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Undirected *ortho*-selectivity in C–H borylation of arenes catalyzed by NHC platinum(0) complexes

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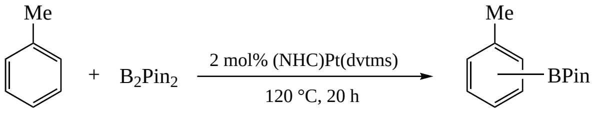
Borylation of arenes with bis(pinacolato)diboron catalyzed by sterically encumbered NHC platinum complexes proceeds predominantly at *ortho*-position even in the absence of a directing group (*o* : *m* : *p* ratio up to 10 : 3 : 1). The similar borylation with pinacolborane would proceed less selectively.



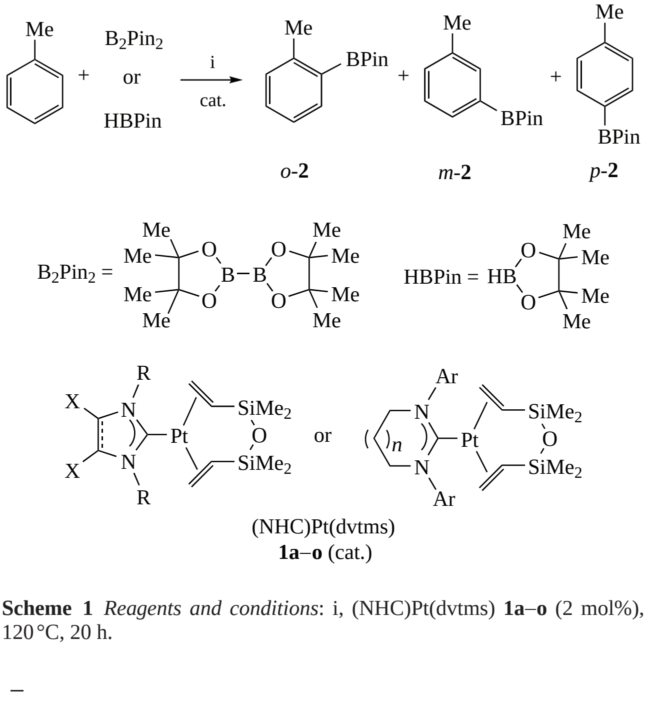
o : *m* : *p* up to 10 : 3 : 1

Keywords: N-heterocyclic carbenes, platinum(0) complexes, borylation, arenes, organoboron compounds, regioselectivity, catalysis.

Platinum complexes are efficient catalysts of hydrosilylation,[1] hydroboration and diboration,[2] examples of catalytic C–H functionalization of aromatic compounds employing platinum catalysts[3] are also known. To the best of our knowledge, just a few works on C–H borylation of arenes mediated by platinum complexes have been published at the time when the manuscript was being prepared. In 2015, Furukawa and co-authors were the first to describe borylation of arenes catalyzed by platinum(0) carbene complexes.[3(*b*)] At the same time, the group of Iwasawa and Takaya independently reported on catalytic C–H borylation of polyfluorinated aromatic compounds using phosphine pincer complexes of platinum.[3(*a*)] As of today, borylation of arenes mediated by platinum complexes bearing carbene ligands has been the most successful due to high stability of these complexes as well as wide variability of the carbene component. However, one of the most important issues associated with selectivity of such borylation of monosubstituted benzenes, *e.g.* toluene, remains open. Moreover, the mechanism of this reaction is poorly studied, and the nature of key intermediates is not known. The question whether pinacolborane (HBPin) released in the course of the reaction would participate in borylation is yet to be answered.

Our ongoing interest in application of N-heterocyclic carbene (NHC) complexes of palladium,[4] gold,[5] and copper[6] in fine organic synthesis triggered our study of catalytic activity of such platinum complexes in borylation of arenes. Here, we report on comparative study of catalytic activity of a series of NHC platinum complexes **1a**–**o** (Scheme 1, for the structural details see Online Supplementary Materials, Scheme S1). When studying the effect of carbene ligand structure on selectivity of the toluene borylation, we have unexpectedly discovered a new phenomenon of high *ortho*-selectivity among C–H functionalization methods that do not rely on a directing group. Also, we demonstrated the possibility of HBPin application for the borylation of arenes. Notably, selectivity of the reaction of HBPin with toluene differs cardinally from that of bis(pinacolato)diboron (B_2Pin_2).

Catalytic properties of the obtained platinum(0) complexes **1a**–**o** were compared in the reaction of borylation of toluene with diboropinacolate (see Scheme 1). The initial series of experiments was aimed to reproduce the results reported by Furukawa[3(*b*)] using toluene as the substrate (Table 1, entry 1). First set of catalytic tests were performed for complexes bearing imidazolium carbenes with varied steric bulk (entries 1–5). In all cases borylation proceeded at all three (*ortho*-, *meta*- and *para*-) positions of toluene. In case of catalyst **1a** (entry 1), total 94% yield was achieved and the isomer ratio was close to statistical with a slight predominance of the *meta*-isomer. Similar results were obtained previously by Chatani.[3(*b*),(*c*)] On moving to catalysts **1b**,**c** with bulkier ligands



Scheme 1 *Reagents and conditions*: i, (NHC)Pt(dvtms) **1a**–**o** (2 mol%), 120 °C, 20 h.

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Table 1 Dehydroboration of toluene with B_2Pin_2 or HBPin catalyzed by (NHC)Pt(dvtms) complexes **1a**–**o**.

Entry	Catalyst	Total yield (%) (*o*-**2** : *m*-**2** : *p*-**2** ratio)	
		with B_2Pin_2	with HBPin
1	ICyPt(dvtms) (**1a**)	94 (1.7 : 2.8 : 1.0)	3 (1.5 : 3.0 : 1.0)
2	IBu^tPt(dvtms) (**1b**)	61 (3.6 : 2.1 : 1.0)	8 (0.6 : 1.8 : 1.0)
3	IPrPt(dvtms) (**1c**)	69 (4.9 : 2.2 : 1.0)	28 (0.8 : 1.9 : 1.0)
4	IPr^*Pt(dvtms) (**1d**)	151 (0.8 : 1.8 : 1.0)[a]	99 (0.3 : 1.8 : 1.0)
5	$IPr^{*OMe}Pt$(dvtms) (**1e**)	73 (1.2 : 1.9 : 1.0)	96 (0.4 : 1.8 : 1.0)
6	$IPr^{Cl}Pt$(dvtms) (**1f**)	92 (3.0 : 2.1 : 1.0)	18 (0.6 : 1.8 : 1.0)
7	$IPr^{Br}Pt$(dvtms) (**1g**)	13 (5.5 : 2.4 : 1.0)	15 (0.6 : 1.7 : 1.0)
8	$IPr^{Me}Pt$(dvtms) (**1h**)	130 (2.2 : 2.1 : 1.0)[a]	23 (0.6 : 1.9 : 1.0)
9	$IMes^{Me}Pt$(dvtms) (**1i**)	71 (2.8 : 2.1 : 1.0)	5 (1.4 : 2.4 : 1.0)
10	SIMesPt(dvtms) (**1j**)	28 (2.6 : 2.6 : 1.0)	4 (0.7 : 2.5 : 1.0)
11	SIPrPt(dvtms) (**1k**)	52 (4.1 : 2.2 : 1.0)	14 (0.5 : 1.8 : 1.0)
12	(6-Mes)Pt(dvtms) (**1l**)	39 (4.1 : 2.1 : 1.0)	14 (0.8 : 2.8 : 1.0)
13	(6-Dipp)Pt(dvtms) (**1m**)	129 (5.3 : 2.6 : 1.0)[a]	54 (1.2 : 2.3 : 1.0)
14	(7-Mes)Pt(dvtms) (**1n**)	64 (5.4 : 2.2 : 1.0)	14 (1.0 : 2.6 :1.0)
15	(7-Dipp)Pt(dvtms) (**1o**)	130 (9.6 : 2.8 : 1.0)[a]	62 (1.5 : 2.4 : 1.0)

[a] Relative yields were calculated based on stoichiometric amounts of the limiting reactant (B_2Pin_2).

(entries 2 and 3), yields drop to 61 and 69%, respectively. Simultaneously, the increase in *ortho*-selectivity was observed.

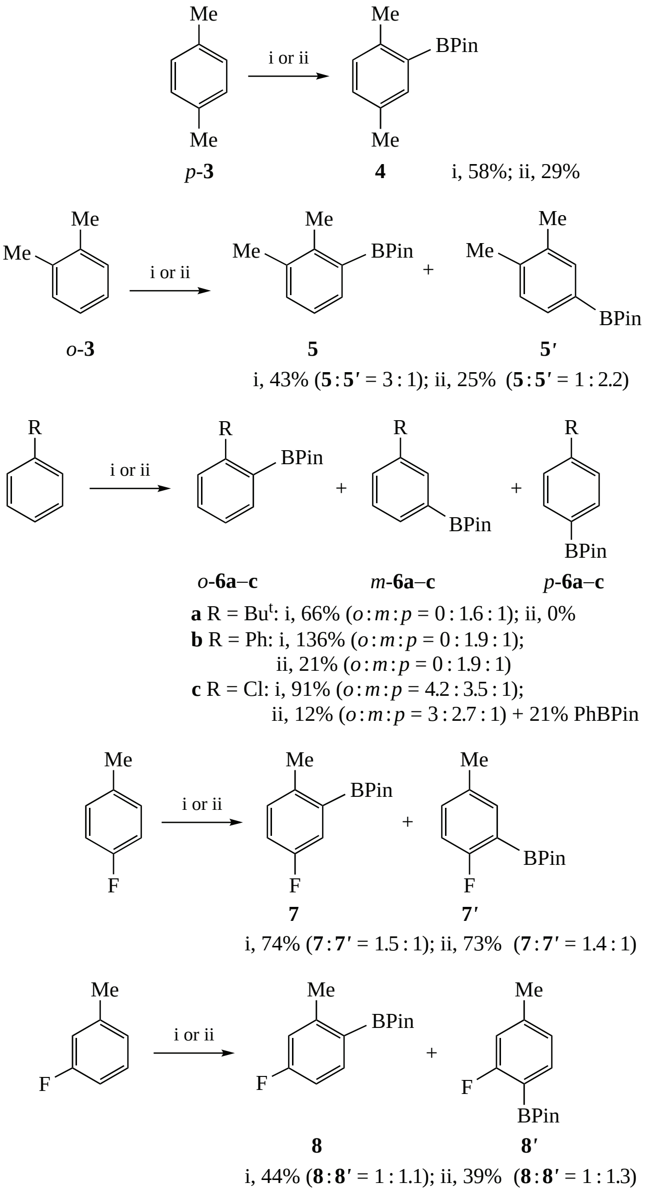
However, further increase in steric bulk of carbene ligand (**1d** and **1e**, see Table 1, entries 4 and 5) leads to a drop of *ortho*-selectivity. Notably, in case of bulky catalyst **1d,** the total yield of products formally exceeded 100% (entry 4). One may suppose that in this case not only B_2Pin_2 but also HBPin (which is formed in the course of the reaction) can serve as borylating reagent. Analogously to complex **1d**, in case of catalyst **1h**, the yield of products exceeded 100% (entry 8).

Next, we tested complexes **1j**–**o** with saturated five-, six- and seven-membered ring carbene backbone[7] bearing bulky Mes and Dipp substituents at the nitrogen atoms. In this series of experiments the following trend can be clearly traced: upon transition from less bulky Mes-substituted carbenes to bulkier Dipp-substituted ones, drastic increase in yield and significant growth of *ortho*-selectivity take place (see Table 1, entry 10 *vs.* 11, entry 12 *vs.* 13, entry 14 *vs.* 15). Analogously, upon expansion of the ring, and corresponding increase in steric bulk of a carbene ligand, the yields and *ortho*-selectivity grow simultaneously (entries 10, 12, 14 *vs.* entries 11, 13, 15). As a result, in this series the highest yield (130%) and the best *ortho*-selectivity (*o* : *m* : *p* = 9.6 : 2.8 : 1.0) were observed for complex bearing seven-membered ring Dipp-substituted carbene **1o** (entry 15).

Attempted borylation of toluene in air with the use of catalyst **1c** gave only traces of products. When the reaction was performed in a sealed vessel which was not pre-flushed with dry argon, the yield turned to be 18% (*cf.* 69% under argon, see Table 1, entry 3). Apparently, catalytically active species and/or intermediates are air-sensitive.

Then we studied borylation of various arenes mediated by complexes **1o** and **1d**, which demonstrated the highest activity and selectivity in toluene borylation (Scheme 2). In most cases, catalyst **1o** was more active than **1d**. Interestingly, borylation of *o*-xylene catalyzed by **1o** gave mostly *ortho*-isomer **5** while in case of **1d** there was virtually no selectivity. Reaction of biphenyl mediated by **1o** led to products *m*/*p*-**6b** in excessive (> 100%) yield, which was probably due to participation of HBPin in the whole process. The absence of *ortho*-isomer is presumably caused by steric bulk of the phenyl substituent.

Borylation of chlorobenzene mediated by **1o** proceeds efficiently while, in case of **1d**, the total yield of products *o*/*m*/*p*-**6c** is low (12%), the side product, PhBPin, is formed in > 20% yield.



Scheme 2 *Reagents and conditions*: i, B_2Pin_2, (NHC)Pt(dvtms) **1o** (2 mol%), 120 °C, 20 h; ii, B_2Pin_2, (NHC)Pt(dvtms) **1d** (2 mol%), 120 °C, 20 h.

Both catalysts have shown virtually the same activity in borylation of *p*- and *m*-fluorotoluenes (products **7**,**7′** and **8**,**8′**, respectively, see Scheme 2). Although fluorine acts as a directing group in many C–H functionalization reactions,[8] in these two cases the ratio of isomers is close to statistical.

Previously, Furukawa has shown that HBPin was unreactive under platinum-catalyzed conditions with benzene.[3(*b*)] In this study as indicated above (see Table 1, entries 4, 8, 13, 15), we accounted yields higher than 100 % for participation of HBPin in the course of borylation. Therefore, we conducted control borylation of toluene with HBPin under the same conditions as for B_2Pin_2. In all cases the amount of *ortho*-substitution product decreased considerably compared to the case with B_2Pin_2, while the ratio between the *para*- and *meta*- isomers varied about the statistical distribution of 1 to 2. The most active catalysts in these experiments are complexes bearing highly sterically hindered imidazolium NHC ligands **1e** and **1d** (see Table 1, entries 4 and 5). Markedly, these complexes ensure the poorest *ortho*-selectivity. In the series of experiments (entries 11–15) using complexes **1k**–**o** bearing 5-, 6- and 7-membered ring carbenes, analogously to the reaction with B_2Pin_2, some regularities can be traced, namely, expansion of the ring size as well as the increase in steric bulk of the aryl group (Dipp *vs.* Mes), which leads to increase in the product yields. However, contrary to borylation with B_2Pin_2, predominant formation of *meta*-isomers occurred.

In conclusion, a series of fifteen (NHC)Pt(dvtms) complexes was tested as catalysts in borylation of toluene with B_2Pin_2. The nature of a carbene ligand significantly affect the catalytic activity and selectivity of the reaction. Most surprising specific feature of the platinum NHC complexes is the unusual *ortho*-selectivity of C–H activation in monosubstituted benzenes: *o*/*m*/*p* ratio amounts to ~ 10 : 3 : 1 in borylation of toluene under catalysis with (7-Dipp)Pt(dvtms). Further mechanistic studies to rationalize this effect are needed. We have found that the borylation could be also performed with HBPin being the secondary product in the process with B_2Pin_2; this was the reason why in some cases with B_2Pin_2 the product yields would exceed 100%.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.005.

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