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Heterolytic carbon–iodine bond cleavage by a palladium(I) metalloradical⁺

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The well-defined Pd(I) metalloradical [Pd(PtBu₃)₂]⁺ reacts with aryl and alkyl iodides at room temperature, yielding [Pd(PtBu₃)(µ-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 lowcoordinate 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).^{1,2} Whilst the Pd(0)/Pd(II) redox couple remains the workhorse, processes invoking single electron transfer and Pd(II) and Pd(III) intermediates have been attracting growing attention.³ Well-defined monomeric examples of the former are rare,⁴ but as part of work in our group we recently reported the synthesis of [Pd(PtBu₃)₂][PF₆] **1** by one-electron oxidation of [Pd (PtBu₃)₂] with [Fc][PF₆].⁵ 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) solvent⁶ 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 $[Pd(PtBu_3)(\mu-I)]_2$ 2 and phenyl phosphonium salt $[PtBu_3Ph][PF_6]$ 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 $PtBu_3$ with excess phenyl iodide which did not lead to formation of **3a**, even under considerably more forcing reaction conditions.

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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 [Pd (PtBu₃)₂Ph][PF₆] **4a** ($\lambda_{max} = 305$ nm, δ_{31P} 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,⁷ with the latter pathway evidently more pronounced in the presence of excess phenyl iodide. Addition of 5 equivalents of PtBu₃ 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 $Pd(\pi)$



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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 ([PtBu₃H][PF₆]). 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 (B, Z' = 2) and 4c (C): thermal ellipsoids at 30% probability, minor disordered components (3× 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-dimethyoxyphenyl iodide in DFB at room temperature resulted in formation of the persistent Pd(II) aryls [Pd $(PtBu_3)_2Ar [PF_6]$ (Ar = 2-(MeO)C₆H₄, 4b; 2,6-(MeO)_2C₆H₃, 4c) alongside $[PtBu_3X]^+$ (X = 2-(MeO)C₆H₄, 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 $\lambda_{\rm max}$ = 310/321 nm and ³¹P resonances at δ 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 $PtBu_3$, but in this case liberated Pd(0) was retained in solution as $[Pd(PtBu_3)_2]$. 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 $[Pd(PtBu_3)]^+$ followed by halogen atom abstraction from the resulting Pd(III) derivative,⁸ and (b) auto-catalytic aryl halide activation,⁹ *e.g.* **1** + ArI + **2** \rightarrow **3** + 1 $\frac{1}{2}$ **2**, where the C–I bond is added across the Pd(I)–Pd(I) bond in **2**.† 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).¹⁰

To explore the reaction scope, **1** was also reacted with adamantyl and *tert*-butyl iodide. Consistent with intermediate formation of $[Pd(PtBu_3)_2Ad][PF_6]$ **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 $[PtBu_3Ad][PF_6]$ **3d** with >75% selectivity after 8 days. In the case of *tert*-butyl iodide, however, the putative Pd(n) alkyl $[Pd(PtBu_3)_2tBu][PF_6]$ **4e** appears to undergo rapid β -hydrogen elimination as a mixture of **2**, $[PtBu_3H][PF_6]$, 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(i)-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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