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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

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† 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>

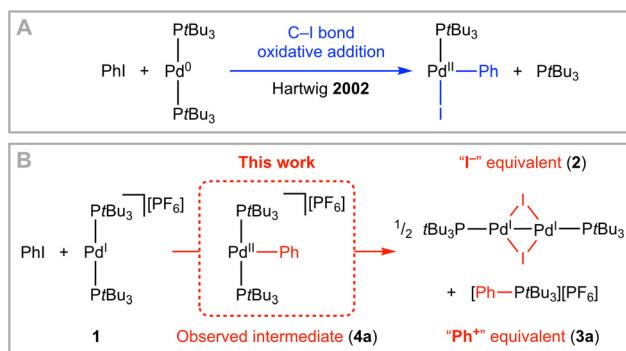
## Heterolytic carbon–iodine bond cleavage by a palladium(**i**) metalloradical†

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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.

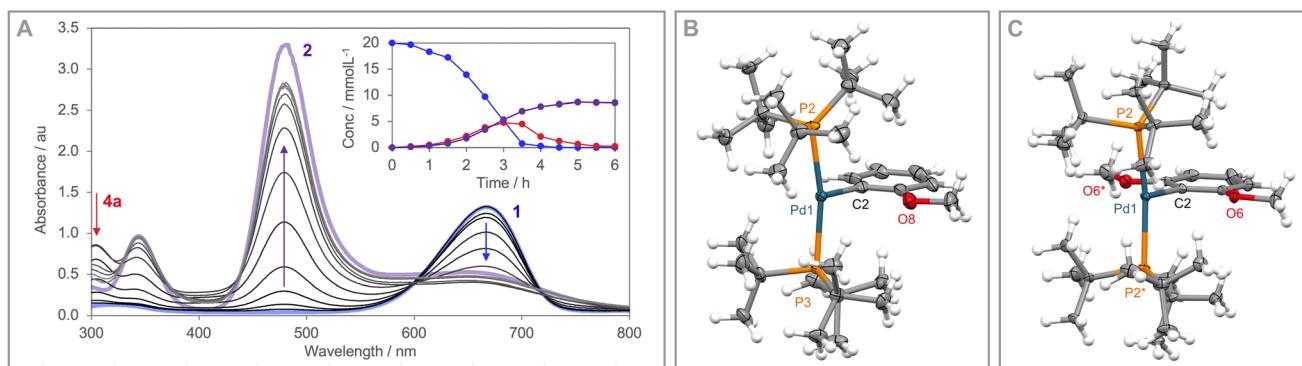
When the reaction was repeated using 1.5 equivalents of phenyl iodide a larger proportion of **3a** was generated and periodic monitoring using UV/vis and NMR spectroscopy indicated complete consumption of **1** within 4 h, sigmoidal reaction kinetics (Fig. 1A), and intermediate formation of a diamagnetic 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.





**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 [Pd(PtBu<sub>3</sub>)<sub>2</sub>Ar][PF<sub>6</sub>] (Ar = 2-(MeO)C<sub>6</sub>H<sub>4</sub>, **4b**; 2,6-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, **4c**) alongside [PtBu<sub>3</sub>X]<sup>+</sup> (X = 2-(MeO)C<sub>6</sub>H<sub>4</sub>, **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 <sup>31</sup>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 PtBu<sub>3</sub>, but in this case liberated Pd(0) was retained in solution as [Pd(PtBu<sub>3</sub>)<sub>2</sub>]. 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 [Pd(PtBu<sub>3</sub>)]<sup>+</sup> 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. **1** + ArI + **2**  $\rightarrow$  **3** + **1**<sub>2</sub><sup>+</sup>**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 [Pd(PtBu<sub>3</sub>)<sub>2</sub>Ad][PF<sub>6</sub>] **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 [PtBu<sub>3</sub>Ad][PF<sub>6</sub>] **3d** with >75% selectivity after 8 days. In the case of *tert*-butyl iodide, however, the putative Pd(II) alkyl

[Pd(PtBu<sub>3</sub>)<sub>2</sub>tBu][PF<sub>6</sub>] **4e** appears to undergo rapid  $\beta$ -hydrogen elimination as a mixture of **2**, [PtBu<sub>3</sub>H][PF<sub>6</sub>], 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.

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