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The active role of NHC ligands in platinum-mediated tandem hydroboration–cross coupling reactions

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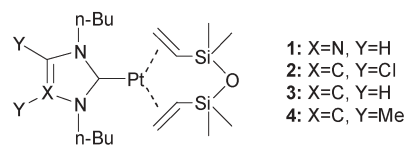
Stable N-heterocyclic platinum–carbene complexes are the first example of platinum-mediated regioselective H–B addition to vinylarenes and alkynes, allowing consecutive cross coupling reactions with the same catalytic system.

The catalytic insertion of unsaturated moieties into a B–H bond through the hydroboration protocol is an effective strategy for selectively obtaining organoboron derivatives,[1] an important class of compounds used as synthetic intermediates[2] especially for constructing carbon frameworks.[3] Although hydroboration can also be performed under non-catalytic conditions, the search for optimised selectivity on the target organoborane compounds requires metal-mediated catalysis to be used. The most efficient catalysts for hydroboration appear to be rhodium complexes,[4] especially for asymmetric B–H addition to alkenes.[5] However, iridium, palladium, ruthenium, niobium, titanium, zirconium and lanthanide-based catalysts are an interesting alternative.[1] We were aware that hydroboration with platinum-based catalysts and catecholborane had not been reported even though they had been successfully used in catalytic B–B addition to alkenes and alkynes.[6] To the best of our knowledge, there are only two significant precedents: Pt(II)-catalysed hydroboration of terminal olefins with polyboranes[7] and Pt(0)-catalysed hydroboration of allenes with pinacolborane.[8] To verify whether Pt(0) could be a better alternative to the hydroboration/oxidation of vinylarenes (Scheme 1), we first used the readily available Pt(PPh$_3$)$_4$ complex, which provided 18% conversion from styrene with catecholborane, under standard reaction conditions after 3 h at room temperature (Table 1, entry 1). This poor result, in comparison with the uncatalysed reaction (entry 0), was accompanied by the lack of regioselectivity, hence producing the Markovnikov and the anti-Markovnikov alcohol derivatives, together with phenylethane.
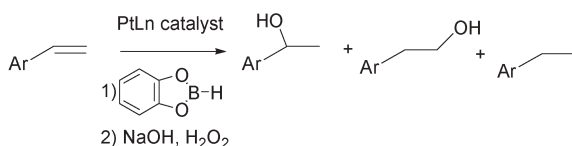
This preliminary result may explain why phosphine-based Pt catalysts for the hydroboration of alkenes are so scarce. B–H addition to alkenes probably requires a phosphine dissociative

Scheme 1 Pt-based catalytic hydroboration/oxidation of vinylarenes.

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pre-step to allow the formation of the hydridoboryl platinum complex, as has been suggested previously.[9] Phosphine-free platinum catalytic systems, such as Pt(COD)Cl$_2$, which have proved to be very effective in the catalytic diboration of terminal alkenes, alkynes and aldimines,[10] show much higher conversion under the same reaction conditions (Table 1, entry 2), although the system lacks selectivity. Addition of PPh$_3$ to this catalyst clearly decreases the activity. The extent of this decrease depends on the amount of phosphine added (entries 2–5), in agreement with analogous catalytic B–B transformations.[11] Palladium complexes modified with electronically different phosphines and phosphites provided less than 25% of branched isomer (entries 6 and 7), while diphosphines (dppm and dppb) resulted in complete loss of activity. Taking all this into consideration, we explored the possibility of performing H–B addition of alkenes with N-heterocyclic carbene (NHC) Pt(0) complexes, since they are an effective alternative to phosphines in numerous catalytic examples.[12–14] We recently reported that compounds 1 and 2 were very efficient in the diboration of alkenes, alkynes and allylic sulfones.[15]

When complexes 1 and 2 were initially tested in our model reaction with styrene as the substrate, the conversion was complete within 3 h and the regioselectivity was surprisingly high for the branched alcohol, 85–90% (Table 1, entries 8 and 10). No hydrogenated byproduct was detected. It is worth mentioning that the catalytically active species are still active at the end of the reaction, because subsequent addition of a second and third amount of styrene and catecholborane leads to the desired products without any measurable decrease in catalytic activity. Even more important is the observation that after several days at ambient temperature the platinum–NHC complexes are still active in sharp contrast to many of the rhodium–phosphine precursors of catalysts. The use of catecholborane as the hydroborating reagent was beneficial because the addition of pinacolborane provided a lower conversion but also a low regioselectivity (Table 1, entry 9). Alternative NHC ligands with more basic properties in complexes 3 and 4, resulted in activity comparable to that displayed by 1 and 2 but lead to lower selectivity.

Complex 2 (0.025 mmol) was dissolved in 1 mL of thf-d$_8$ in a sealable NMR tube, and freshly distilled HBcat (0.025 eq.) was added via syringe. Despite the immediate change to a brownish colour, no specific signals were detected in the hydride region of the ^{1}H NMR spectra. Then 0.5 mmol of styrene and 0.5 mmol of

Table 1 Platinum-catalysed hydroboration/oxidation of styrene with catecholborane[a]

Entry	Catalytic system	Conv.[b] (%)	Branched[b] (%)	Linear[b] (%)	Hydrog.[b] (%)
0	—	14	Trace	99.9	—
1	Pt(PPh$_3$)$_4$	18	17	18	65
2	Pt(COD)Cl$_2$	100	49	51	—
3	Pt(COD)Cl$_2$ + 1PPh$_3$	92	15	85	—
4	Pt(COD)Cl$_2$ + 2PPh$_3$	0	—	—	—
5	Pt(COD)Cl$_2$ + 4PPh$_3$	0	—	—	—
6	Pt(COD)Cl$_2$ + 1PCy$_3$	71	25	59	15
7	Pt(COD)Cl$_2$ + 1P(OR)$_3$[c]	80	19	28	53
8	**1**	100	85	15	—
9	**1**[d]	19	52	48	—
10	**2**	100	90	10	—
11	**3**	100	71.5	28.5	—
12	**4**	82	65	35	—

[a] *Standard conditions*: Styrene : catechol borane : Pt complex = 0.5 : 0.55 : 0.025; solvent: THF; T = 25 °C, 3 h. [b] Determined by ^{1}H NMR and GC. [c] P(OR)$_3$ = Tris(2,4-di-*tert*-butylphenyl)phosphite. [d] Hydroborating reagent: pinacolborane.

HBcat were added to monitor the product formation under these conditions. Fig. 1 shows the styrene consumption within the first 3.5 h following the disappearance of the doublet at 5.7 ppm in the ^{1}H NMR spectra. Similarly, Fig. 2 shows the branched and linear product formation under these reaction conditions, attending to the increasing doublet at 1.5 ppm for the branched boronate ester, and the triplet at 1.6 ppm for the linear boronate ester.

In order to check whether the applicability of **1** and **2** could be extended to other substrates, we studied the hydroboration of other terminal and internal vinylarenes and vinylalkanes, as well as allylic systems such allylsulfones (Table 2). As can be seen, the selectivity on the branched derivative increases with the electron
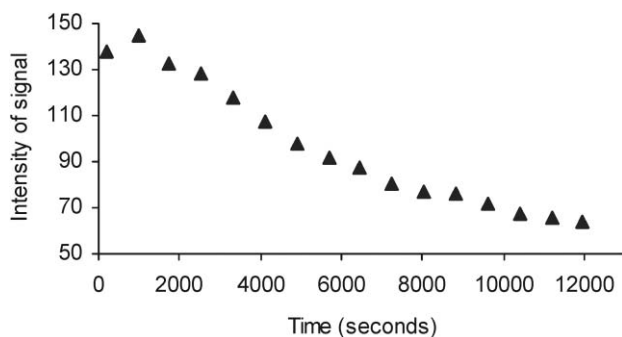
Fig. 1 Monitoring the disappearance of styrene.
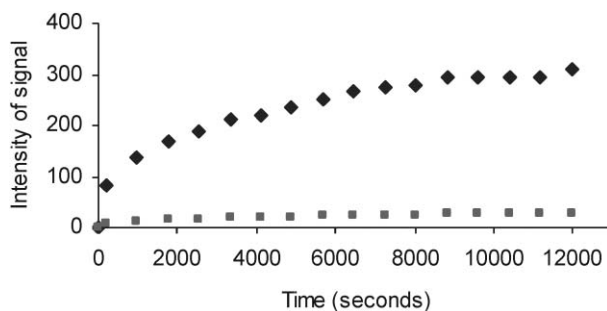
**Fig. 2** Monitoring the appearance of branched (◆) and linear (■) boronate esters.

withdrawing properties of the aryl substituent (entries 1, 2 and 9, 10). Internal vinylarenes also favour the formation of the branched isomer, up to values about 97% for the 1-phenyl-1-propanol. However, the conversion is lower than with terminal substrates, because the C=C bond is more hindered (entries 3, 4 and 11, 12). Complex **2** also provided small amounts of hydrogenated product in the hydroboration of indene and *trans*-β-methylstyrene. Interestingly, the catalytic hydroboration of vinylalkenes inverts the selectivity with respect to the other vinylarenes used (entries 5 and 6). Vinylcyclohexane and *tert*-butylethene mainly afforded the linear alcohol with complex **1**, probably because a η^3-metal–alkene intermediate cannot be formed in the catalytic cycle.[16] Finally, **1** and **2** are efficient catalysts in the hydroboration of phenyl allyl sulfones, although the regioselectivity is moderate because the hydrogenated product is also formed (entries 7, 8 and 13).

The versatility of the platinum-catalyzed hydroboration reaction is further substantiated by the H–B addition to alkynes. In this case, complex **2** provided branched and linear alkenylboronic esters in moderate selectivity, within 3 h at room temperature in THF (Scheme 2). Styrene was also formed under these reaction conditions. In comparison, the uncatalysed hydroboration of

Table 2 Platinum catalyzed hydroboration–oxidation of alkenes with catecholborane[a]

Entry	Substrate	Pt system	Conv.[b] (%)	Branched[b] (%)	Linear[b] (%)	Hydrog.[b] (%)
1		**1**	100	90	10	—
2		**1**	100	74	26	—
3		**1**	60	87	13	—
4		**1**	77	92	8	—
5		**1**	100	5	95	—
6		**1**	100	15	85	—
7		**1**	41	69	21	10
8[c]		**1**	72	53	29	18
9		**2**	100	92	8	—
10		**2**	95	70	21	9
11		**2**	70	77	9	14
12		**2**	77	97	3	—
13[c]		**2**	73	64	21	15

[a] *Standard conditions*: Alkene : catecholborane : Pt complex = 0.5 : 0.55 : 0.025; solvent: THF. T = 25 °C, 3 h. [b] Determined by ^{1}H NMR and GC [c] 3 eq. catecholborane.
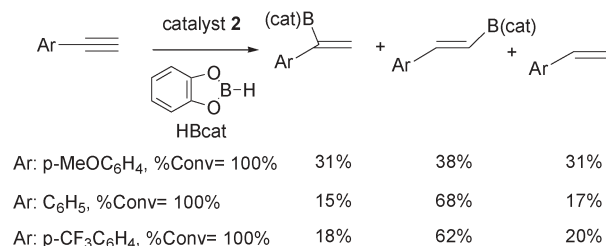
Scheme 2 Pt-based catalytic hydroboration of arylalkynes.
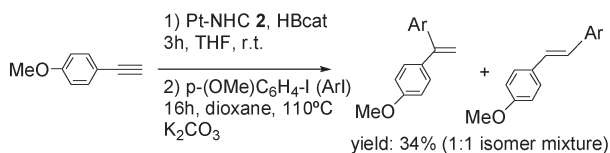
Scheme 3

alkynes required elevated temperatures[17] and the rhodium(I) mediated hydroboration of phenylethylene in the presence of variable amounts of PPh$_3$, resulted in a more complex mixture of byproducts.[18] However, the regioselectivity towards the alkenyl boronate isomer was optimal with alternative catalytic systems, such as Cp$_2$Ti(CO)$_2$, Cp$_2$ZrHCl and nickel complexes modified with phosphines.[19]

One significant advantage of Pt-based catalysts in the hydroboration of olefins over the catalysts such as Rh-based, is their potential ability to perform the tandem H–B addition/cross coupling reaction, under the same catalytic system. In a preliminary study, we tested the catalytic activity of complex **2** in the one-pot hydroboration of alkynes/Suzuki–Miyaura coupling reaction. Addition of 4-iodoanisole to the 1-ethynyl-4-methoxy-benzene hydroboration mixture in presence of K$_2$CO$_3$, afforded the coupling product in 34% yield, as a 1 : 1 mixture of isomers, after heating to 110 °C for 16 h in dioxane (Scheme 3). The platinum catalyst affects both the hydroboration and the Suzuki–Miyaura coupling. It should be noted that there are few examples in the literature of Pt-catalysing this type of cross coupling reaction.[20]

In summary, we have shown that platinum(0)–carbene complexes afford an effective alternative for the catalytic regioselective hydroboration of alkenes, and that they can be applied in the one-pot tandem H–B addition/Suzuki–Miyaura coupling reaction, under the same catalytic system.

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