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Stille Cross-Coupling Reactions with Tin Reagents Supported on Ionic Liquids

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Dedicated to Professor François Huet on the occasion of his retirement

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New ionic-liquid-supported tin reagents were synthesized and used in Stille cross-coupling reactions. High yields of biaryls were obtained under low-temperature, solvent-free, ligand-free conditions, with simple purification techniques. Moreover, the tin compound could be recycled up to five times without significant loss of reactivity. An expanded catalytic cycle for the Stille cross coupling reaction is proposed in order to explain side products that were formed under certain reaction conditions.

Introduction

Over the last two decades, Stille cross-coupling reactions have emerged as versatile methods for C–C coupling reactions.[1] Unfortunately, disadvantages such as contamination of coupling products by tin residues limit the scope of these reagents, especially for the synthesis of pharmaceutical products. Efforts have been made to overcome these problems over the last few years, leading to the use of, for example, solid-phase synthetic methods, monoorganotin reagents, fluorous phases, and phosphonium reagents.[2] In the development of more practical methodologies, room-temperature ionic liquids (RTILs) have been found to be very useful as reaction media for a wide range of organic reactions catalyzed by transition metals.[3] Indeed, ionic liquids have been used in Stille-type reactions involving aryl bromides and iodides,[4] Suzuki cross-coupling reactions,[5] or Grignard reactions.[6] In addition, task-specific ionic liquids (TSILs) have been applied to supported reagents, for example, to support iodobenzoate compounds for Suzuki cross-coupling reactions[7a] or to support a (carbene)ruthenium complex catalyst in ring-closing metathesis,[7b] and also as soluble supports for syntheses using small organic molecules.[8]

As an extension, we considered the use of TSILs for supporting tin reagents on ionic liquids for use in Stille cross-coupling reactions. Figure 1 shows the general strategy: different tin reagents are linked to an imidazolium-based ionic liquid (IL) through an alkyl chain spacer. The influences of chain length, of substituents on the tin moiety, and of counter anions were investigated.

Figure 1. General strategy.

Preliminary experiments with phenyl iodide and bromide, published in a recent communication,[9] showed the potential of these covalently supported tin reagents through their combination of the positive aspects of ILs with Stille cross-coupling reactions (e.g., low reaction temperatures, solvent- and ligand-free conditions). Moreover, the key disadvantage of Stille cross-coupling – its toxic tin residue by-products – was reduced. In this paper, based on preliminary results, we wish to report a comprehensive summary of the use of ionic-liquid-supported tin reagents for cross-coupling reactions involving substituted phenyl halides, iodopyridines, iodothiophenes, iodonaphthalenes, and benzoyl chloride. In addition, the effects of different catalysts and the recyclability of the tin reagents are also described.

Results and Discussion

1. Preparation of IL-Supported Tin Reagents

Initially, hydrostannylation of the terminal double bond of an ionic liquid was attempted (Scheme 1). Ionic liquid **2** was synthesized from 1-methylimidazole (**1**) and 4-bro-

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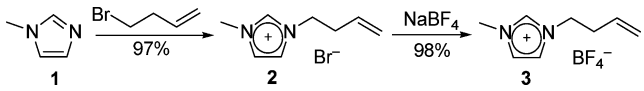
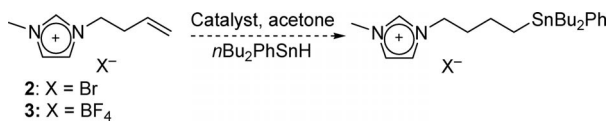
mobut-1-ene,[3,10] without solvent, in high yield and purity (by washing with diethyl ether). Furthermore, the bromide anion could be exchanged for the tetrafluoroborate anion to afford **3**.[3c,11]



Scheme 1. Synthesis of the ionic liquids starting from 1-methylimidazole.

The hydrostannylation reaction was then studied with nBu$_3$SnH and nBu$_2$SnPhH.[12] Unfortunately, this reaction failed to take place, whatever the method used (AIBN[12] or Pd(OH)$_2$;[13] Table 1).

Table 1. Hydrostannylation reactions.



Tin reagent	Catalyst	T [°C]	Time [h]	Yield [%]
Bu$_2$PhSnH	AIBN	80	2	–[a]
Bu$_2$PhSnH	AIBN	70	3	–[a]
Bu$_2$PhSnH	Pd(OH)$_2$	20	4	–[a]
Bu$_3$SnH	AIBN	100	6	–[a]
Bu$_3$SnH	AIBN	100	6	–[a]
Bu$_3$SnH	Pd(OH)$_2$	100	6	–[a]

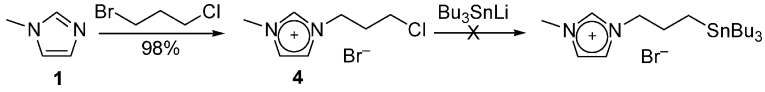
[a] Recovered starting materials and tin degradation products.

Consequently, we decided to use stannyllithium and halogen substitution in the alkyl chain, and so ILs containing halogen atoms in their alkyl chains were synthesized (Scheme 2). On employment of 1-methylimidazole with 1,3-dibromopropane or 1,4-dibromobutane, double substituted products were observed both at low temperatures and at low concentrations. However, use of 1-bromo-3-chloropropane led to the ionic liquid **4** in high yield. Unfortunately though, the subsequent reaction with lithium tributylstannane on ionic liquid **4** did not take place, possibly due to the positive charge on the imidazolium moiety, which might make it more difficult to substitute the chlorine atom, due to a higher bond strength. Research in this area by, for example, atomistic and molecular dynamics simulations is still ongoing.[14]

We turned then our attention to another strategy and decided to synthesize ionic liquids from the starting imidazoles **5** (Table 2). In this strategy the substitution would be carried out first, followed by the formation of the ionic liquid simply by addition of methyl iodide. This procedure turned out to be the method of choice, especially for long side chains or for 2-substituted starting materials. From imidazole (**5a**), 2-methylimidazole (**5b**), or 2-phenylimidazole (**5c**), ionic-liquid-supported tin reagents **8** and **9** were prepared. Whereas the product **7b** could be purified by column chromatography, providing the pure product in 73% yield, all other separations failed at the first step of the reaction sequence because of the similar polarities of products and starting materials. After conversion into the ionic liquids, the products **8a**, **8c**, and **8d** were then purified by extraction. Overall yields between 32 and 72% were obtained. In two cases the anions were exchanged for BF_4^-, thus affording **9a** and **9c** in good yields. Compounds **8c** and **8d** were not used in Stille cross-coupling reactions, due to their higher melting points and the reduced accessibility.

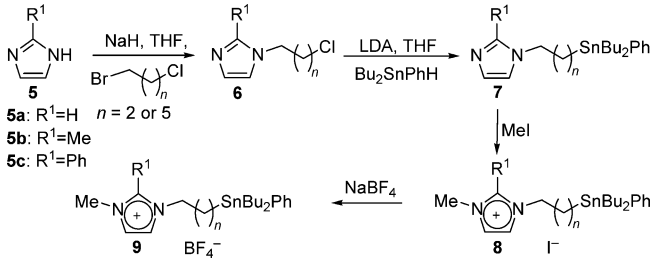
2. Stille Cross-Coupling in the Presence of IL-Supported Tin Reagents

In the first trials, Stille cross-coupling reactions under standard conditions were unsuccessful (Table 3). Copper,



Scheme 2. Synthesis of IL-supported tin reagents starting from 1-methylimidazole.

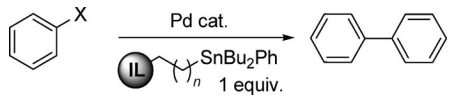
Table 2. Synthesis of IL-supported tin reagents starting from imidazoles **5**.



Entry	**5**	n	**6**	Yield [%][a]	**7**	Yield [%]	**8**	Yield [%]	**9**	Yield [%]
1	**5a**	2	**6a**[15]	82	**7a**	n.d.	**8a**	44[b]	**9a**	99
2	**5a**	5	**6b**	96	**7b**	73[a]	**8b**	99[a]	–	–
3	**5b**	2	**6c**	73	**7c**	n.d.	**8c**	32[b]	**9c**	74
4	**5c**	2	**6d**	65	**7d**	n.d.	**8d**	44[b]	–	–

[a] After purification. [b] Two steps, purification.

Table 3. Stille reactions with ionic-liquid-supported tin reagents.



Entry	IL	*n*	Anion	X	Conditions[a]	Time [h]	Conversion [%][b]	$Bu_2Sn\ Ph_2$ [%][b]
1	**9a**	2	BF_4^-	Br	A	16	32	57
2	**9a**	2	BF_4^-	Br	B	16	–	15
3	**8b**	5	I^-	I	C	40	52	27
4	**9c**	2	BF_4^-	I	C	16	–	43
5	**8b**	5	I^-	I	D	40	9	7
6	**8a**	2	I^-	I	E	160	98	–
7	**8b**	5	I^-	I	E	112	98	–
8	**8b**	5	I^-	I	F	160	87	–
9	**8b**	5	I^-	I	G	160	93	–

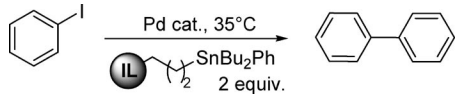
[a] Conditions: A: $Pd_2Cl_2(PhCN)_2$ (5 mol-%), CuI (10 mol-%), $AsPh_3$ (10 mol-%), [BMIM]BF_4 (0.5 mL), 80 °C; B: $Pd(PPh_3)_4$ (5 mol-%), CuI (10 mol-%), $AsPh_3$ (10 mol-%), [BMIM]BF_4 (1 mL), 80 °C; C: $Pd(PPh_3)_4$ (5 mol-%), CuI (10 mol-%), 80 °C; D: $Pd(PPh_3)_2Cl_2$ (5 mol-%), CuI (10 mol-%), 35 °C; E: Pd_2dba_3·$CHCl_3$ (5 mol-%), 35 °C; F: Pd_2dba_3·$CHCl_3$ (5 mol-%), [BMIM]PF_6 (0.5 mL), 35 °C; G: $Pd(dba)_2$ (5 mol-%), 35 °C. [b] Determined by GC.

which is often mentioned as a co-catalyst for palladium-catalyzed cross-coupling reactions,[16] was then tested in combination with **8a**, **8b**, **9a**, and **9c**. When [BMIM]BF_4 was used as co-solvent under the same conditions, the catalyst $Pd_2Cl_2(PhCN)_2$ was able to promote the reaction (32%/16 h; Entry 1), but $Pd(PPh_3)_4$ was not (Entry 2). The formation of $(n\text{Bu})_2SnPh_2$ in relatively high proportions of up to 57% (Entries 1–5) was observed. In addition, high temperatures were necessary to perform the catalytic reactions (Entries 1–4). At low temperatures, slow conversion was observed, and $Ph_2Sn(n\text{Bu})_2$ was also formed (Entry 5). No reaction took place when $Pd(PPh_3)_4$ was used without copper iodide.

Interestingly, we found that the catalysts Pd_2dba_3·$CHCl_3$ and $Pd(dba)_2$ provided good yields of the desired products. With our tin reagents supported on ionic liquids, the cross-coupling reactions were successful even at low reaction temperatures without addition of copper salts or ligands (Entries 6–9).[6,17] A first reaction with the triorganotin IL **8a** and the catalyst Pd_2dba_3·$CHCl_3$ showed a level of conversion of 98% (Entry 6). At 35 °C without solvents, no side products such as $Ph_2Sn(n\text{Bu})_2$ were formed. Under the same conditions, the cross-coupling reaction with the tin IL **8b** led to biphenyl at a 98% level of conversion after 112 h (Entry 7). With use of [BMIM]PF_6[18] as co-solvent, the coupling rate was reduced, and the reaction gave a level of conversion of 87% after a prolonged reaction time (Entry 8). The catalyst $Pd(dba)_2$ proved to be slightly less reactive in the cross-coupling reaction than Pd_2dba_3·$CHCl_3$ (93% for Entry 9 vs. 98% for Entry 7). Because the IL-supported tin reagents **8** showed very good results in Stille cross-coupling reactions, they were preferred to the tin compounds **9**, which each required an additional synthetic step.

Starting from these positive results, we continued our investigations, aiming at increasing levels of conversion and using different substrates. Initially, larger amounts of the ionic liquid **8a** were used. In all cases, very high levels of conversion could be achieved with 2 equiv. of **8a** (Table 4) within 6 h in the presence of Pd_2dba_3·$CHCl_3$, to afford a product in 94% yield. With Pd_2dba_3, the rate of conversion was lower, and the reaction was complete after 24 h. Remarkably, palladium on charcoal could be used as a catalyst with a result comparable to that obtained with Pd_2dba_3 (Entry 3). Notably, no side products were observed in any case. For all further described reactions, unless otherwise mentioned, 2 equiv. of the tin reagent were used.

Table 4. Stille reactions with aryl iodides.

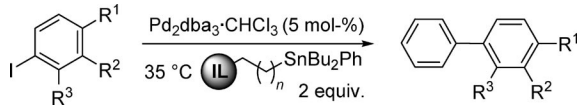


Entry	Conditions[a]	Time [h]	Conversion [%][b]	Yield [%][c]
1	E	6	100	94
2	H	24	100	–
3	I	24	100	–

[a] Conditions: E: Pd_2dba_3·$CHCl_3$ (5 mol-%), 35 °C; H: Pd_2dba_3 (5 mol-%), 35 °C; I: Pd/C (10%) (5 mol-%), 35 °C. [b] Determined by GC. [c] Isolated yield.

We then directed our attention to other substituted substrates (Table 5). In general, alkyl- and methoxyiodobenzenes needed longer reaction times than unsubstituted iodobenzenes except in the case of iodotoluene; the other substrates needed more than 5 d to reach the maximum level of conversion. Surprisingly, the cross-coupling reaction with iodotoluene was faster with **8b** than with **8a** (1 d vs. 4 d for total conversion; Entries 1–2). The ^{119}Sn NMR spectrum of the coupling product was recorded to determine the presence of possible tin residues, but no signal was observed (in Entry 1, for example). On the other hand, no significant difference could be observed with 4-*tert*-butyliodobenzene (Entries 3–4). The 2,4-dimethoxy compound displayed the lowest level of conversion. Increasing reaction times did not improve the conversion. Disadvantageously, the formation of biphenyl was observed in all reactions. The product/biphenyl ratio depends on the aryl substrate; it is

Table 5. Stille reactions with substituted aryl iodides.



Entry	IL	*n*	R^1	R^2	R^3	Time [d]	Conversion [%][a]	Product [%][a]	Ph–Ph [%][a]
1	**8a**	2	Me	H	H	4	100	60	40
2	**8b**	5	Me	H	H	1	100	64	36
3	**8a**	2	*t*Bu	H	H	5	82	55	33
4	**8b**	5	*t*Bu	H	H	5	87	58	33
5	**8b**	5	OMe	H	OMe	5	79	60	24
6	**8b**	5	H	CO_2H	H	5	–[b]	–[b]	–[b]
7	**8b**	5	H	H	CO_2H	5	–[b]	–[b]	–[b]
8	**8a**	2	H	CO_2Me	H	3	92	67	24
9	**8b**	5	H	CO_2Me	H	1	100	72[c]	20
10	**8a**	2	H	H	CO_2Me	1	100	59	41
11	**8b**	5	H	H	CO_2Me	3	100	86	14
12	**8b**	5	OCF_3	H	H	1	100	87	13
13	**8b**	5	F	H	F	1	100	97	3
14[d]	**8b**	5	H	Cl	H	2.5	93	51	19[e]

[a] Determined by GC. [b] Not detectable by GC. [c] Isolated yield. [d] 1 equiv. of IL was used. [e] Homocoupled product: 23%.

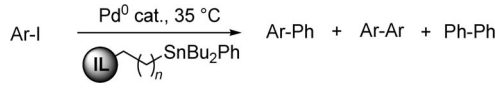
at its maximum in the case of iodotoluene (40 and 36% of biphenyl produced for Entries 1–2) and at its minimum for 1-iodo-2,4-dimethoxybenzene (24% of biphenyl for Entry 5).

We then employed iodobenzoic acid derivatives in cross-coupling reactions. Although the trials with the free acids were unsuccessful, their esters gave high levels of conversion and yields (Table 5). Again, though, a difference between the tin reagents used in the reactions was apparent. With the tin IL **8b**, methyl 3-iodobenzoate could be completely converted into the product in good yield: 72% in only 1 d (Entry 9). For the reaction of methyl 2-iodobenzoate, in contrast, the tin reagent **8a** showed the higher reactivity (Entry 10). In this case, however, the higher amount of biphenyl was also formed.

Better results were obtained with iodobenzenes substituted with electron-withdrawing group(s) [4-(trifluoromethoxy) and 2,4-difluoro], which afforded the biaryls with excellent yields and levels of conversion within 24 h (Entries 12–13). Especially in the case of 1,3-difluoro-4-iodobenzene, the unwanted biphenyl side-product was observed only in small amounts. In contrast with these results, the cross-coupling with 1-chloro-3-iodobenzene (Entry 14) afforded the main product (51%) together with biphenyl (19%) and the homocoupled product (23%).

Because pyridine derivatives are highly useful building blocks and intermediates for the synthesis of insecticides, herbicides, pharmaceuticals, food flavorings, dyes, rubber chemicals, adhesives, paints, etc.,[19] we tried to perform a cross-coupling reaction with an iodo-substituted pyridine. Only 1 equiv. of the ionic liquid was used, and a reaction time of 4 d was necessary to reach the maximum conversion in both cases (Table 6, Entries 1–2). Interestingly, the $Pd(dba)_2$ catalyst was better here, because only a 4% yield of biphenyl was obtained (Entry 2). Surprisingly, when 2 equiv. of the tin reagent supported on ionic liquid were used (Entry 3), with the tin compound **8a** the reaction time was reduced to 3 d. Moreover, with the tin ionic liquid **8b** (Entry 4), total conversion was reached after only 2.5 d (61% yield), but with an amount of biphenyl of 26%. No tin signal was detectable in the ^{119}Sn NMR spectrum of the coupling product (Entry 4).

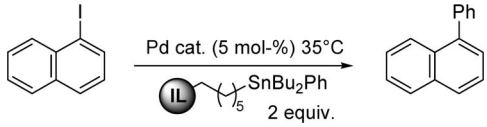
Table 6. Stille reaction with 3-iodopyridine and iodothiophenes.



Entry	IL	*n*	Ar	Conditions[a]	Time	Conversion [%]	Product [%][b]	Ar–Ar	Ph–Ph [%][b]
1	**8a**	2	3-pyridinyl	E	4 d	84[c]	70	0	14
2	**8a**	2	3-pyridinyl	H	4 d	92[c]	88	0	4
3	**8a**	2	3-pyridinyl	E	3 d	99[d]	91	0	8
4	**8b**	5	3-pyridinyl	E	2.5 d	100[d]	61[e]	0	26
5	**8b**	5	2-iodothienyl	E	16 h	100[d]	33	21	46
6	**8b**	5	2-iodothienyl	I	16 h	90[d]	32	18	40
7	**8b**	5	3-iodothienyl	E	16 h	100[d]	38	18	44

[a] Conditions: E: $Pd_2dba_3·CHCl_3$ (5 mol-%); H: $Pd(dba)_2$ (5 mol-%); I: Pd/C (10%) (5 mol-%). [b] Determined by GC. [c] Only 1 equiv. of the ionic-liquid-supported tin reagent was used. [d] 2 equiv. of the ionic-liquid-supported tin reagent were used. [e] Isolated yield.

Table 7. Stille reaction with iodonaphthalene.



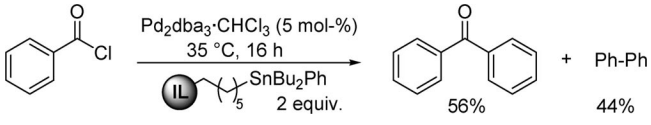
Entry	Conditions[a]	Time [h]	Conversion [%][b]	Product [%][b]	Ph–Ph [%][b]	Naphthalene [%][b]
1	I	66	86	54	27	10
2	J	66	82	53	24	11
3	K	66	95	59	28	10
4	E	17	100	67	22	11

[a] Conditions: I: Pd/C (10%, 5 mol-%); J: $Pd(OAc)_2$ (5 mol-%); K: $PdCl_2(PhCN)_2$ (5 mol-%); E: $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol-%). [b] Determined by GC.

We next used thiophenes, which showed slightly different product spectra. Under all conditions, large amounts of biphenyl – between 40 and 46% – were produced after a 16 h reaction time (Entries 5–7). The desired products were obtained in yields between 32 and 38%. The third products were the homocoupled products (Table 6).

We also investigated the coupling of 1-iodonaphthalene in the presence of the tin IL **8b** under different conditions (Table 7). With $Pd_2(dba)_3{\cdot}CHCl_3$ as catalyst, full conversion was observed after only 17 h, with an amount of biphenyl of 22% (Entry 4). In this case, we also observed the formation of naphthalene in 11% yield.

The Stille reaction with benzoyl chloride was also possible, and, after 16 h, complete conversion of the starting material was observed (determined by GC). The reaction afforded the coupling product in 56% yield, and a 44% yield of the biphenyl by-product was formed (Scheme 3).

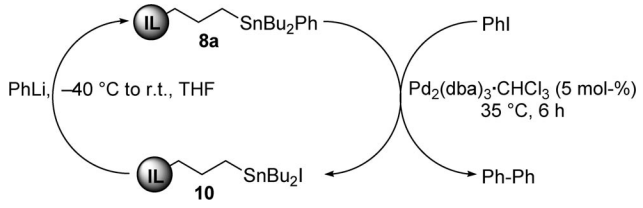


Scheme 3. Stille reaction with benzoyl chloride.

It is possible to recycle the tin compound/palladium catalyst system at the end of the reaction. Products and remaining starting materials and/or side products are extracted by organic solvents such as pentane, which is immiscible with the ionic liquid, whereas the ionic liquid phase still contains the halogenotin-supported ionic liquid **10** (Table 8). Simple addition of PhLi to a solution of compound **10** in THF regenerates the Stille starting material **8a** (Scheme 1). The tin reagent could be recycled five times without appreciable loss of effectiveness (Table 8). The 2-positions in imidazolium ionic liquids are known to be relatively acidic, leading to substitution and exchange.[20] In our case, however, no substitution at the 2-position of imidazolium **10** was observed with phenyllithium.

In our Stille coupling reaction, the formation of biphenyl and/or homocoupled products was observed. Unlike in the case of arylboronic acids,[21] there is no self-coupling of the

Table 8. Recycling of the tin compounds.



Run	Conversion [%][b]
1	100
2[a]	100
3[a]	99
4[a]	97
5[a]	96

[a] Recovered tin reagent **8a** from the previous cycle. [b] Determined by GC.

tin reagents **8** under Pd^0 catalysis conditions. We believe that because of the nature of the substrate the catalysts are destabilized and diverge from the standard catalytic cycle steps ("oxidative addition, transmetalation, *trans*/*cis* isomerization, reductive elimination"; Figure 2). In a published kinetic and mechanistic investigation of the transmetalation reaction with organotin reagents[22] it was discovered that two different catalyst species are formed simultaneously in the transmetalation step on platinum(II). In particular, one of these species is considered to react a second time with a tin compound. This would lead to different products in the Stille cross-coupling reaction.

To provide support for this proposed alternative cycle, we synthesized a new supported tin reagent with a methoxy substituent on the phenyl group (compound **14**, Scheme 4). This, under Stille cross-coupling conditions, afforded predominantly the desired product **15** and 3,3′-dimethoxybiphenyl (**16**) originating from the alternative cycle. In our proposed alternative cycle the Pd^2L_2ArR reacts a second time with our stannane IL (Sn1). In this additional transmetalation step $Pd^2L_2R_2$ is formed. After the subsequent *trans*/*cis* isomerization and reductive elimination, the biaryl R–R is eliminated. In addition, the IL–$SnBu_2Ar$ intermediate (Sn3) could lead to homocoupled products (Ar–Ar) af-

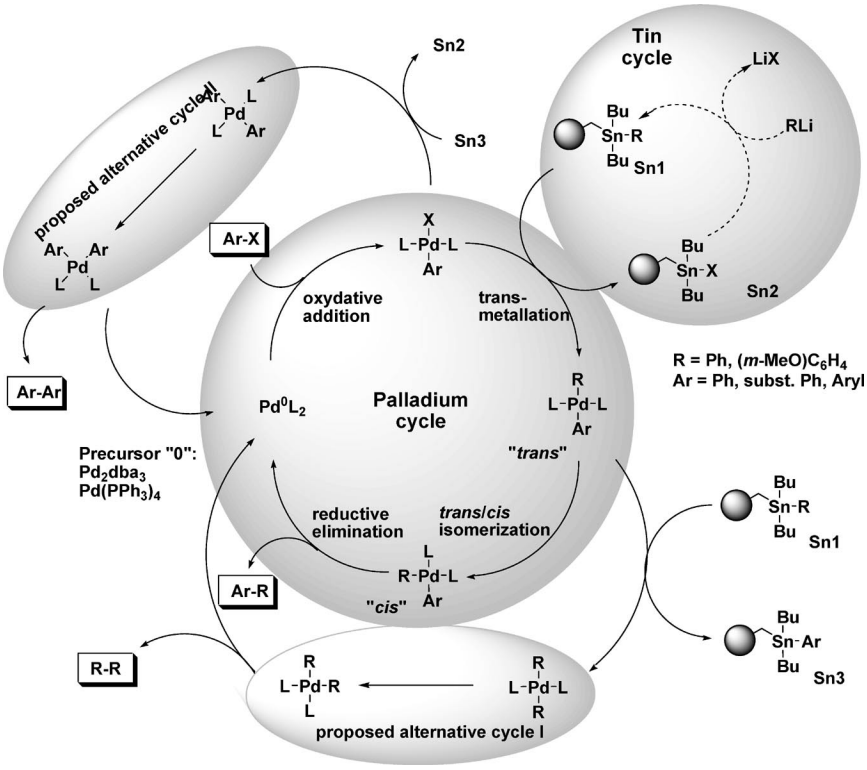
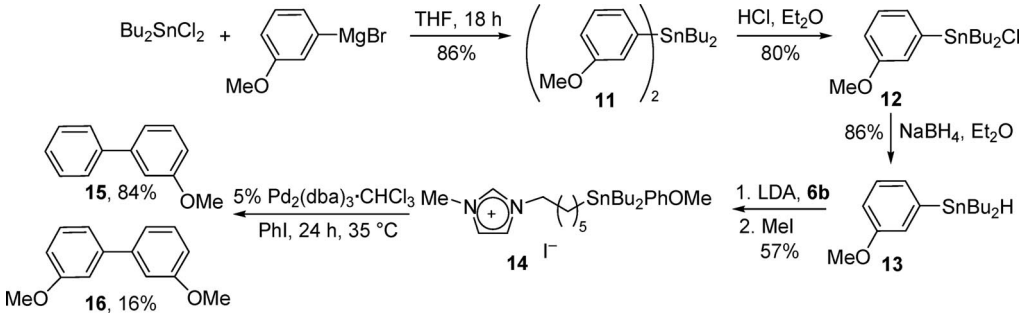


Figure 2. Catalytic cycle with proposed alternative pathway.



Scheme 4. Ionic-liquid-supported tin-substituted reagents and Stille coupling.

ter passing through the transmetalation step a second time. For example, in Table 5 (Entry 14) and Table 6 (Entries 5–7) we have shown that the homocoupling products (3,3′-dichlorobiphenyl and 2,2′-bithiophene) were formed.

Conclusions

New tin reagents supported on ionic liquids were synthesized and successfully used under Stille cross-coupling reactions. High yields of coupled products were obtained under low-temperature, solvent-free conditions. Moreover, the tin compounds could be recycled up to five times without significant loss of reactivity. The best results were achieved with Pd_2dba_3·$CHCl_3$ catalyst, which does not require additional additives or ligands. This reduces costs and simplifies the workup procedure. We have also proposed an expanded catalytic cycle for the Stille cross-coupling reaction to explain side products that were formed under certain reaction conditions.

Experimental Section

1-{3-[Dibutyl(phenyl)stannyl]propyl}-1*H*-imidazole (7a):[9] Dibutylphenyltin hydride (1.37 g, 4.4 mmol) was slowly added at –78 °C to a solution of lithium diisopropylamide (4.5 mmol) in dry THF (20 mL). The resulting mixture was stirred at –50 °C for 1 h and subsequently added at –50 °C to a solution of 1-(3-chloropropyl)-1*H*-imidazole (**6a**, 0.60 g, 4.1 mmol) in dry THF (15 mL). The mixture was then allowed to warm to room temp. and stirred for 18 h. Water (5 mL) was slowly added, and the mixture was stirred at room temp. for an additional 15 min. CH_2Cl_2 (50 mL) was added to this mixture, and the organic phase was successively washed with H_2O (2 × 20 mL) and brine (10 mL). The aqueous layer was ex-

tracted with CH_2Cl_2 (3 × 20 mL), and the combined organic phase was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude product (1.78 g) was then purified by column chromatography [silica gel: 20 g; solvent: CH_2Cl_2 to CH_2Cl_2/MeOH (98:2) and then CH_2Cl_2/MeOH/diethyl ether (96:2:2)] to yield the liquid product as a mixture of **7a** with the starting material **6a** (1.70 g, 67% product, 33% starting material). This mixture was used directly in the next reaction step. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.28–7.42 (m, 6 H), 7.04 (s, 1 H), 6.84 (s, 1 H), 3.86 (t, J = 7.2 Hz, 2 H), 1.01–2.00 (m, 16 H), 0.88 (t, J = 7.3 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.6, 137.1, 136.3, 129.3, 128.3, 128.2, 118.7, 50.6, 29.0, 28.7, 27.3, 13.6, 9.4, 5.8 ppm. IR (neat): $\tilde{\nu}$ = 2955, 2924, 2870, 2850, 1504, 1462, 1427, 1375, 1281, 1227, 1107, 1074, 906, 808, 725, 698, 662, 594, 503, 446 cm^{-1}. HRMS: calcd. for $C_{20}H_{32}N_2Na^{120}Sn$ [M + Na]$^+$ 443.1485; found 443.1482.

1-{3-[Dibutyl(phenyl)stannyl]propyl}-3-methyl-1*H*-imidazolium Iodide (8a):[9] In a dried sealed tube, crude 1-{3-[dibutyl(phenyl)stannyl]-propyl}-1*H*-imidazole (**7a**, 1.68 g) was dissolved in methyl iodide (1 mL) and stirred at 40 °C overnight. The mixture was cooled to room temp., and the excess methyl iodide was evaporated under reduced pressure. A CH_2Cl_2/ethyl acetate/diethyl ether (90:5:5) mixture was added, and the organic phase was washed with water to remove the impurities having remained from the previous step and then separated, dried with $MgSO_4$, filtered, and concentrated under reduced pressure to yield **8a** (0.99 g, 1.8 mmol, 44%, over two steps) as a colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.11 (s, 1 H), 7.33–7.44 (m, 5 H), 7.30 (m, 1 H), 7.04 (m, 1 H), 4.23 (t, J = 7.2 Hz, 2 H), 4.09 (s, 3 H), 2.03–2.11 (m, 2 H), 1.11–1.57 (m, 14 H), 0.89 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.4, 136.8, 136.5, 128.5, 128.4, 123.7, 121.7, 53.3, 37.1, 29.0, 28.1, 27.3, 13.7, 9.5, 5.4 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –42.2 ppm. IR (neat): $\tilde{\nu}$ = 3061, 2953, 2922, 2868, 2850, 1568, 1456, 1425, 1375, 1167, 1072, 1020, 864, 727, 700, 656, 617, 594, 503, 447 cm^{-1}. HRMS: calcd. for $C_{21}H_{35}N_2{}^{120}Sn$ 435.1822; found 435.1825.

1-{6-[Dibutyl(phenyl)stannyl]hexyl}-1*H*-imidazole (7b):[9] Dibutylphenyltin hydride (3.45 g, 11.1 mmol) was slowly added at –78 °C to a solution of lithium diisopropylamide (11.3 mmol) in dry THF (40 mL). The resulting mixture was stirred at –50 °C for 1 h and was subsequently added at –50 °C to a solution of 1-(6-chlorohexyl)-1*H*-imidazole (**6b**, 1.57 g, 8.5 mmol) in dry THF (20 mL). The mixture was then allowed to warm to room temp. and stirred for 18 h. Water (5 mL) was slowly added, and the mixture was stirred at room temp. for an additional 15 min CH_2Cl_2 (100 mL) was added to this mixture, and the organic phase was successively washed with H_2O (20 mL) and brine (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the organic combined phases were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude product (4.69 g) was then purified by column chromatography [silica gel; solvent: CH_2Cl_2 to CH_2Cl_2/MeOH (98:2) and then CH_2Cl_2/MeOH/diethyl ether (96:2:2)] to yield the pure product **7b** as a colorless oil (2.86 g, 6.2 mmol, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.29–7.45 (m, 6 H), 7.05 (s, 1 H), 6.87 (s, 1 H), 3.87 (t, J = 7.2 Hz, 2 H), 1.68–1.75 (m, 2 H), 1.64 (br. s, 2 H), 1.50–1.57 (m, 5 H), 1.27–1.37 (m, 8 H), 0.89–1.07 (m, 5 H), 0.88 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.8, 137.1, 136.5, 129.3, 128.1, 128.0, 118.8, 47.0, 33.7, 31.0, 29.1, 27.4, 26.6, 26.0, 13.7, 9.6, 9.5 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –43.9 ppm. IR (neat): $\tilde{\nu}$ = 2955, 2922, 2850, 1504, 1462, 1427, 1282, 1228, 1074, 808, 725, 698, 662, 596, 503, 446 cm^{-1}. HRMS: calcd. for $C_{23}H_{39}N_2{}^{120}Sn$ 463.2135; found 463.2138.

1-{6-[Dibutyl(phenyl)stannyl]hexyl}-3-methyl-1*H*-imidazolium Iodide (8b):[9] In a dried sealed tube, crude 1-{3-[dibutyl(phenyl)stannyl]-hexyl}-1*H*-imidazole (**7b**, 1.02 g, 2.2 mmol) was dissolved in methyl iodide (0.5 mL) and stirred at 40 °C overnight. The mixture was allowed to cool to room temp., and the excess methyl iodide was evaporated under reduced pressure to yield **8b** (1.33 g, 2.2 mmol, 99%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.17 (s, 1 H), 7.29–7.46 (m, 6 H), 7.20 (s, 1 H, 4-H), 4.25 (t, J = 7.5 Hz, 2 H), 4.11 (s, 3 H), 1.83–1.90 (m, 2 H), 0.98–1.57 (m, 20 H), 0.88 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.7, 136.8, 136.8, 136.4, 128.0, 123.6, 121.8, 50.1, 37.1, 33.5, 30.1, 29.0, 27.3, 26.5, 25.6, 13.6, 9.5, 9.4 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –43.8 ppm. IR (neat): $\tilde{\nu}$ = 3061, 2953, 2922, 2848, 1568, 1462, 1427, 1375, 1165, 1072, 862, 727, 700, 656, 617, 505, 447 cm^{-1}. HRMS: calcd. for $C_{24}H_{41}N_2{}^{120}Sn$ 477.2291; found 477.2296.

Dibutylbis(3-methoxyphenyl)stannane (11): A solution of 3-$MeOC_6H_4MgBr$ in THF (1.2 mol L^{-1}, 24.00 mmol, 20 mL) was added dropwise over a period of 30 min to a solution of Bu_2SnCl_2 (3.64 g, 12.00 mmol) in THF (9 mL). The solution was heated at reflux for 18 h. The THF was evaporated under reduced pressure, and the residue was dissolved in Et_2O (20 mL). The organic layers were washed with H_2O (3 × 10 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL), and the combined organic phases were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to yield **11** (4.56 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.32 (m, 2 H), 6.99–7.12 (m, 4 H), 6.85–6.88 (m, 2 H), 3.80 (s, 6 H), 1.57–1.70 (m, 4 H), 1.26–1.40 (m, 8 H), 0.88 (t, J = 7.3 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 141.7, 122.3, 113.5, 35.0, 28.9, 27.3, 13.6, 10.4 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –69.6 ppm. IR (neat): $\tilde{\nu}$ = 2899, 1569, 1474, 1408, 1282, 1241, 1223, 1180, 1100, 1039, 819, 773, 693, 655, 432 cm^{-1}. HRMS (CI methane): calcd. for $C_{22}H_{33}O_2Sn$ [M + H]$^+$ 449.1503; found 449.1495.

Dibutylchloro(3-methoxyphenyl)stannane (12): A solution of HCl in Et_2O (2 M, 3 mL, 6 mmol) was added dropwise at 0–5 °C over 5 min to a solution of dibutylbis(3-methoxyphenyl)stannane (**11**, 2.66 g, 5.94 mmol) in Et_2O (25 mL). The mixture was stirred at room temp. for an additional 1 h, and was then treated with H_2O (3 × 20), and brine (10 mL). The aqueous layer was extracted with Et_2O (3 × 20 mL), and the combined organic phases were dried with $MgSO_4$, filtered, concentrated under reduced pressure, and distilled (125 °C, 0.04 Torr) to yield **12** as a yellow oil (1.78 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90–7.38 (m, 4 H), 3.83 (s, 3 H), 1.67–1.75 (m, 4 H), 1.49–1.57 (m, 4 H), 1.35–1.45 (m, 4 H), 0.92 (t, J = 7.3 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 142.6, 129.7, 127.5, 120.8, 115.2, 55.2, 27.8, 26.8, 17.8,13.6 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –70 ppm. IR (neat): $\tilde{\nu}$ = 2955, 2853, 1734, 1583, 1571, 1475, 1462, 1411, 1376, 1284, 1242, 1228, 1181, 1038, 866, 776, 692, 657, 511, 432 cm^{-1}. HRMS (CI methane): calcd. for $C_{15}H_{25}OSn$ [M – Cl]$^+$ 341.0927; found 341.0929.

Dibutyl(3-methoxyphenyl)tin Hydride (13): A solution of $NaBH_4$ (0.548 g, 14.50 mmol) in H_2O (5 mL) was added dropwise with vigorous stirring (Caution: hydrogen evolution!) at 0–8 °C over a period of 10 min to a solution of dibutylbis(3-methoxyphenyl)stannane (**12**, 1.81 g, 4.82 mmol) in Et_2O (25 mL). The mixture was stirred at room temp. for an additional 45 min. The organic phase was then washed with H_2O (2 × 50 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL), and the combined organic phases were dried with $MgSO_4$, filtered, and concentrated under vacuum to yield **13** as a yellow oil (1.41 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84–7.29 (m, 5 H), 5.43 (m, 1 H), 1.14–1.63 (m, 12

H), 0.89 (t, J = 7.3 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 140.7, 127.8, 121.6, 113.1, 54.0, 28.4, 26.3, 12.6, 8.4 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = 83.0 ppm. IR (neat): $\tilde{\nu}$ = 2954, 2923, 1814, 1582, 1570, 1474, 1462, 1409, 1282, 1240, 1225, 1181, 1041, 773, 693, 673, 656, 529, 494, 429 cm^{-1}. HRMS (CI methane): calcd. for $C_{15}H_{25}OSn$ $[M - H]^+$ 341.0927; found 341.0942.

1-{6-[Dibutyl(3-methoxyphenyl)stannyl]hexyl}-1*H*-imidazolium Iodide (14): Dibutyl(3-methoxyphenyl)tin hydride (1.25 g, 3.67 mmol) was slowly added at –78 °C to a solution of lithium diisopropylamide (4.30 mmol) in dry THF (20 mL). The resulting mixture was stirred at –50 °C for 1 h and subsequently added at –50 °C to a solution of 1-(6-chlorohexyl)-1*H*-imidazole (**6b**, 0.622 g, 3.34 mmol) in dry THF (20 mL). The mixture was then allowed to warm to room temp. and stirred at room temp. for further 18 h. Water (5 mL) was slowly added, and the mixture was stirred at room temp. for an additional 15 min. CH_2Cl_2 (100 mL) was added to this mixture, and the organic phase was successively washed with H_2O (20 mL) and brine (10 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude 1-{6-[dibutyl(3-methoxyphenyl)stannyl]hexyl}-1*H*-imidazole. In a dried sealed tube, crude 1-{6-[dibutyl(3-methoxyphenyl)stannyl]hexyl}-1*H*-imidazole (1.52 g) was dissolved in methyl iodide (1.12 mL) and stirred at 40 °C for 16 h. The mixture was allowed to cool to room temp., and the excess methyl iodide was evaporated under reduced pressure. A CH_2Cl_2/ethyl acetate/ether (90:5:5) mixture was added, and the organic phase was washed with water to remove the ionic liquid side product having remained from the previous step, separated, dried with $MgSO_4$, filtered, and concentrated under reduced pressure to yield **14** (1.19 g, 57%, over two steps) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1 H), 6.82–7.60 (m, 6 H), 4.26 (t, J = 7.5 Hz, 2 H), 4.11 (s, 3 H), 3.81 (s, 3 H), 1.83–2.01 (m, 2 H), 0.98–1.60 (m, 20 H), 0.88 (t, J = 7.3 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 143.2, 136.5, 128.9, 128.8, 123.9, 122.1, 122.0, 113.0, 55.1, 50.1, 37.1, 33.6, 30.2, 29.0, 27.3, 26.6, 25.6, 13.7, 9.6, 9.5 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –41.5 ppm. IR (neat): $\tilde{\nu}$ = 2955, 2853, 1734, 1583, 1571, 1475, 1462, 1411, 1376, 1284, 1242, 1228, 1181, 1038, 866, 776, 692, 657, 511, 432 cm^{-1}. HRMS (CI methane): calcd. for $C_{25}H_{43}N_2OSn$ $[M - I]^+$ 507.2397; found 507.2482.

Stille Cross-Coupling Reactions. Representative Procedure: Pd_2dba_3·$CHCl_3$ (11 mg, 5 mol-%) was added to a Schlenk tube containing the ionic-liquid-supported tin compound **8b** (247 mg, 0.41 mmol). The reaction tube was closed, and heated at 35 °C for 15 min. After the mixture had cooled to ambient temperature, iodobenzene (23 μL, 42 mg, 0.205 mmol) was added, and the tube was evacuated and back-filled with nitrogen five times. The mixture was heated at 35 °C for the required time. The reaction was checked by GC of the pentane extract. When complete (GC > 98%), pentane (10 mL) was added to the mixture and stirred for 30 min. The stirring was stopped, and the pentane phase was separated. This was repeated twice, and the combined pentane phases were then filtered through a short pad of silica gel and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography [silica gel; pentane/EtOAc (90:10)] to afford the product biphenyl (30 mg, 95%). After the coupling reaction, the product was determined by GC-MS. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.34–7.62 (m, 10 H) ppm.

Ionic Liquid Recycling Procedure: Pd_2dba_3·$CHCl_3$ (18 mg, 5 mol-%) was added to a Schlenk tube containing the ionic liquid **8a** (394 mg, 0.70 mmol). The reaction tube was closed, and heated at 35 °C for 15 min. After the mixture had cooled to ambient temperature, iodobenzene (40 μL, 72 mg, 0.35 mmol) was added, and the tube was evacuated and back-filled with nitrogen five times. The mixture was heated at 35 °C for 6 h. After the mixture had cooled, pentane (10 mL) was added, and the mixture was stirred for 30 min. The stirring was stopped and the pentane phase was separated. This was repeated twice, and the combined pentane phases were then filtered through a short pad of silica gel and concentrated under reduced pressure. Levels of conversion were determined by GC analysis of the filtrate. In order to recycle the ionic liquid, the ionic liquid residue was dissolved in CH_2Cl_2 (10 mL) and filtered through a short pad of Celite® to remove insoluble materials. The filtrate was concentrated under reduced pressure to afford the ionic liquid **10**, which was treated with PhLi (0.78 mL, 1.4 mmol, 1.8 mol L^{-1}) at –40 °C for 2 h in dry THF (5 mL). The mixture was then allowed to warm to room temp. and stirred for 6 h. Water (5 mL) was slowly added, and the mixture was stirred at room temp. for an additional 15 min. CH_2Cl_2 (10 mL) was added to this mixture, and the organic phase was successively washed with H_2O (2 × 10 mL) and brine (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic phases were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to afford the ionic liquid **8a**, used for the next run without further purification. This cycle could be repeated five times according to the typical procedure described above.

Supporting Information (see footnote on the first page of this article): Additional experimental procedures; selected ^{1}H and ^{13}C NMR spectra.

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