warwick.ac.uk](mailto:a.b.chaplin@warwick.ac.uk)

† Electronic supplementary information (ESI) available: Full experimental details, including characterisation of new compounds and spectroscopic data for selected reactions, and mechanistic sketch. CCDC 2172989 (**3a**), 2172990 (**3b**), 2172991 (**4b**), 2172992 (**4c**) and 2172993 ( $[\text{PtBu}_3\text{H}]\text{[PF}_6]$ ). For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2dt02152h>





**Fig. 1** (A) UV-vis spectra collected during the reaction of **1** with phenyl iodide, with inset showing time course profiles of **1**, **2** and **4a**. Solid-state structures of **4b** ( $Z' = 2$ ) and **4c** (C): thermal ellipsoids at 30% probability, minor disordered components (3x tBu groups in **4b**) and anions omitted for clarity. Selected bond lengths and angles for **4b**: Pd1–P2, 2.3967(13) Å; Pd1–P3, 2.4345(12) Å; Pd1–C2, 1.998(6) Å; all Pd1–Me > 3.0 Å; P2–Pd1–P3, 168.24(5)°; Pd11–P12, 2.4168(12) Å; Pd11–P13, 2.4192(11) Å; Pd11–C12/C12A, 1.991(5)/1.971(5) Å; all Pd11–Me > 3.0 Å; P12–Pd11–Pd13, 169.39(4)°; **4c**: Pd1–P2, 2.4151(14) Å; Pd1–C2, 1.975(7) Å; all Pd1–Me > 3.0 Å; P2–Pd1–P2\*, 168.91(7)°. \* = symmetry equivalent atom.

aryl derivatives by attenuating onward reductive elimination. Gratifyingly, reactions of **1** with 2-methoxyphenyl iodide and 2,6-dimethoxyphenyl iodide in DFB at room temperature resulted in formation of the persistent Pd(II) aryls  $[\text{Pd}(\text{PtBu}_3)_2\text{Ar}]^+[\text{PF}_6^-]$  ( $\text{Ar} = 2\text{-}(\text{MeO})\text{C}_6\text{H}_4$ , **4b**;  $2,6\text{-}(\text{MeO})_2\text{C}_6\text{H}_3$ , **4c**) alongside  $[\text{PtBu}_3\text{X}]^+$  ( $\text{X} = 2\text{-}(\text{MeO})\text{C}_6\text{H}_4$ , **3b**; **I**) and **2** within 24 h. These low coordinate complexes were successfully isolated from solution, in modest yield following purification by column chromatography (32%, **4b**; 38%, **4c**), and fully characterised; including in the solid state by single crystal X-ray diffraction (Fig. 1B and C). The spectroscopic features of **4b/c** are congruent with those attributed to **4a**, with absorption maxima at  $\lambda_{\text{max}} = 310/321$  nm and  $^{31}\text{P}$  resonances at  $\delta = 62.0/65.3$ . Isolated **4b** undergoes slow reductive elimination of **3b** in DFB at room temperature ( $t_{1/2} = 3$  days), alongside precipitation of palladium black. The rate is unchanged in the presence of excess  $\text{PtBu}_3$ , but in this case liberated  $\text{Pd}(0)$  was retained in solution as  $[\text{Pd}(\text{PtBu}_3)_2]$ . In contrast, **4c** showed no onward reactivity after 14 days in DFB at room temperature.

We tentatively propose that the aforementioned reactions involve a combination of (a) concerted oxidative addition of the C–I bond to  $[\text{Pd}(\text{PtBu}_3)]^+$  followed by halogen atom abstraction from the resulting Pd(III) derivative,<sup>8</sup> and (b) auto-catalytic aryl halide activation,<sup>9</sup> e.g.  $\text{1} + \text{ArI} + \text{2} \rightarrow \text{3} + \text{1} \frac{1}{2}\text{2}$ , where the C–I bond is added across the Pd(I)–Pd(I) bond in **2**.<sup>†</sup> The former may initiate the latter, which we suggest becomes the main kinetic pathway in the case of phenyl iodide where reductive elimination of **3a** is fast. Work by Schoenebeck and co-workers with Pd(I) dimers provides precedent for the proposed C–I bond activation step in (b).<sup>10</sup>

To explore the reaction scope, **1** was also reacted with adamantyl and *tert*-butyl iodide. Consistent with intermediate formation of  $[\text{Pd}(\text{PtBu}_3)_2\text{Ad}]^+[\text{PF}_6^-]$  **4d**, treatment of **1** with 1.5 equivalents of adamantyl iodide in DFB at room temperature resulted in heterolytic C–I bond cleavage and a 1 : 2 mixture of **2** and  $[\text{PtBu}_3\text{Ad}]^+[\text{PF}_6^-]$  **3d** with >75% selectivity after 8 days. In the case of *tert*-butyl iodide, however, the putative Pd(II) alkyl

$[\text{Pd}(\text{PtBu}_3)_2\text{tBu}]^+[\text{PF}_6^-]$  **4e** appears to undergo rapid  $\beta$ -hydrogen elimination as a mixture of **2**,  $[\text{PtBu}_3\text{H}]^+[\text{PF}_6^-]$ , and isobutylene was obtained under the same conditions, but after 24 h.

Taken together, these findings unequivocally demonstrate the capacity of Pd(I)-based metalloradicals to activate C–I bonds under mild conditions. Whilst the associated mechanism is complex, generation of Pd(II)-aryls/alkyls suggests that through judicious selection of substrates and reaction conditions this reactivity could be effectively harnessed in catalysis.

## Conflicts of interest

The authors declare no conflicts of interest.

## Acknowledgements

We thank the EPSRC (MJGS; DTP studentship) and Royal Society (ABC; UF100592, UF150675) for financial support.

## Notes and references

- (a) J. P. Stambuli, M. Bühl and J. F. Hartwig, *J. Am. Chem. Soc.*, 2002, **124**, 9346–9347; (b) F. Barrios-Landeros, B. P. Carrow and J. F. Hartwig, *J. Am. Chem. Soc.*, 2009, **131**, 8141–8154.
- Note  $[\text{Pd}(\text{PtBu}_3)(\text{Ph})\text{I}]$  has been shown to decompose to **2** and biphenyl: E. Galardon, S. Ramdeehul, J. M. Brown, A. Cowley, K. K. Hii and A. Jutand, *Angew. Chem., Int. Ed.*, 2002, **41**, 1760–1763.
- (a) X. Sun, X. Dong, H. Liu and Y. Liu, *Adv. Synth. Catal.*, 2021, **363**, 1527–1558; (b) Q. Simpson, M. J. G. Sinclair, D. W. Lupton, A. B. Chaplin and J. F. Hooper, *Org. Lett.*, 2018, **20**, 5537–5540; (c) Q. Liu, X. Dong, J. Li, J. Xiao, Y. Dong and H. Liu, *ACS Catal.*, 2015, **5**, 6111–6137.



4 (a) J. Liu, M. M. Bollmeyer, Y. Kim, D. Xiao, S. N. MacMillan, Q. Chen, X. Leng, S. H. Kim, L. Zhao, K. M. Lancaster and L. Deng, *J. Am. Chem. Soc.*, 2021, **143**, 10751–10759; (b) J. Luo, G. N. Tran, N. P. Rath and L. M. Mirica, *Inorg. Chem.*, 2020, **59**, 15659–15669; (c) M. C. MacInnis, J. C. DeMott, E. M. Zolnhofer, J. Zhou, K. Meyer, R. P. Hughes and O. V. Ozerov, *Chem.*, 2016, **1**, 902–920.

5 T. Troadec, S. Tan, C. J. Wedge, J. P. Rourke, P. R. Unwin and A. B. Chaplin, *Angew. Chem., Int. Ed.*, 2016, **55**, 3754–3757.

6 S. D. Pike, M. R. Crimmin and A. B. Chaplin, *Chem. Commun.*, 2017, **53**, 3615–3633.

7 This suggestion is supported by an increased baseline UV/vis absorption over time and the reactivity of isolated **4b**.

8 A Pd(III) species resulting from the reaction of a Pd(I) dithiopyridinophane complex with phenyl iodide has recently been reported: G. N. Tran, B. S. Bouley and L. M. Mirica, *ChemRxiv*, 2022. DOI: [10.26434/chemrxiv-2022-9c7kg-v2](https://doi.org/10.26434/chemrxiv-2022-9c7kg-v2).

9 F. Barrios-Landeros, B. P. Carrow and J. F. Hartwig, *J. Am. Chem. Soc.*, 2008, **130**, 5842–5843.

10 (a) C. Fricke, T. Sperger, M. Mendel and F. Schoenebeck, *Angew. Chem., Int. Ed.*, 2021, **60**, 3355–3366; (b) K. J. Bonney, F. Proutiere and F. Schoenebeck, *Chem. Sci.*, 2013, **4**, 4434–4439.

