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Air-Stable, Phosphine-Free Anionic Palladacyclopentadienyl Catalysts: Remarkable Halide and Pseudohalide Effects in Stille Coupling

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Abstract: The Stille cross-coupling of allylic and benzyl bromides is shown to proceed efficiently using phosphine-free dinuclear anionic palladacyclopentadienyl catalysts possessing bridging (*N*,*O*)-imidate ligands. The type of bridging anion influences the catalytic activity considerably. Halide anions such as chloride, bromide or iodide also influence the catalytic activity but to a far lesser extent than the pseudohalide imidate anions (from succinimide or phthalimide). A Baldwin-type cooperative effect is seen with **7a** using CuI as a co-catalyst, in the presence of two equivalents of CsF in DMF at 40 °C. In toluene, these additives slow down substrate turnover.

Keywords: C–C bond formation; copper(I) salts; cross-coupling; halide effects; palladium

Palladium-catalysed cross-coupling processes have solved numerous synthetic problems, notably in natural product synthesis,[1] pharmaceutical targets,[2] fluorescent DNA base analogues and biological probes.[3] The C–C and C–X (X = heteroatom) bond-forming technologies, such as Buchwald–Hartwig, Heck, Kumada, Negishi, Sonogashira, Suzuki and Stille, represent just a few of the key transformations widely used.[4] In recent years, broader substrate scope has become accessible through the development of highly active Pd catalysts,[5] particularly for aryl chlorides, where palladacycles have been studied extensively (as precatalysts).[6] The palladacyclic unit is believed to degrade under the reaction conditions to slowly release neutral or anionic Pd(0) as the catalytically active species – the latter species contains a halide ligand.[7]

Generally, the manipulation of the metal halide functionality is a highly valuable method for tuning the reactivity of transition metal complexes (in catalysts or in stoichiometric processes).[8] Importantly, alteration of the halide does not usually perturb the reaction system such that catalysis inhibition is seen, but more often promotes changes in reactivity and/or selectivity. The steric and electronic effects of the specific type of halide will delicately alter the electronic properties of other ligands bound to the metal, thereby producing changes in metal reactivity. Halides can also participate in bonding with a metal centre, e.g., Pd(0) or neutral Pd(II), generating anionic species such as "X–Pd(0)$^-$" or "X–Pd(II)$^-$",[9] which ultimately increases the nucleophilicity of the metal centre, but potentially offers the opportunity to influence the metal reactivity through changes in halide (X).

As the nucleofuge concentration increases during the course of a cross-coupling reaction, one predicts that anionic Pd(0) adducts will contain halides derived from the organohalide substrate. However, sub-stoichiometric quantities of halide and pseudohalide additives (as low as 10 mol %) often affect catalyst activity and lifetime in these reactions – the degree of halide binding to Pd therefore depends on the type of organohalide substrate employed and any additives used.[10]

The influence of imidate-type ligands, derived from succinimide (succ), phthalimide (phal) and maleimide (mal), and their influence in cross-coupling processes has been of recent interest to us, particularly in Stille coupling.[11] The discovery of the useful precatalyst *cis*-bis(triphenylphosphine)palladium(II)(bromo)succinimide (*cis*-**1**, Figure 1), for Stille coupling of allylic and

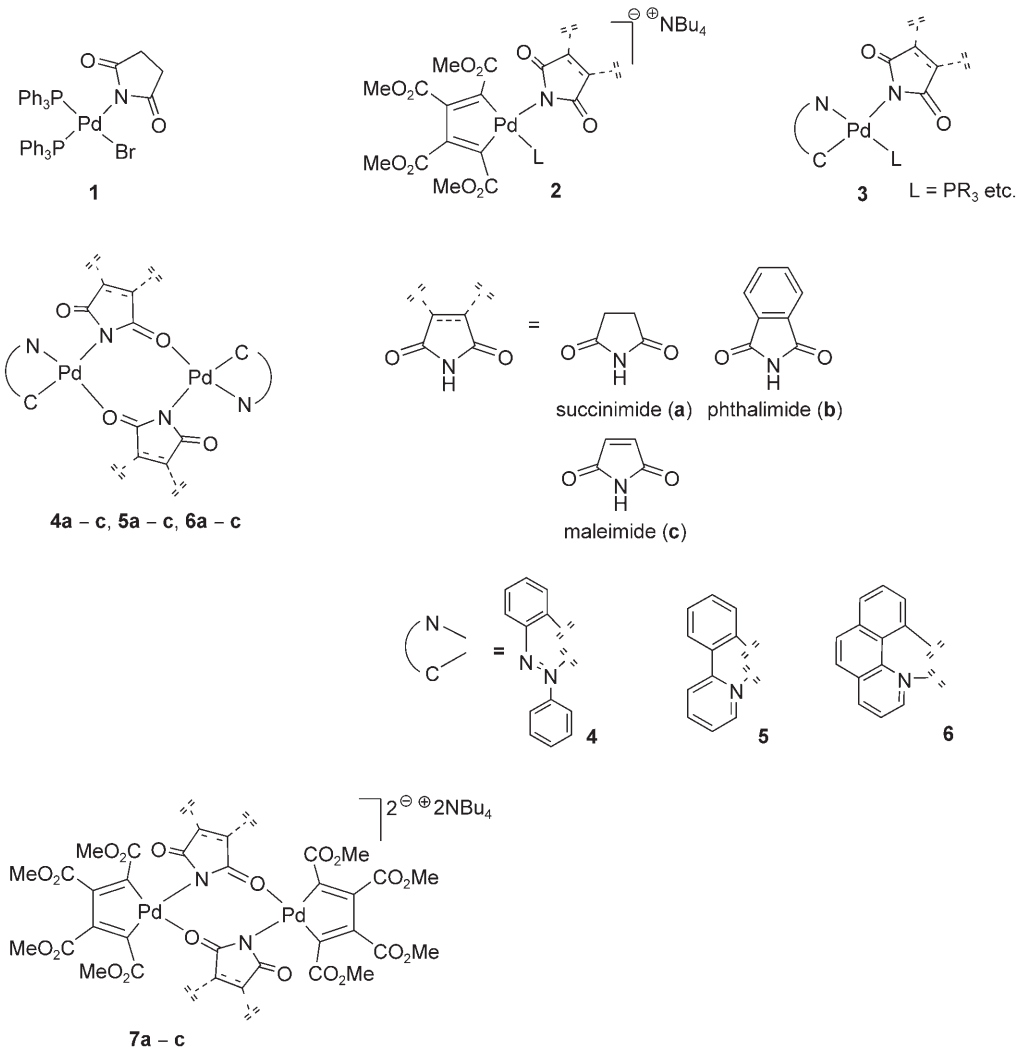


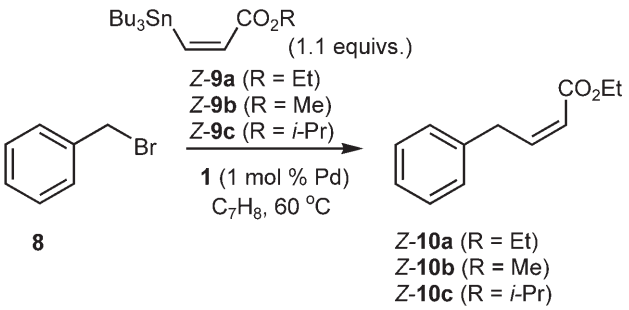
Figure 1. Neutral and anionic palladium(II) complexes containing imidate ligands.

benzylic bromides with organostannanes has led to the finding that the succinimide ligand, a rather unusual pseudohalide with a subtle blend of σ-donating and π-accepting ability, imparts interesting selectivity for benzylic substrates over activated aryl bromides, when compared to common Pd(0)/(II) catalysts/precatalysts.[12]

Second generation precatalysts have been synthesised and evaluated in Stille (**2**),[13] Suzuki and Sonogashira reactions (**3**–**6**).[14] Differences in reactivity were observed against small changes in structure of the Pd/L assembly. Overall, it appears that the ligand backbone plays a *kamikaze* role in initiating the active palladium catalyst. Our first studies in this specific report are focused toward the application of phosphine-free neutral and anionic dinuclear Pd(II) imidate complexes (**4**–**7**) as catalysts/precatalysts for Stille coupling to study further halide and pseudohalides effects.

The reaction of benzyl bromide **8** with *cis*-vinylstannyl ester *Z*-**9a** to give *Z*-**10a** represents the benchmark for initial catalyst screening (Scheme 1).[12] Crucially, the reaction requires preservation of the geometry and position of the double bond. Organostannane *Z*-**9** is also relatively deactivated.[12d]

Complexes **4**–**7** were tested using standard conditions developed previously[12e] by our group (toluene, 1 mol % Pd, 60 °C – referred to as method A) (Table 1).



Scheme 1. Stille coupling mediated by *cis*-**1**.

All reactions were analysed after 0.75 hours and then followed to completion. With catalyst *cis*-**1**, 48% conversion in *Z*-**10a** was observed (entry 1). The reaction is essentially quantitative after 3 hours. For the palladacyclic dimers containing an azobenzene backbone (**4a–c**), low conversions were observed after 0.75 hours, although reasonable yields resulted after 18 hours (entries 2–4). The yields improved for the 2-phenylpyridine-derived palladacyclic dimers (**5a–c**) (entries 5–7). Notable differences were seen between the imide ligands after 18 hours (for **5a**, 86%; **5b**, 73%; **5c**, 56%). Alteration of the palladacyclic backbone to a phenanthroline improved the yields after 0.75 hours (entries 8–10), showing similar catalytic activity to **1**. Turning our attention to the anionic palladacyclopentadienyl complexes (**7a–c**), significantly higher catalytic activity was observed (entries 11–13). For example, for the succinimide complex **7a**, 65% conversion was observed after 0.75 hours, and 99% after 3 hours (entry 11). The phthalimide complex **7b**, showed higher activity (77% after 0.75 hours and 99% after 3 hours) (entry 12). The yield dropped for the maleimide complex **7c** (entry 13). At this stage we were intrigued by the differences observed on changing the pseudohalide from succinimide, through to phthalimide and maleimide. Co-additives, in the form of soluble organic halides, were added to **7a** to assess their affect on catalytic activity (entries 14–17). We were surprised to find that TBAF (0.05 equivs.) had a dramatic affect causing the conversion to drop from 65% to 9% after 0.75 hours (entry 14).[15] Conversion was better for TBAC, TBAB and TBAI, but essentially catalysis was slowed by addition of the halide co-additives – fluoride retarded catalysis the most, with bromide having the minimum effect of the halides studied.

Interested by the effect of the halide co-additives, the μ^2-hydroxy- (**7d**) and μ^2-halo-anionic palladacyclopentadienyl complexes (**7e–g**, Figure 2) were evaluated in the benchmark reaction (Table 2).

The hydroxy complex **7d** showed poor catalytic activity (entry 1). Product conversion was higher for the chloro, bromo and iodo complexes (**7e–g**) relative to **7d**, with the bromide showing the best catalytic activity (entry 3). However, these yields are notably lower than the succinimide and phthalimide relatives **(7a** and **7b**). This series of results indicates the importance associated with the specific type of halide/pseudohalide for catalytic activity.

In screening various organostannanes for the reaction we determined that the reactivity of *Z*-**9** was greatly affected by the size of the ester group. For example, in comparison with the ethyl ester in *Z*-**9a**, the methyl ester (*Z*-**9b**) reacted more quickly (Table 3).

In this series, the succinimide (**7a**), phthalimide (**7b**), chloro (**7e**), bromo (**7f**) and iodo (**7g**) functions again showed significant differences in reactivity (entry 1). In stark contrast, the *i*-propyl ester (*Z*-**9c**) was even less reactive than *Z*-**9a** and *Z*-**9b**

Table 1. Catalyst precursor screening for Stille coupling of **8** + *Z*-**9a** → *Z*-**10a**.[a]

Entry	[Pd] precursor catalyst	Reaction time [hours]	Yield [%][b]
1	**1**	0.75 (3)	48 (98)
2	**4a**	0.75 (18)	13 (57)
3	**4b**	0.75 (18)	18 (64)
4	**4c**	0.75 (18)	6 (31)
5	**5a**	0.75 (18)	23 (86)
6	**5b**	0.75 (18)	18 (73)
7	**5c**	0.75 (18)	21 (56)
8	**6a**	0.75 (18)	45 (85)
9	**6b**	0.75 (18)	53 (81)
10	**6c**	0.75 (18)	38 (67)
11	**7a**	0.75 (3)	65 (99)
12	**7b**	0.75 (3)	77 (99)
13	**7c**	0.75 (3)	48 (94)
14	**7a** + TBAF[c]	0.75 (3)	9 (49)
15	**7a** + TBAC[c]	0.75 (3)	22 (74)
16	**7a** + TBAB[c]	0.75 (3)	38 (87)
17	**7a** + TBAI[c]	0.75 (3)	29 (80)

[a] Reaction conditions as for Scheme 1; The Pd catalyst loading = 1 mol % Pd (0.01 equiv.).
[b] Numbers in brackets are yields after KF work-up and column chromatography.
[c] Tetrabutylammonium salt added (0.05 equivs.); TBAF = tetrabutylammonium fluoride; TBAC = tetrabutylammonium chloride; TBAB = tetrabutylammonium bromide; TBAI = tetrabutylammonium iodide.

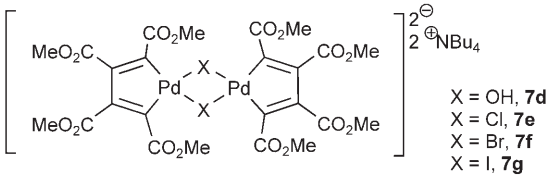


Figure 2. Anionic palladium(II) complexes containing μ^2-hydroxy- and μ^2-halide bridging ligands.

Table 2. Effect of μ^2-hydroxy- and μ^2-halide-bridging ligands in Stille coupling of **8** + *Z*-**9a** → *Z*-**10a**.[a]

Entry	[Pd] precursor catalyst	Reaction time [hours]	Conversion [%][b]
1	**7d**	0.75 (3)	15 (33)
2	**7e**	0.75 (3)	34 (78)
3	**7f**	0.75 (3)	42 (85)
4	**7g**	0.75 (3)	31 (69)

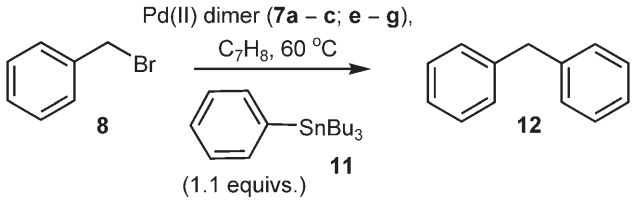
[a] Reaction conditions as for Scheme 1 and Table 1.
[b] Conversion calculated by GC analysis against an internal standard (dodecane).

The reaction of **8** with phenylstannane **11** to give diphenylmethane **12** was evaluated next (Scheme 2 and Table 4).

Table 3. Substituent effect in the vinylstannyl ester (*Z*-**9**).[a]

Entry	$Bu_3SnCH{=}CHCO_2R$	Reaction time [hours]	Conversion [%][b]
1	R = Me (*Z*-**9b**)		
	7a	0.75 (3)	85 (99)
	7b	0.75 (3)	93 (99)
	7e	0.75 (3)	59 (88)
	7f	0.75 (3)	71 (99)
	7 g	0.75 (3)	62 (94)
2	R = *i*-Pr (*Z*-**9c**)		
	7a	0.75 (3)	40 (84)
	7b	0.75 (3)	34 (91)

[a] Reaction conditions as for Scheme 1 and Table 1.
[b] Conversion calculated by GC analysis against an internal standard (dodecane).



Scheme 2. Stille coupling of benzyl bromide **8** with phenylstannane **11** to give **12**.

Table 4. Reaction of **8** with $PhSnBu_3$ **11** to give **12**.[a]

Entry	[Pd] precursor catalyst	Reaction time [hours]	Conversion [%][b]
1	**7a**	6 (12)	37 (81)
2	**7b**	6 (12)	44 (93)
3	**7c**	6 (12)	32 (78)
4	**7e**	6 (12)	14 (41)
5	**7f**	6 (12)	31 (67)
6	**7g**	6 (12)	24 (62)

[a] Reaction conditions as for Scheme 1 and Table 1.
[b] Conversion calculated by GC analysis against an internal standard (dodecane).

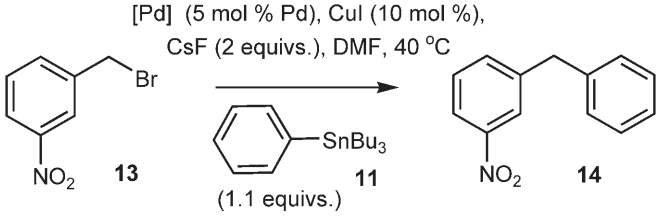
The reaction was monitored after 6 and 12 hours. The best yields were observed for **7a** and **7b** (entries 1 and 2). Of the halide complexes, the poorest activity was seen for **7e** (entry 4) and the best for **7f** (entry 5).

We were interested in evaluating whether cooperative effects with CuI and CsF would be observed in DMF at 40 °C (Method B). In a recent study, Baldwin and co-workers have revealed a remarkable cooperative effect between CuI and CsF, when using $Pd(PPh_3)_4$ (5 mol %) as the catalyst, which was most striking when employing DMF as the solvent in Stille coupling.[16] The benchmark reaction (**8** + *Z*-**9a** → *Z*-**10a**) was used to probe whether the cooperative effect was operative for the phosphine-free complex **7a** using method B (Table 5).

Table 5. Cooperative effect with CsF and CuI in the reaction of **8** + *Z*-**9a** → *Z*-**10a**.[a]

Entry	[Pd] precursor catalyst	Reaction time [hours]	Conversion [%][b]
1	**7a**	0.75 (3)	0 (10)
2	**7a** + CuI[c]	0.75 (3)	10 (48)
3	**7a** + CsF[d]	0.75 (3)	2 (12)
4	**7a** + CuI + CsF[e]	0.75 (3)	89 (99)
5	$Pd(PPh_3)_4$ + CuI + CsF[f]	0.75 (3)	62 (99)
6	**7a** + CuI[g]	0.75 (3)	5 (27)
7	**7a** + CsF[h]	0.75 (3)	0 (8)
8	**7a** + CuI + CsF[i]	0.75 (3)	8 (33)
9	**7a** + CuI + CsF[j]	0.75 (3)	17 (57)

[a] As for Scheme 1, using DMF as the solvent, 5 mol % Pd, 40 °C.
[b] Conversion calculated by GC analysis against an internal standard (dodecane).
[c] 10 mol % CuI added.
[d] 2 equivalents of CsF added.
[e] Both CuI (10 mol %) and CsF (2 equivs.) added.
[f] Identical catalyst system and conditions employed by Baldwin and co-workers.
[g] Reaction conditions as for Scheme 1 (Method A); The Pd catalyst loading = 1 mol % Pd (0.01 equiv.). CuI was added (0.05 equivs.).
[h] As for [g], using catalytic CsF (0.05 equivs.) (without added CuI).
[i] As for [g], using CuI (0.05 equivs.) and CsF (0.05 equivs.).
[j] As for [g], CuI (0.05 equivs.) and CsF (2 equivs.).



Scheme 3. Stille coupling of 3-nitrobenzyl bromide **13** with phenylstannane **11** to give **14**.

In the absence of CuI and CsF, complex **7a** (5 mol % Pd) was a poor catalyst in DMF (entry 1). Lower reaction concentrations gave similar results – ruling out the formation of Pd clusters. Sluggish substrate turnover was seen with either CuI or CsF (entries 2 and 3). However, the cooperative effect clearly exists when **7a**, CuI and CsF were used in tandem (entry 4). For comparison purposes, a yield of 89% conversion was attained for **7a** after 0.75 hours, whereas using $Pd(PPh_3)_4$, 62% conversion was seen after the same time (entries 4 and 5). The effect of a Cu(I) co-catalyst was also assessed using Method A, which resulted in negligible conversion (entry 6). The addition of CsF (0.05 equivs.) also resulted in very low conversion (entry 7). Perhaps unsurprisingly, when CuI and CsF were both added low conversions were also seen (entries 8 and 9).

Table 6. Other examples.[a]

Entry	[Pd] precursor catalyst	Reaction time [hours]	Conversion [%][b]
1	**7a**[c]	3 (6)	50 (97)
2	**7b**[c]	3 (6)	66 (99)
3	**7a**[d]	2 (4)	85 (99)
4	**7b**[d]	2 (4)	89 (99)
5	**7a**[d]	3 (6)	32 (81)
6	**7b**[e]	3 (6)	37 (84)

[a] As for Scheme 3.
[b] Conversion calculated by GC analysis against an internal standard (dodecane).
[c] Using Method A with no additional additives (1 mol% Pd).
[d] Using Method B.
[e] Using Method B, but using 1 mol% Pd.

We also tested both Methods A and B for the reaction of 3-nitrobenzyl bromide **13** with **11** to give **14** (Scheme 3 and Table 6).

The conversions for **7a** and **7b**, using Method A with no additional additives, were 50% and 66% after 3 hours, and essentially quantitative conversion after 6 hours (entries 1 and 2). Conversions were higher for both **7a** and **7b** using Method B, where again quantitative conversions were seen (entries 3 and 4). For lower Pd catalyst loadings, for direct comparison with Method A, inferior catalyst activity was noted (entries 5 and 6).

It is clear from the above results that **7a** and **7b** are the best catalysts (using Method A). A library of substrates were screened using **7a** as the catalyst (similar yields are seen for **7b** for selected examples given in Table 7).

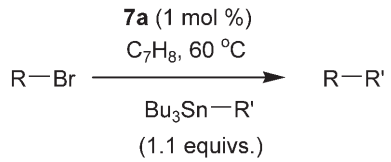
In this series of compounds, good to excellent yields were observed. In all cases, the alkene regio- and stereoselectivity were preserved from the vinylstannyl starting material. The yields for these products are higher, and the Pd catalyst concentrations lower, than the best previously reported results for these reactions.[12c,12d]

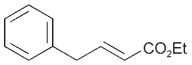
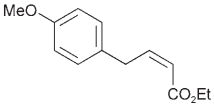
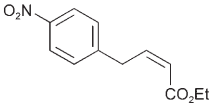
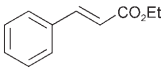
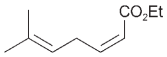
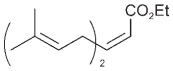
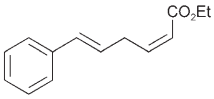
A series of other substrates was screened with **7a** using Method B (Table 8). Again, high yields were observed throughout the series of examples (entries 1–7). In entries 3 and 7, **7a** compares favourably against $Pd(PPh_3)_4$.

A mechanism accounting for the CuI/CsF cooperative effect in reactions mediated by **7a** (X′ = succinimide) in DMF is tentatively suggested in Scheme 4 (as a modification to that previously postulated for $Pd(PPh_3)_4$).[16] We can assume the *in situ* generation of an organocuprate in DMF, which is expected to be more reactive than the organostannane in the transmetallation step of the catalytic cycle. Two related cycles are presented: (1) a neutral catalytic cycle (Pathway A) and (2) an anionic catalytic cycle (Pathway B). Given that we have not detected any side-products that would result from degradation of the palladacyclopentadienyl unit *via* reaction with the organostannane, the oxidation states (Y) of the various Pd intermediates, in the reactions mediated by **7a** or related complexes, remain unknown. The dominant pathway cannot be confirmed at this stage. However, the pronounced halide/pseudohalides effect detailed *vide supra* undoubtedly indicates a role for anionic ligands in the catalytic cycle. Alteration of the halide/pseudohalide ligand (as in **7b**–**7g**), and their affect on catalytic activity with respect to the cooperativity of catalytic Cu(I) and stoichiometric CsF, will form part of a more detailed study that will be reported in due course.

Overall, we have identified that dinuclear anionic palladacyclopentadiene complexes **7a**–**c** are active catalysts for Stille coupling. They represent the first anionic Pd(II) catalysts that do not possess a donor ligand, e.g., PR_3 or NR_3. Of particular note was the finding that remarkable halide and pseudohalide effects were observed with these complexes, indicating that the anionic ligand either stabilises or enhances the reactivity of the

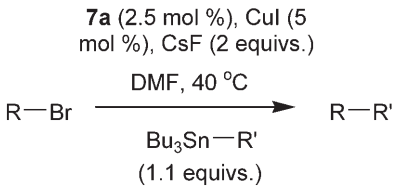
Table 7. Products from the Stille coupling of allylic or benzylic substrates with organostannanes, mediated by **7a** (using Method A).[a]

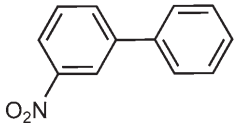
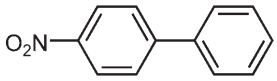
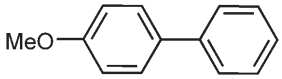
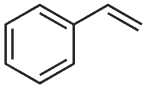
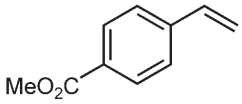
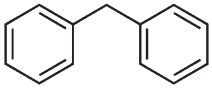
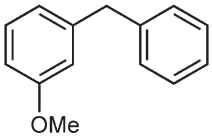


Entry	Coupled Product	Yield [%][b]
1		95
2		82
3		75
4		90
5		81
6		92 (85)[c]
7		86 (81)[c]

[a] Reaction conditions: allylic/benzylic bromide (0.25 mmol), organostannane (0.3 mmol), **7a** (0.5 mol %; 1 mol % Pd), $C_6H_5CH_3$ (2.5 mL) at 60 °C, under an inert atmosphere of N_2, 6 hours.
[b] Yields after KF work-up and column chromatography.
[c] Yields in brackets are using **7b** instead of **7a**.

Table 8. Selected other Stille couplings of organobromides with organostannanes mediated by **7a** in combination with CuI (10 mol%) and CsF (2 equivs.) (using Method B).[a]



Entry	Coupled Product	Conversion [%][b]
1		99 (2 h)
2		93 (3 h)
3		94 (4 h);[c] 97 (2 h)[d]
4		74 (2 h)
5		97 (8 h)
6		98 (6 h)
7		96 (4 h)[e]

[a] Reaction conditions: allylic/benzylic bromide (0.25 mmol), organostannane (0.3 mmol), **7a** (2.5 mol %; 5 mol % Pd), CuI (5 mol %), CsF (2 equivs.), DMF (2.5 mL) at 60 °C, under an inert atmosphere of N_2, 6 hours.

[b] Yields are conversion by GC analysis against an internal standard (dodecane).

[c] Using 4-methoxybromobenzene.

[d] Using 4-methoxyiodobenzene. After one hour, 60% conversion was seen. $Pd(PPh_3)_4$ showed 34% conversion after 1 hour, and 87% after 2 hours.

[e] After 2 hours, 58% conversion observed. $Pd(PPh_3)_4$ showed 41% conversion after 2 hours, and 83% after 4 hours.

active Pd catalyst species. For the reaction of **8** + *Z*-**9a** → *Z*-**10**, the order of reactivity was **7b** (phthal) = **7a** (succ) > **7c** (mal) > **7f** (Br) > **7e** (Cl) > **7g** (I) > **7d** (OH). Previous studies with mono-nuclear relatives, containing various activating donor ligands (PR_3, NR_3 etc.), indicate that they are considerably less active than the di-nuclear species.[13] Baldwin-type cooperative effects (CuI and CsF)[16] were observed in reactions conducted in DMF, but not in toluene. In the latter solvent, the additives reduce the rate of catalysis. It should be noted that an increase in catalyst concentration is required for high catalytic activity using method B [for both **7a** and $Pd(PPh_3)_4$] and that it is more cumbersome to remove DMF than toluene. Interestingly, the results using **7a** and Method B, indicate that the role of Cu(I) is to activate the organostannane and not to act as a donor ligand scavenger (given the absence of donor ligand in **7a**), although one should not rule out the formation of bimetallic catalyst intermediates. Future studies will focus on identifying the active catalyst species in these reactions.

Experimental Section

General Remarks

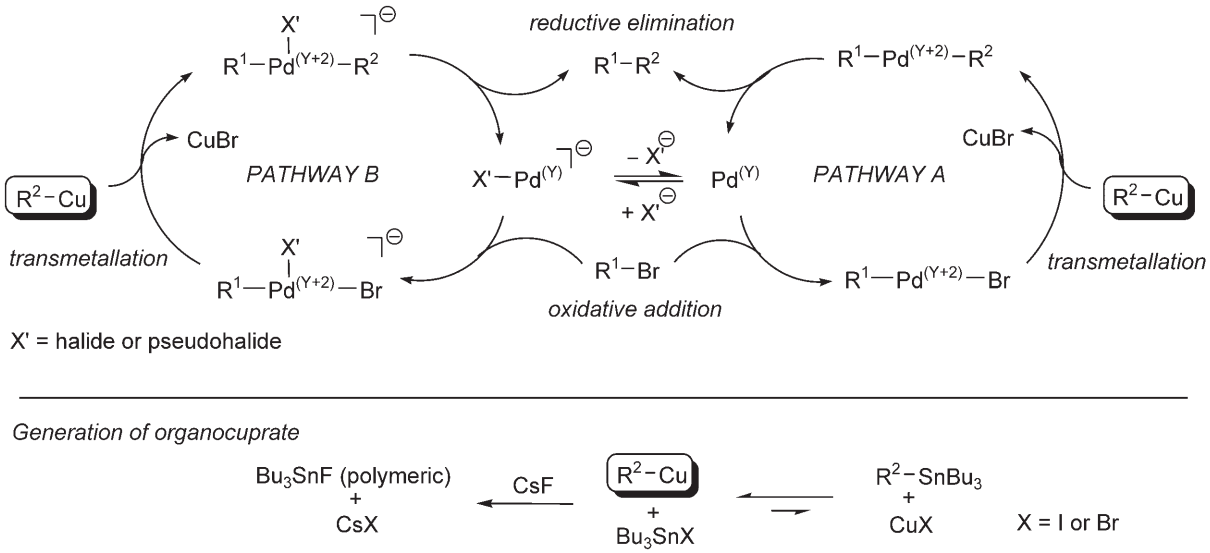
See reference for general experimental information.[12d] Complexes **4**–**6**[14] and **7a**–**c**[13] have been previously prepared and characterized. $Pd(PPh_3)_4$ was freshly prepared from the reaction of $Pd(PPh_3)_2Cl_2$ in DMSO with hydrazine at 120 °C (the catalytic activity of commercial material was generally poor when compared to freshly prepared material, which was stored under argon).

Stille Coupling Procedure (Method A)[12]

Following a similar procedure to that previously reported by our group:[12d] To a solution of the organohalide (0.25 mmol, 1 equiv.) and the organostannane (0.3 mmol, 1.2 equivs.) in dry degassed (freeze-pump-thaw cycles) toluene (2.5 mL) and dodecane (0.1 equiv.; internal standard) was added the palladium catalyst (0.0025 mmol, 0.01 equiv.). The mixture was placed under a dry N_2 atmosphere and heated to 60 °C in the dark (the flask was covered with domestic foil) for the time specified in the text. All reactions were monitored by TLC, GC or GC/MS analysis [GC samples were quenched by addition of a 1 M solution of HCl (0.25 mL) to the analysis sample (0.1 mL), then extracted into EtOAc (2 × 0.5 mL) and passed through a plug of silica ca. 1 g; samples were then analyzed directly]. On completion, the reaction was cooled to ambient temperature, then saturated aqueous KF (2.5 mL) added and the mixture stirred vigorously for 1 hour. The mixture was filtered through Celite®, and the residue rinsed with Et_2O (2 × 5 mL), washed with saturated aqueous NaCl (2 × 2.5 mL) and dried ($MgSO_4$). Concentration under vacuum and subsequent purification by column chromatography, using EtOAc/hexane or PE mixtures, gave the products as oils.

Stille Coupling Procedure (Method B)

Following a similar procedure to that reported by Baldwin and co-workers:[16] To a solution of the organohalide (0.25 mmol, 1 equiv.) and the organostannane (0.3 mmol, 1.2 equivs.) in de-



Scheme 4. Proposed mechanism for Stille coupling in the presence of catalytic CuI and stoichiometric CsF in reactions mediated by **7a** (X′ = succinimide) in DMF (Pathway A is a neutral catalytic cycle and Pathway B is an anionic cycle; the oxidation state "Y" is not specified).

gassed (freeze-pump-thaw cycles) DMF (2.5 mL), was added the palladium catalyst (0.0125 mmol, 0.05 equivs.), CuI (0.0125 mmol, 0.05 equivs.) and CsF (0.5 mmol, 2 equivs.). The mixture was heated to 40 °C for the times indicated in the text. GC analysis and work-up were similar to Method A.

The following compounds have been previously characterised: ethyl 3-(tributylstannyl)-2*Z*-propenoate (*Z*-**9a**),[12d] methyl 3-(tributylstannyl)-2*Z*-propenoate (*Z*-**9b**),[17] ethyl (2*Z*)-4-phenyl-2-butenoate (*Z*-**10a**),[12d] methyl (2*Z*)-4-phenyl-2-butenoate (*Z*-**10b**),[18] isopropyl (2*Z*)-4-phenyl-2-butenoate (*Z*-**10c**),[19] diphenylmethane (**12**),[12d] 3-nitrophenyl(phenyl)methane (**14**), ethyl (2*Z*)-4-(4′-nitrophenyl)-2-butenoate (entry 2, Table 7),[12d] ethyl (2*Z*)-4-(4′-methoxyphenyl)-2-butenoate (entry 3, Table 7),[12d] ethyl (1*E*)-2-phenylpropenoate (entry 4, Table 7),[12d] ethyl (2*Z*,5*E*)-6,10-dimethyl-2,5,9-undecatrienoate (entry 6, Table 7),[12d] ethyl (2*Z*,5*E*)-6-phenyl-2,5-hexadienoate (entry 7, Table 7),[12d] 3-nitrobiphenyl (entry 1, Table 8),[20] 4-nitrobiphenyl (entry 2, Table 8),[21] 4-methoxybiphenyl (entry 3, Table 8),[14] methyl 4-vinylbenzoate (entry 5, Table 8),[22] 3-methoxyphenyl(phenyl)methane (entry 7, Table 8).[12d]

Isopropyl 3-(Tributylstannyl)-2Z-propenoate (*Z*-9c)

AIBN (0.073 g, 1.4 mmol) was added to a neat mixture of isopropyl propynoate (5 g, 44 mmol) and tributyltin hydride (13.2 mL, 49 mmol) and heated to 60 °C for 24 hours. The mixture was then cooled to room temperature and purified by column chromatography using petroleum ether (40–60 °C):EtOAc (95:5, v:v) as the eluent. This gave the *Z*-isomer (6.1 g, 34%), followed by the *E*-isomer (9.7 g, 54%) as colourless oils.

Data for *Z*-**9c**: $R_f = 0.70$ (PE:EtOAc, 9:1, v:v); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.78–1.09$ (m, 21H), 1.24–1.34 (m, 6H), 1.43–1.56 (m, 6H), 4.99 (septet, 1H, $J = 7.1$ Hz), 6.64 (d, 1H, $J = 12.7$ Hz, satellite peaks observed: $J_{^{117}Sn\text{-}H} = 112.0$ Hz, $J_{^{119}Sn\text{-}H} = 114.0$ Hz), 7.07 (d, 1H, $J = 12.7$ Hz, satellite peaks observed: $J_{^{117}Sn\text{-}H} = 58.0$, $J_{^{119}Sn\text{-}H} = 59.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 11.0$, 13.7, 20.4, 27.3, 29.0, 67.7, 135.6, 156.6, 167.3; MS (EI): $m/z = 405$ (25, M^+), 347 (100), 305 (30), 291 (10); HR-MS (EI): $m/z = 401.18109$, calculated for (M^+): 401.18045.

Data for *E*-**9c**: $R_f = 0.60$ (PE:EtOAc, 9:1, v:v); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.78–1.09$ (m, 21H), 1.24–1.34 (m, 6H), 1.43–1.56 (m, 6H), 4.99 (septet, 1H), 6.22 (d, 1H, $J = 12.9$ Hz, satellite peaks observed: $J_{^{117}Sn\text{-}H} = 58.0$ Hz, $J_{^{119}Sn\text{-}H} = 61.0$ Hz), 7.67 (d, 1H, $J = 12.9$ Hz, satellite peaks observed: $J_{^{117}Sn\text{-}H} = 53.0$, $J_{^{119}Sn\text{-}H} = 56.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 11.0$, 13.7, 20.4, 27.3, 29.0, 67.7, 137.6, 153.2, 167.3; MS (EI): $m/z = 405$ (25, M^+), 347 (100), 305 (30), 291 (10); HR-MS (EI): $m/z = 401.18109$, calculated for(M^+): 401.18045.

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