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Silylstannation of terminal alkynes using a recyclable palladium(0) catalyst immobilised in an ionic liquid

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Silylstannanes can be regioselectively added across terminal alkynes in a quantitative fashion in the presence of a palladium(0) catalyst immobilised in the [bmim]PF_6 ionic liquid which can be recycled without loss of activity.

Ionic liquids have seen use in many applications owing to their unique properties.[1] Being ionic in nature, they provide a solvent environment unobtainable with traditional molecular solvents. They often contain poorly-coordinating anions and thus form a new class of polar, non-coordinating solvents. As such, ionic liquids have been used in several catalytic reactions involving many different catalysts.[2] Several catalysts have been immobilised in ionic liquids and successfully recycled as a result of the involatile nature of ionic liquids. These include palladium catalysts for use in Stille,[3] Suzuki,[4] and Heck coupling reactions,[5] as well as several other coupling reactions,[6] a chromium catalyst for asymmetric epoxide openings,[7] a chiral manganese epoxidation catalyst,[8] and a ruthenium catalyst for asymmetric alkene hydrogenations.[9] Few reactions involving organometallic reagents have been performed in ionic liquids, possibly stemming from the relatively high acidity of the proton on C-2 of the *N*,*N′*-dialkylimidazolium ring on which the most prevalent ionic liquids are based. One such ionic liquid is 1-*n*-butyl-3-methylimidazolium hexafluorophosphate, [bmim]PF_6, the ionic liquid used in this study (Fig. 1). The synthesis and reactivity of organozinc reagents has been studied in a non-imidazolium-based ionic liquid, showing the potential of some organometallic reactions in ionic liquids.[10]

Silylstannanes are versatile organometallic reagents in organic synthesis. These compounds contain a silicon–tin bond and are easily synthesized by generating a trialkyltin anion followed by a quench with a trialkylsilyl chloride.[11] The resulting silylstannanes can be added across unsaturated organic compounds *via* a palladium catalyst to afford a bifunctional organic dianion equivalent containing both carbon–silicon and carbon–tin bonds.[11,12] These products can then be selectively destannylated or desilylated, substitutions can be made for the silyl or stannyl groups, or they can participate in such reactions as Stille couplings. As the addition of silylstannanes across unsaturated systems uses expensive palladium catalysts, immobilisation of the palladium catalyst in an ionic liquid that allows recycling of the catalyst without loss of activity was seen as a potentially useful application of ionic liquids in synthesis. This would also add to the growing number of organometallic reactions shown to proceed in ionic liquids.

We report herein the regioselective addition of silylstannanes to terminal alkynes in the presence of a palladium(0) catalyst. This reaction proceeds cleanly, giving a terminally silylated, internally stannylated alkene as a single *cis*-bismetallated isomer.[11a] Yields obtained using the catalyst immobilised in an ionic liquid affords equal to improved isolated yields of adducts. This system also allows facile product isolation and easy recycling of the immobilised catalyst without loss of activity. The silylstannane employed, trimethyl(tributylstannyl)silane ($Bu_3SnSiMe_3$), was easily synthesized *via* deprotonation of tributyltin hydride with LDA followed by a quench with chlorotrimethylsilane[11] or was purchased from Aldrich. This was stirred with one of three terminal alkynes containing various functional groups—phenylacetylene, 1-decyne, and 5-hexyn-1-ol—in the [bmim]PF_6 ionic liquid.[13] 1–5 mol% $Pd(PPh_3)_4$ was immobilised in the dry ionic liquid, as this has been shown to be the best palladium species to catalyse silylstannations of terminal alkynes.[11a] The reaction was generally carried out with diethyl ether as a co-solvent and heated to 70 °C. When 5 mol% of the Pd(0) catalyst was used the mixture of catalyst and ionic liquid appeared turbid and underwent some colour change to a reddish-brown with subsequent cycles of the reaction. The possibility that this is an indication for the formation of some other active catalytic species is under investigation. However, when 1 mol% of the catalyst was used the bright yellow colour characteristic of the Pd(0) catalyst was maintained. Products were easily isolated *via* ether extraction of the ionic liquid, the yields of which are presented in Table 1.†

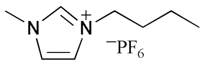
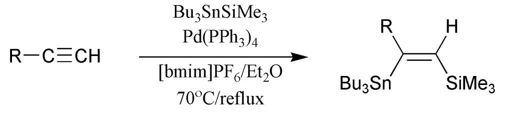
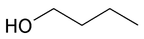
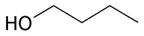


Fig. 1 [bmim]PF_6.

The silylstannations of the three alkynes proceeded readily in the [bmim]PF_6 ionic liquid in the presence of both 5 mol% and 1 mol% $Pd(PPh_3)_4$. As expected, the reactions carried out with 1 mol% palladium required slightly longer reaction times than those with 5 mol%; however, these are not inordinately long as these reactions have generally been carried out at 70 °C for 24–48 h in refluxing tetrahydrofuran.[11a] All reactions proceeded quantitatively by gas chromatography and isolated yields were also quite high. The isolated yield of the 5-hexyn-1-ol adduct was the same as that previously reported for a 4-pentyn-1-ol adduct; although, this reaction shows that the reagents tolerate a degree of alkyne functionality (it has been shown that a wide variety of functional groups are tolerated by this reaction in THF).[11a] A 91% yield was previously reported for the reaction of phenylacetylene with $Bu_3SnSiMe_3$[11a] and a 52% yield was reported for the reaction of 1-hexyne with the same silylstannane,[12a] both reactions being performed in THF with 1 mol% $Pd(PPh_3)_4$. In [bmim]PF_6 99% isolated yields of the adducts formed with phenylacetylene and 1-decyne were obtained. This may be a result of the ionic liquid facilitating product isolation as it is exhaustively extracted from the ionic liquid with multiple ether washes. Since the reactants and

Table 1 Silylstannations of terminal alkynes



Entry	R group	mol% Pd	Rxn time (h)	Yield (%)[a]
1[b]	Ph	5	18	100 (78)
2	Ph	1	20	100 (99)
3	 HO	5	18	100 (89)
4	 HO	1	24	100 (87)
5	C_8H_{17}	5	15	99 (97)
6	C_8H_{17}	1	24	99 (99)

[a] GC yield (isolated yield in brackets). [b] Reaction performed without ether.

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products form an upper layer in those reactions conducted without ether and also since products can be efficiently isolated from this system *via* ether extraction it follows that when a biphasic system is used the majority of the reactants and products reside in the upper ethereal layer. Small portions of the reactants partition into the catalyst/ionic liquid layer where the bismetallation occurs and then the products, once formed, partition predominantly back into the upper ethereal layer leaving behind the regenerated Pd(0) catalyst in the ionic liquid layer. It is also possible that the reaction is proceeding further to completion in the ionic liquid than when it is performed neat or in THF. Ether was not used as a cosolvent in the first addition of $Bu_3SnSiMe_3$ across phenylacetylene (Table 1, entry 1) and the isolated yield was only 78%. Ether was used from this point forward since phenylacetylene was partially evaporating and condensing onto the flask walls, thus lowering the isolated yields of adducts. Evaporation of the ether was avoided through use of a dried reflux condenser attached to the reaction flask. Temperature was maintained at a constant 70 °C using an oil bath heated by a thermally controlled hotplate. All subsequent isolated yields from reactions using ether as a cosolvent were higher.

The identities of the isolated compounds were confirmed by GC/MS as well as by ^1H and ^{13}C NMR. The ^1H NMR spectra were especially useful as they helped confirm the stereochemistry of the silylstannylated alkene product. Coupling constants for the Sn–H coupling to the lone vinylic proton are known to be around 180 Hz for *trans* coupling but are around 100 Hz for *cis* and geminal coupling.[11a] The Sn–H vinylic coupling constant for all isolated adducts was 160–178 Hz, indicating *trans* coupling and that only *cis*-bismetallated adducts were formed. As well, only a single peak was present in the GC trace, indicating only one isomer.

Ionic liquids have been described as being potential "green solvents" mainly due to their involatility, since they cannot contaminate the atmosphere and can be reused. The silylstannation of alkynes is also a green reaction as it exhibits total "atom economy" in that all atoms of the starting reagents are incorporated into the products and no by-products are produced. Recycling of the $Pd(PPh_3)_4$/[bmim]PF_6 catalyst/ionic liquid system was relatively straight forward. After a reaction was performed in 1.0 mL of [bmim]PF_6 containing 1 or 5 mol% $Pd(PPh_3)_4$ and the products were extracted under an inert atmosphere, a further amount of $Bu_3SnSiMe_3$ and the desired alkyne were injected followed by 5.0 mL of dry ether and the reaction was repeated. The results of these recycling experiments are presented in Table 2.

The recycling experiments were monitored by gas chromatography and showed that the catalyst/ionic liquid system could be recycled at least four times with negligible loss in activity (Table 2, entries 1–4), even with only 1 mol% $Pd(PPh_3)_4$ (Table 2, entries 5 and 6). Gas chromatography performed on the final ether extracts after each cycle showed no traces of either starting materials or products. The only products formed were the bismetallated alkene, unreacted $Bu_3SnSiMe_3$, and a small amount of $Bu_3SnSnBu_3$. The appearance of the distannane product was not surprising as silylstannanes are known to equilibrate with the possible hexaalkyldistannane and hexaalkyldisilane compounds through a disproportionation reaction catalysed by $Pd(PPh_3)_4$.[11a] Use of equimolar amounts of silylstannanes and alkynes should avoid the formation of the distannane adduct and give the expected product cleanly.

Table 2 Recycling of $Pd(PPh_3)_4$/[bmim]PF_6 for silylstannations of terminal alkynes with $Bu_3SnSiMe_3$ for 16–20 h

Entry	Alkyne	mol% Pd	Cycle	Yield (%)[a]
1[b]	Phenylacetylene	5	1	100
2[b]	Phenylacetylene	5	2	100
3[b]	Phenylacetylene	5	3	100
4[b]	Phenylacetylene	5	4	100
5	Phenylacetylene	1	1	100
6	Phenylacetylene	1	2	97
7	5-Hexyn-1-ol	5	1	100
8	5-Hexyn-1-ol	5	2	97
9	1-Decyne	5	1	99
10	1-Decyne	5	2	100

[a] GC yield. [b] Reaction performed without ether.

In summary, we have shown that the ionic liquid [bmim]PF_6 can be used as a solvent for the palladium-catalysed reaction of silylstannanes with terminal alkynes to afford 1-trimethylsilyl-2-tributylstannylalk-1-enes in quantitative yields. We have shown that the palladium catalyst can be immobilised in the ionic liquid phase and reused at least four times without appreciable loss in activity. The reaction proceeds cleanly and the use of the ionic liquid allows for easy product/catalyst separation and product isolation. It is likely that the system can be recycled many more than four times, allowing extensive, simple recycling of expensive palladium catalysts to form the highly synthetically useful silylstannylated alkene products. These aspects of this system as well as the use of other palladium catalysts and kinetic studies are currently underway and will be a topic of a subsequent full account of this research.

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Notes and references

† *Representative silylstannation procedure*: 1.0 mL [bmim]PF_6 was dried under vacuum at 60 °C for 2 h. $Pd(PPh_3)_4$ (0.05 or 0.01 mmol) was added in an argon glove box and stirred to dissolve. $Bu_3SnSiMe_3$ (1.2 mmol) was injected under nitrogen *via* needle and syringe while stirring, followed by the desired alkyne (1.0 mmol). 5.0 mL freshly dried and distilled diethyl ether was injected and the reaction vessel was fitted with a dry reflux condenser. The biphasic reaction mixture was heated to 70 °C under nitrogen for 18–24 h and was monitored by gas chromatography. Upon completion, the ether layer was removed *via* needle and syringe and the ionic liquid was washed with dry ether (8 × 10 mL). The products were separated from excess $Bu_3SnSiMe_3$ by flash chromatography with hexanes in the cases of phenylacetylene and 1-decyne and with 5:1 hexanes/ethyl acetate in the case of 5-hexyn-1-ol to afford products in near quantitative yield as clear oils. The ionic liquid containing the catalyst could then be reused.

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