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# Imidazol(in)ium carboxylates as *N*-heterocyclic carbene ligand precursors for Suzuki–Miyaura reactions

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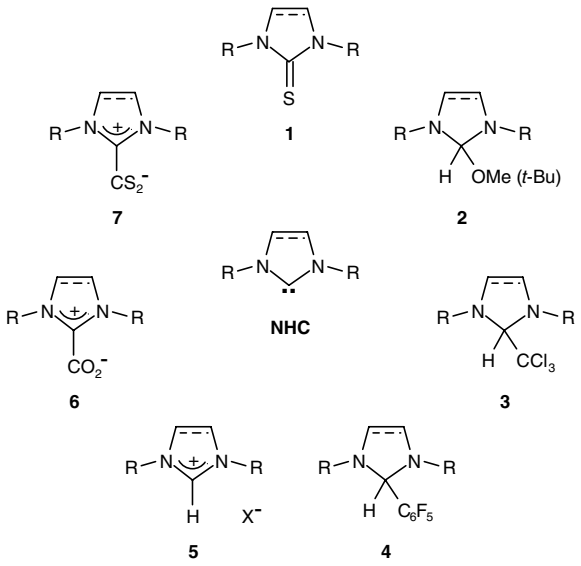
**Abstract**—Simple catalysts formed in situ from palladium acetate and a variety of imidazolium and imidazolinium carboxylates and dithiocarboxylates have been screened in the coupling of aryl halides with *trans*-2-phenylvinylboronic acid. Imidazol(in)ium carboxylates show an excellent activity, which compares to that displayed by the parent imidazol(in)ium chlorides, whereas imidazol(in)ium dithiocarboxylates are poorly efficient. Interestingly, the base employed exerts a profound influence on the trans/cis stereochemistry of the coupling product.


Transition-metal-mediated cross-coupling reactions have revolutionised organic synthesis. Many highly efficient and mild protocols for bond construction have emerged by the mastery of such reactions. Perhaps the most utilised carbon–carbon bond-forming cross-coupling reactions are those that use tin (Stille coupling)[1] and boron derivatives (Suzuki–Miyaura coupling)[2] because of their tolerance of a broad range of functional groups. The Suzuki–Miyaura cross-coupling is particularly valued because boron compounds present many advantages in relation to other organometallic compounds, including ease of accessibility and ultimate product isolation, minimal toxicity and other environmental factors.

Palladium is the metal of choice for the Suzuki–Miyaura reaction. Generally, the best catalysts incorporate strongly electron-donating phosphine ligands with two or three alkyl substituents, such as P*t*-$Bu_3$, $PCy_3$, $PR_2$(*o*-biphenyl) and related ligands.[3] Activity is not limited to catalysts with phosphine ligands: palladium complexes with *N*-heterocyclic carbene (NHC) ligands have also proved to be effective in Suzuki–Miyaura reactions. While such catalysts can be preformed,[4] they are often generated in situ by decomposition of a suitable carbene precursor (Scheme 1) to yield the corresponding free carbenes, which are then ligated to the metal centre.[5] In principle, free carbenes could also be used, but this can lead to problems with handling due to their air and moisture sensitivity. NHCs can be generated by the reductive desulfurisation of thioureas (**1**) on treatment with potassium[6a] or sodium/potassium mixture.[6b] Although high yielding, this protocol is limited to the synthesis of free carbenes and is inappropriate to the




**Scheme 1.** *N*-Heterocyclic carbene precursors.

*Keywords*: Aryl halides; Boronic acids; Homogeneous catalysis; *N*-Heterocyclic carbene ligands; Palladium and compounds; Stilbenes; Suzuki–Miyaura coupling reactions.
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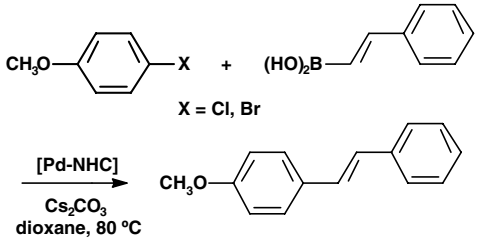
in situ preparation of metal–NHC complexes. The use of neutral carbene precursors that form carbenes by thermal decomposition under mild conditions has also been examined. This methodology was first employed by Enders et al.,[7] who found that 2-alkoxy-substituted species **2** decomposed endothermically with concomitant elimination of alcohol to form the corresponding NHCs. It was also found that **2** could be reacted directly with metal complexes at elevated temperatures via the in situ conversion to the free NHCs. An alternative route was also developed, which employed the trichloromethyl-containing precursor **3**.[8] On the other hand, Waymouth and co-workers very recently showed that the 2-(pentafluorophenyl)imidazoline (**4**) can be used as a simple, air-stable precursor for the synthesis of both free carbene and a carbene adduct of allyl palladium chloride under mild thermolytic conditions, via loss of pentafluorobenzene.[9] Nowadays, however, palladium complexes with NHC ligands are most often formed in situ by deprotonation of the corresponding imidazol(in)ium salts (**5**).[5,10,11]

There are very few examples in the literature of imidazol(in)ium-2-carboxylates (**6**).[12] The most convenient procedure for their synthesis consists of deprotonating imidazol(in)ium salts (**5**) with potassium *tert*-butoxide under an atmosphere of $CO_2$.[13] Furthermore, the reversibility of the formation of imidazolium carboxylates has also been demonstrated under certain conditions. As a support for this observation, Crabtree reported that imidazolium-2-carboxylates can transfer NHCs to a variety of metal salts to produce the corresponding NHC metal complexes with the concomitant release of $CO_2$.[14] In particular, the reaction of *N*,*N*′-dimethyl imidazolium-2-carboxylate with $Pd(OAc)_2$ afforded $[Pd(NHC)_3(OAc)]OAc$ in a 71% isolated yield.[14] While imidazol(in)ium salts (**5**) are often used for the in situ generation of metal–NHC catalysts, to the best of our knowledge imidazol(in)ium carboxylates have never been employed as NHCs sources in transition metal catalysis. Given the prime importance of NHCs in this area, we wondered whether imidazol(in)ium carboxylates (**6**) and dithiocarboxylates[9a,15] (**7**) might actually prove effective in the Suzuki–Miyaura reaction. This indeed turns out to be the case with imidazol(in)ium carboxylates, and we report below the use of simple in situ generated palladium–NHC catalysts for the coupling of aryl halides with boronic acids.

Because of our current interest in the preparation of stilbenoids,[16] we chose for the initial screening of catalyst performance the reaction outlined in Scheme 2 as a typical example of Suzuki–Miyaura coupling. 1,4-Dioxane was used as the solvent and caesium carbonate as the base (non-optimised conditions). The reactions were performed at 80 °C under an inert atmosphere of nitrogen, and the catalyst loading was fixed on 0.5 mol %. The results from this study are summarised in Table 1. As can be seen, catalytic systems **8a–c** and **11a,b** (Scheme 3) generated in situ by deprotonation of the corresponding imidazol(in)ium chlorides show a high activity with *p*-bromoanisole, an electronically deactivated aryl bromide. Whether the carbene precursors were unsaturated (imidazolium chlorides **8**) or saturated (imidazolinium chlorides **11**) and whatever their substitution patterns (**a–c**) the conversions of the *p*-bromoanisole substrate were indeed higher than 85% and corroborated by the isolated yields of 4-methoxystilbene. Interestingly, while the trans isomer of 2-phenylvinylboronic acid was employed as the reagent, some *cis*-4-methoxystilbene was also formed and its abundance slightly increased with the reaction time.




**Scheme 2.** The Suzuki–Miyaura coupling reaction under investigation.

**Table 1.** Experimental data for the Suzuki–Miyaura reaction between *trans*-2-phenylvinylboronic acid and *p*-bromoanisole and *p*-chloroanisole, catalysed by palladium-based systems **8–13**[a]

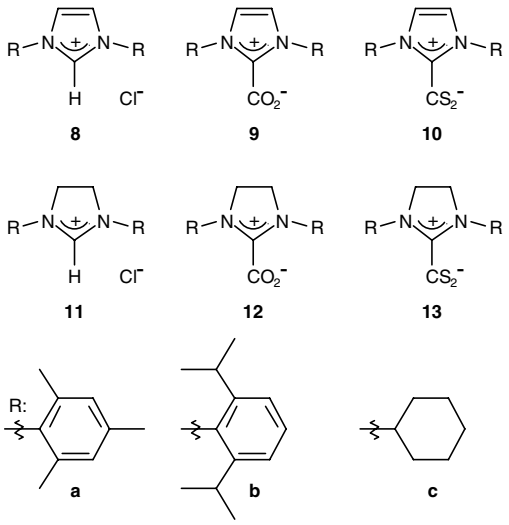
| Catalyst system | Conversion[b] (%) | | Isolated yield[c] (%) |
|---|---|---|---|
| | 8 h | 24 h | 24 h |
| *p-Bromoanisole*[d] | | | |
| **8a** | 95 (95:5) | 100 (88:12) | 97 (88:12) |
| **9a** | 83 (96:4) | 97 (89:11) | 95 (90:10) |
| **10a** | 39 (95:5) | 39 (85:15) | — |
| **8b** | 77 (96:4) | 96 (91:9) | 92 (90:10) |
| **9b** | 67 (95:5) | 91 (89:11) | 90 (88:12) |
| **10b** | 39 (98:2) | 40 (96:4) | — |
| **8c** | 63 (93:7) | 88 (91:9) | 85 (90:10) |
| **9c** | 60 (95:5) | 88 (89:11) | 85 (88:12) |
| **10c** | 13 | 14 | — |
| **11a** | 70 (95:5) | 90 (88:12) | 91 (88:12) |
| **12a** | 65 (94:6) | 87 (90:10) | 87 (90:10) |
| **13a** | 45 (95:5) | 51 (89:11) | — |
| **11b** | 80 (87:13) | 95 (81:19) | 95 (80:20) |
| **12b** | 75 (91:9) | 100 (83:17) | 95 (84:16) |
| **13b** | 19 | 20 | — |
| *p-Chloroanisole*[d] | | | |
| **8a** | 27 (99:1) | 32 (98:2) | — |
| **9a** | 37 (99:1) | 42 (98:2) | — |
| **8b** | 76 (99:1) | 89 (98:2) | 90 (99:1) |
| **9b** | 76 (99:1) | 87 (99:1) | 88 (99:1) |
| **8c** | 10 | 14 | — |
| **9c** | 16 | 20 | — |
| **11a** | 32 | 33 | — |
| **12a** | 19 | 21 | — |
| **11b** | 2 | 2 | — |
| **12b** | 2 | 2 | — |

[a] Experimental conditions: $Pd(OAc)_2$, 0.01 mmol; imidazol(in)ium chloride, imidazol(in)ium carboxylate or dithiocarboxylate, 0.04 mmol; $Cs_2CO_3$, 4 mmol; *trans*-2-phenylvinylboronic acid, 2.4 mmol; 1,4-dioxane, 2 mL; 1 mL of a solution containing 2 mmol of the haloarene and *n*-decane in dioxane; 80 °C, under an inert atmosphere of nitrogen.

[b] Based on the haloarene and determined by GC using decane as an internal standard.

[c] Yields are of isolated, analytically pure material.

[d] Into brackets, the trans:cis stereoselectivity determined by GC.




**Scheme 3.** The carbene ligand precursors under investigation.

We next wondered whether imidazol(in)ium-2-carboxylates **9a**–**c** and **12a**,**b** (Scheme 3) could be used in an analogous fashion and were pleased to find that the Suzuki–Miyaura coupling reaction worked equally well to produce 4-methoxystilbene in an 85–95% yield (Table 1). In addition, an examination of the plots of conversion versus time (Supplementary Fig. 1) revealed that the data for imidazol(in)ium carboxylates **9** and **12** were close to those of imidazol(in)ium chlorides **8** and **11**, indicating that the catalyst structures were very similar, indeed, identical. On the other hand, *cis*-4-methoxystilbene was again formed in increasing amounts with the reaction time. It is likely that under the conditions used (dioxane at 80 °C), the decarboxylation process of imidazol(in)ium carboxylates **9a**–**c** and **12a**,**b** is very fast. Previous studies[13] revealed indeed that compounds **9a** and **9b** in solution in methanol, DMSO and chlorinated solvents, such as chlorobenzene,[11d] decomposed readily at room temperature.

We next shifted our attention to imidazol(in)ium dithiocarboxylates **10a**–**c** and **13a**,**b** (Scheme 3) as NHC sources. We found that the resulting palladium systems showed far lower activity than equivalent systems prepared from imidazol(in)ium chlorides or carboxylates (Table 1 and Supplementary Fig. 1). In view of this, it might be anticipated that carbon disulfide, which should be released upon decomposition of the dithiocarboxylates would partly poison the catalyst. To this end, we performed the Suzuki–Miyaura couplings in the presence of 10 equiv $CS_2$ (compared to palladium) added either at the beginning of the reaction or after 1 h. The results (Supplementary Fig. 2) clearly indicate that $CS_2$ strongly inhibits the catalytic process. In this regard, the extent of the inhibiting/poisoning effect of carbon disulfide should be estimated carefully because the reactions were performed at a temperature (80 °C) higher than the boiling point of $CS_2$ (46 °C): under these conditions, some $CS_2$ was presumably condensed on the cold inner surface of the reaction vessel. The inhibiting/poisoning effect of $CS_2$ could be due to the formation of a palladium complex through the coordination of $CS_2$, which would be poorly active or inactive for the test reaction. An alternative explanation for the low activity of the catalytic systems prepared in the presence of imidazol(in)ium dithiocarboxylates is that palladium–NHC complexes have not been generated in situ, but complexes in which the imidazol(in)ium dithiocarboxylate acts as a ligand. Carbenium dithiocarboxylates have been used so far only rarely as ligands for metal complexes[17] and we are currently investigating the use of imidazol(in)ium dithiocarboxylates as ligands in palladium chemistry.

Having established that imidazol(in)ium chlorides and imidazol(in)ium carboxylates show essentially the same activity in the test reaction of *p*-bromoanisole, we next examined their performance in the coupling of *p*-chloroanisole, a substrate that is more difficult to activate than its bromide counterpart. The results from this study are summarised in Table 1 and they confirm the trends observed with *p*-bromoanisole: imidazol(in)ium chlorides and imidazol(in)ium carboxylates are equipotent carbene precursors.

On the other hand, it is well established in Suzuki–Miyaura chemistry that, in addition to the choice of appropriate ligand, the correct selection of the base can lead to a considerable enhancement in performance. For instance, $Cs_2CO_3$, $K_2CO_3$, KF and $K_3PO_4$ often show a substantially improved activity in the Suzuki–Miyaura reactions compared to sodium and lithium salts. With this in mind, we investigated the effect of the base on the test reaction between *p*-bromoanisole and *trans*-2-phenylvinylboronic acid. Comparing the data summarised in Table 2, it can be seen that the highest conversion to the desired product was obtained when KF was used rather than alkali metal carbonates, irrespective of the choice of the catalyst system. In addition, from the comparison of the different carbonates used (Table 2 and Supplementary Fig. 3), the general trend appeared to be Cs > K > Na > Li. On the other hand, the coupling of *p*-bromoanisole with *trans*-2-phenylvinylboronic acid led to the formation of both trans and cis isomers of the coupled product and, quite unexpectedly, the trans/cis ratio markedly depended on the carbonate used. Thus, the trans isomer was predominantly formed in the presence of caesium carbonate as the base (±90% at the end of the reaction (24 h)), whereas in the presence of lithium carbonate the selectivity was reversed (25–30% trans isomer after 24 h) irrespective of the carbene precursor used. To the best of our knowledge, there are no reports in the literature of such effect of the base employed in Suzuki–Miyaura coupling reactions,[18] and this is an area that obviously needs further attention in the future. Preliminary experiments have demonstrated that pure *trans*-4-methoxystilbene is not isomerised by catalyst system **8a** in dioxane at 80 °C, in the presence of $Li_2CO_3$ or $Na_2CO_3$.[19]

In conclusion, imidazol(in)ium carboxylates make excellent *N*-heterocyclic carbene precursors for the in situ generation of palladium-based catalysts for the Suzuki–Miyaura coupling reactions of haloarenes with *trans*-2-phenylvinylboronic acid. In addition, we have

**Table 2.** Experimental data for the Suzuki–Miyaura reaction of *p*-bromoanisole with *trans*-2-phenylvinylboronic acid, catalysed by systems **8a** and **9a** in the presence of various bases[a]

| Base | **8a** Conversion[b] (trans:cis)[c] (%) | | | | **9a** Conversion[b] (%) (trans:cis)[c] | | | |
|---|---|---|---|---|---|---|---|---|
| | 2 h | 8 h | 24 h | 48 h | 2 h | 8 h | 24 h | 48 h |
| $Li_2CO_3$ | 24 (18:82) | 37 (23:77) | 46 (27:73) | 54 (32:68) | 21 (16:84) | 34 (20:80) | 41 (25:75) | 47 (30:70) |
| $Na_2CO_3$ | 31 (32:68) | 57 (36:64) | 66 (39:61) | 70 (40:60) | 26 (34:66) | 65 (37:63) | 78 (37:63) | 82 (39:61) |
| $K_2CO_3$ | 52 (84:16) | 78 (77:23) | 88 (77:23) | 91 (76:24) | 51 (84:16) | 79 (78:22) | 88 (75:25) | 91 (74:26) |
| $Cs_2CO_3$ | 69 (99:1) | 95 (95:5) | 100 (88:12) | | 54 (99:1) | 83 (96:4) | 97 (89:11) | |
| KF | 88 (88:12) | 100 (86:14) | | | 69 (87:13) | 92 (83:17) | 95 (82:18) | |

[a] Experimental conditions: $Pd(OAc)_2$, 0.01 mmol; imidazolium salt, 0.04 mmol; base, 4 mmol; *trans*-2-phenylvinylboronic acid, 2.4 mmol; 1,4-dioxane, 2 mL; 1 mL of a solution containing 2 mmol of *p*-bromoanisole and *n*-decane in dioxane; 80 °C, under nitrogen.
[b] Based on *p*-bromoanisole and determined by GC using decane as an internal standard.
[c] Trans:cis stereoselectivity of 4-methoxystilbene determined by GC.

also found serendipitly that the inorganic base markedly affects the trans/cis stereochemistry of the target compound.

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## Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tetlet.2006.09.139.

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19. Reaction conditions: (a) $Pd(OAc)_2$, 0.01 mmol; imidazolium chloride **8a**, 0.04 mmol; $Na_2CO_3$, 4 mmol; *trans*-4-methoxystilbene, 2.0 mmol; 1,4-dioxane, 3 mL; 80 °C, under an inert atmosphere of nitrogen for 150 h; (b) $Pd(OAc)_2$, 0.01 mmol; imidazolium chloride **8a**, 0.04 mmol; $Li_2CO_3$ or $Na_2CO_3$, 2 mmol; *trans*-4-methoxystilbene, 1.0 mmol; *trans*-2-phenylvinylboronic acid, 0.2 mmol; 1,4-dioxane, 3 mL; 80 °C, under an inert atmosphere of nitrogen for 150 h.