

Letter

# Oxidative Cross-Coupling of Boron and Antimony Nucleophiles via Palladium(I)

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**Supporting Information** 

**ABSTRACT:** The use of an isolatable, monomeric Pd(I) complex as a catalyst for the oxidative cross-coupling of arylantimony and aryl-boron nucleophiles is reported. This reaction tolerates a wide variety of substrates, with >20:1 selectivity for cross-coupled products. This strategy offers a new approach to achieving the selective cross-coupling of nucleophiles.

ransition-metal-catalyzed cross-coupling reactions are keystone transformations in contemporary organic chemistry.<sup>1</sup> Selectivity in these reactions has classically been achieved by exploiting the complementary metal-based reactivity of electrophilic and nucleophilic substrates. The electrophilic reagent is first oxidatively added to the metal catalyst, typically involving insertion into a carbon-halogen bond, before subsequent transmetalation with the nucleophilic coupling partner, enabling product formation through bond forming reductive elimination. While many successful coupling reactions exploit this sequence of events,<sup>2</sup> alternative strategies based on two nucleophiles or two electrophiles are comparatively underdeveloped.<sup>3</sup> In recent years, coupling approaches involving single-electron redox events have emerged, with visible-lightpromoted photoredox catalysis a particularly prominent example.<sup>4</sup> Other single-electron transfer mediated processes proceed through internal redox mechanisms<sup>5</sup> or use external oxidants.<sup>6</sup> These alternative coupling approaches are made viable by transition-metal-based catalysts with accessible M(n)/M(n + 1) redox couples and, for this reason, have largely been associated with complexes of first row metals such as Ni,<sup>5,7</sup> Cu,<sup>8</sup> and Fe.<sup>9</sup>

Despite widespread use in cross-coupling reactions, the redox chemistry of palladium catalysts has largely been confined to the Pd(0)/Pd(II) couple. It has been speculated that Pd(I) intermediates are involved in radical atom transfer reactions<sup>10</sup> and Kumada couplings (Scheme 1, eq 1).<sup>10,11</sup> Dimeric Pd(I) phosphine complexes have shown catalytic application in trifluoromethylthiolation reactions (Scheme 1, eq 2).<sup>12</sup> They have also proven to be valuable sources of low-coordinate Pd(0), allowing effective catalysis of carbon–carbon bond forming reactions via a conventional Pd(0)/Pd(II) cycle.<sup>13</sup>

Recently, one of us demonstrated the facile one-electron oxidation of  $Pd(P^tBu_3)_2(1)$  using ferrocenium hexafluorophosphate ([Fc][PF<sub>6</sub>]) and subsequent isolation of  $[Pd(P^tBu_3)_2][PF_6](2)$ .<sup>14</sup> This straightforward method for





generation of monomeric palladium bis(phosphine) metalloradicals led us to speculate that the associated Pd(0)/Pd(I)redox couple could be exploited catalytically in single-electron transfer reactions. Herein, we report a highly selective oxidative coupling of organoboron- and organoantimony-based aryl nucleophiles mediated by commercially available 1 and  $[Fc][PF_6]$  or preformed 2 (Scheme 1, eq 3).

While exploring the reactivity of 2, we noted that 2 equiv of this complex promoted the selective two-electron oxidative coupling of SbPh<sub>3</sub> and aryl trifluoroborate salt 4a to deliver

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Received: June 26, 2018
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biaryl **5a** in 78% yield. We looked to develop a catalytic version of this coupling by examining the use of **1**, with  $[Fc][PF_6]$  as the stoichiometric oxidant to generate **2** *in situ*, with the addition CsF (Table 1). Pleasingly, this reaction gave extremely high

Table 1. Oxidative Coupling of Aryl Nucleophiles					
M <mark>Ph<sub>x</sub> †</mark> Kl	F <sub>3</sub> B 4a	OCH <sub>3</sub>	10 mol% 1, [Fc][PF <sub>6</sub> ], CsF (2 THF, 16 h	Ph 5 Bequiv) 5 H <sub>3</sub> CO	OCH <sub>3</sub>
entry	$MPh_x$	t, °C	ratio Ph/ <b>4a</b> / oxidant	variation	yield <b>5a</b> , % <sup>a</sup> (ratio <b>5a:6</b> ) <sup>b</sup>
1	SbPh <sub>3</sub>	rt	3:1:2	_	67 (>20:1)
2	SbPh <sub>3</sub>	60	1:2:3	_	86 (>20:1)
3	SbPh <sub>3</sub>	60	1:2:3	2 as cat.	84 (>20:1)
4	SbPh <sub>3</sub>	60	1:2:3	no Pd cat.	<5
5	SbPh <sub>3</sub>	60	1:2:0	no oxidant	<5
6	SbPh <sub>3</sub>	60	1:2:1 <sup>c</sup>	O <sub>2</sub> oxidant	<5
7	$SbPh_3$	60	1:2:3	AgBF <sub>4</sub> oxidant	54
8	SbPh <sub>3</sub>	60	1:2:3	Selectfluor oxidant	70
9	SbPh <sub>3</sub>	60	1:2:3	no CsF	8 <sup><i>d</i></sup>
10	$BPh_3$	rt	3:1:2	_	31 (2:1)
11	$\mathrm{SnPh}_4$	rt	4:1:2	_	$nd^{e}$ (1:4.5)
12	$PbPh_4$	rt	4:1:2	-	44 (11:1)
13	$BiPh_3$	rt	3:1:2	-	54 (4:1)

<sup>*a*</sup>Isolated yield. <sup>*b*</sup>Determined by <sup>1</sup>H NMR analysis of crude mixture. <sup>*c*</sup>Performed under 1 atm of O<sub>2</sub>. <sup>*d*</sup>Significant polymerization of solvent observed. <sup>*c*</sup>Not determined.

selectivity for the cross-coupling, delivering biaryl **5a** in 67% yield (Table 1, entry 1). Using 0.33 equiv of the antimony reagent (1 equiv with respect to the phenyl group), all three aryl groups could be transferred at 60 °C, using a 2:3 ratio of **4a**/  $[Fc][PF_6]$  to give an 86% yield of **5a** (entry 2).

Replacing catalyst 1 with the preformed Pd(I) salt 2 had little effect on yield, while the reaction failed in the absence of a palladium catalyst (Table 1, entries 3 and 4). The electron-rich Pd(PCy<sub>3</sub>)<sub>2</sub> complex was also a successful catalyst, while Pd(PPh<sub>3</sub>)<sub>4</sub> and Pd<sub>2</sub>dba<sub>3</sub> gave reduced yields of 44% and 40%. The addition of excess Hg(0) to the reaction mixture did not affect the yield, suggesting that the reaction is not catalyzed by heterogeneous palladium. Moreover, monitoring the conversion of the reaction over time did not show any evidence of an induction period (see Supporting Information (SI)).

The reaction did not proceed in the absence of the oxidant, while  $O_2$  as the oxidant gave only a trace amount of product (Table 1, entries 5, 6). A screen of alternative oxidants (see SI) identified AgBF<sub>4</sub> and Selectfluor as viable reagents, consistent with a pathway involving single-electron oxidation of palladium (Table 1, entries 7, 8).<sup>15a,b</sup> Low conversion was observed in the absence of CsF, along with the formation of a THF-derived polymer.

We also examined the use of nonantimony-based aryl transfer reagents, to determine if this oxidative coupling strategy could be applied more generally to other pairs of nucleophiles. Coupling of **4a** with triphenylborane gave a 2:1 mixture of the cross-coupled product **5a** and the dimer **6** along with biphenyl. Tetraphenyltin gave predominantly **6**, while tetraphenyllead and triphenylbismuth showed useful selectivity toward the cross-coupled biaryl (Table 1, entries 10-13). Gratifyingly, of the five coupling partners tested, four were viable, highlighting the orthogonal reactivity enabled by this approach.

With the optimized reaction conditions established, we next set about applying this coupling to a number of aryl-borate and antimony compounds (Figure 1). All triaryl-antimony reagents were synthesized in one step from commercially available SbCl<sub>3</sub> and were bench stable. While triarylantimony reagents have seen limited use as nucleophiles in organic synthesis,<sup>15c</sup> they offer improved stability compared with organometallic reagents based on Mg or Zn, and when all three aryl groups are utilized, better atom economy than most B- or Sn-based reagents. Care should



<sup>a</sup> 1 equiv of **3** with respect to anyl group (0.33 equiv of Sb), <sup>b</sup> 1 equiv. of **3** and 1 equiv of **4** used, <sup>c</sup>Bu<sub>4</sub>NBF<sub>3</sub>-aryl salts used <sup>d</sup> Boronic acid used

Figure 1. Scope of the boron/antimony coupling.

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be taken, however, due to the potential toxicity of antimonybased reagents.

Using SbPh<sub>3</sub>, electron-rich and -poor fluoroborate salts were well tolerated, giving the biaryls in good yields (Figure 1, 5a–g). Sb(4-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)<sub>3</sub> was also effectively coupled, employing aryl and heteroaryl fluoroborate salts including benzofuran (5k) and thiophene boronic acid (5l). Sb(4-C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub> was coupled with a variety of aryl and heteroaryl fluoroborates in good yields (5n– $\mathbf{r}$ ).<sup>16</sup> Heteroaryl antimony reagents were also incorporated, with the benzothiophene and furan derived reagents coupling in 45–92% yields (5t– $\mathbf{x}$ ). Alkyl and alkenyl fluoroborate reagents were also examined, but did not deliver the desired products. Tris(phenylethynyl)stibane was also synthesized, but proved to be unstable under the reaction conditions.

While we attribute the role of  $[Fc][PF_6]$  to the previously established,<sup>14</sup> one-electron oxidation of Pd(0) during catalysis, we sought to preclude the possible formation of aryl radicals<sup>17</sup> or Sb(V) species by oxidation of the coupling partners. The cyclic voltammograms of SbPh<sub>3</sub> and 4a in THF/[<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] show irreversible oxidation waves, but only at potentials >0.9 V higher than Fc/[Fc]<sup>+</sup> (see SI).<sup>18</sup> Consistent with this observation, treatment of SbPh<sub>3</sub> or 4a with [Fc][PF<sub>6</sub>] in the presence of TEMPO gave no detectable biaryl formation or TEMPO adduct. Likewise their catalytic coupling is unaffected in the presence of the known radical trap 1,1-diphenylethylene. Finally, treatment of SbPh<sub>3</sub> with [Fc][PF<sub>6</sub>] at 60 °C in THF returned the starting material in quantitative yield after 16 h.<sup>19</sup>

Informed by the reactivity of conceptually related dimeric Pd(I) pincer complexes,<sup>20</sup> we propose the mechanism depicted in Scheme 2 for the cross-coupling. The critical step involves



radical oxidative addition of an aryl-antimony bond across two Pd(I) centers giving a Pd(II)-aryl and Pd(II)-stibide.<sup>21</sup> The Pd(II)-aryl species could mediate the formation of the biaryl product via a conventional metalation/reductive elimination sequence, while the Pd(II)-stibide could react with fluoride to regenerate the common zerovalent palladium species. There is literature precedent for reaction of M–Sb moieties with fluoride

leading to formation of new Sb–F bonds, lending support to the latter conjecture.  $^{\rm 22}$ 

In an attempt to provide experimental support for our proposal, reactions of isolated Pd(I) salts with Sb(2- $C_6H_4OCH_3$ )<sub>3</sub> (**3w**) in THF were studied using <sup>31</sup>P NMR spectroscopy: although, under the catalytic coupling conditions **3w** performed poorly (Table 2, **5w**), the large steric profile is attractive from a practical perspective. Stoichiometric reaction of **3w** with [Pd(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>] (**2**) under catalytically relevant conditions (60 °C, 16 h) resulted in complete consumption of the metalloradical and formation of a complex reaction mixture containing [HP<sup>t</sup>Bu<sub>3</sub>]<sup>+</sup> ( $\delta$  52.4) and a new compound that was subsequently characterized as [Pd<sub>2</sub>(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub>( $\mu$ -C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)( $\mu$ -SbC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)]<sup>+</sup> (7, two geometric isomers in a 1:1 ratio;  $\delta$  87.4, 86.6; Figure 2). The conversion to 7 is only moderate



**Figure 2.** Solid-state structure of one of the isomers of 7. Thermal ellipsoids for selected atoms at the 30% probability level; minor disordered component (Pd<sub>2</sub>Sb core), <sup>t</sup>Bu hydrogen atoms, and  $[BAr_4^F]^-$  anion omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1–Pd2, 2.7918(6); Pd1–Sb3, 2.4723(5); Pd2–Sb3, 2.5026(5); Pd1–P4, 2.299(15); Pd2–P5, 2.3223(14); Pd1–C6, 2.135(6); Pd2–C6, 2.137(5); Pd2–Pd1–P4, 161.04(5); Pd1–Pd2–P5, 153.70(4); Pd1–Sb3–Pd2, 68.274(15); Pd1–C6–Pd2, 81.62(18).

under these conditions (ca. 20%), but increased when carried out at room temperature (ca. 45%). Using 0.5 equiv of Sb(2- $C_6H_4OCH_3$ )<sub>3</sub> and employment of the weakly coordinating  $[BAr_4^F]^-$  anion  $(Ar^F = 3,5-(CF_3)_2C_6H_3)^{23}$  resulted in a slower reaction but gave enhanced production of 7 (ca. 50%). Isolation proved difficult, but was realized in low yield by manual separation of single crystals and successive recrystallization.

The structure of 7 contains an unusual combination of bridging aryl and stibinidene ligands and a significant Pd–Pd bond (2.7918(6) Å).<sup>24</sup> We assign formal Pd(II) and Sb(III) oxidation states, with the latter consistent with pronounced pyramidalization at the metalloid ( $\sum$ angles@Sb3 = 265.7°). Scheme 2 reconciles how 7 could be formed, with the transient presence of a reactive three-coordinate Pd(II)-aryl cation evidenced through isolation of the aryl phosphonium salt [P<sup>t</sup>Bu<sub>3</sub>(2-C<sub>6</sub>H<sub>4</sub>OMe)][BAr<sup>F</sup><sub>4</sub>].<sup>25</sup> Although presumably an off-cycle species, in the context of the proposed mechanism the formation of 7 directly evidences Sb–C bond cleavage and single-electron oxidation events at palladium. Only partial decomposition (ca. 10%) to 1 was observed on reaction of 7 with excess K[F<sub>3</sub>BC<sub>6</sub>H<sub>4</sub>F] and CsF in THF (60 °C, 16 h).

In summary, we have presented the first synthetic application of a well-defined monomeric Pd(I) species, facilitating the oxidative cross-coupling of aryl-boron and aryl-antimony nucleophiles. This strategy offers a new approach for achieving selectivity in palladium catalyzed cross-coupling reactions and demonstrates that single-electron redox events at palladium can be harnessed for new catalytic organic transformations.

# ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01989.

Full experimental data, including synthetic procedures, characterization data, and NMR spectra (PDF)

## **Accession Codes**

CCDC 1839868 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

We acknowledge financial support from the Australian Research Council, through a DECRA award (J.F.H.) and Discovery Programs (D.W.L.), the EPSRC (M.J.G.S.; DTP studentship), and the Royal Society (A.B.C.; UF100592, UF150675).

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