Palladium–NHC complexes do catalyse the diboration of alkenes: mechanistic insights†

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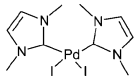
Novel catalytic activation of the B–B bond by palladium(II)–NHC complexes in presence of a mild base (NaOAc) and an excess of diboron reagent enables chemoselective 1,2-diboration of alkenes, suggesting the heterolytic cleavage of diboron rather than oxidative addition of a B–B bond to the metal.

Palladium and platinum complexes efficiently catalyse the activation of inter-element σ-bonds such as S–B,[1] Si–B,[2] Ge–B[3] and Sn–B[4] that are added to alkynes and alkenes. In contrast, catalytic diboration reactions have mainly used catalysts based on platinum, rhodium and, to a lesser extent, the group 11 metal complexes.[5] Palladium complexes are ineffective in these reactions, although they were shown to be efficient in diboration of allenes[6] and borylative cyclisation of 1,6-enynes.[7] Computational studies by Morokuma[8] and Sakaki[9] have postulated that oxidative addition of B–B cannot take place in palladium complexes because it is an endothermic process with an extremely low reverse barrier. In fact, it is well known that oxidative adducts are produced by the reaction of Pt(0) and Rh(I) complexes with diboron reagents,[10] but the corresponding palladium complexes have not ever been detected. In this paper, we wish to report the first example of the Pd-catalysed diboration of alkenes. We would like to point out that the reaction is completely chemoselective for diborane derivative formation and no other byproducts are detected. A catalytic pathway, other than the one that involves the oxidative addition of diboron to Pd species, is suggested.

We first explored a series of standard Pd(0) and Pd(II) complexes in the catalytic diboration of styrene as a model reaction. In accordance with the results of Miyaura *et al.*,[11] the palladium(0) complex $Pd(PPh_3)_4$ was as ineffective as $Pd(dba)_2$. Alternative palladium(II) complexes such as $Pd(OAc)_2$, $PdCl_2$, $PdCl_2(COD)$, $PdCl_2(PhCN)_2$ and $PdCl_2(PPh_3)_2$ did not lead to the formation of any diboronate esters when bis(catecholato)diboron, (B_2cat_2), was added to a solution of the precursor of catalyst (5 mol%) and styrene in THF under argon. In this context, we turned our attention to N-heterocyclic carbene (NHC) ligands, because we have recently demonstrated their efficient role as basic ligands in the catalytic diboration of alkenes and alkynes with Ag[12] and Au,[13] and more conveniently with Pt[14] and Cu.[15] Although Pd–NHC complexes have been extensively used in the cross-coupling reaction,[16] to the best of our knowledge they have never been involved in any B addition to unsaturated compounds. The NHC–palladium compounds **1–6** were prepared[17] in order to test their activity in the catalytic diboration of styrene, in an attempt to find a correlation between the coordination mode of the ligand, the nature of the counterion and the efficient catalytic activity. Under standard reaction conditions, only complexes **5–6** showed the incipient formation of phenylethyl diboronate esters at room temperature, (Table 1, entries 1–4). In addition to the diborated product, branched and linear monoborated byproducts were also observed in conjunction with alkenylboronate derivatives. This result was very encouraging because it represents the first example of Pd catalysing this type of reaction. The addition of a mild base markedly improves the total chemoselectivity on the diborated product (entries 5–9), NaOAc being the most effective among those used. An excess of diboron reagent was required to afford a total conversion within 4 h at room temperature (entry 6).



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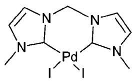

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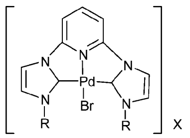

3:R= Me; **a**:X=Br; **b**:X=PF_6
4:R= n-Bu; **a**:X=Br; **b**:X=PF_6
5:R= Bn; X=Br
6:R= *p*NO_2-Bn; **a**:X=Br; **b**:X=PF_6; **c**:X=BF_4

Among all the palladium complexes explored, complexes **2** and **6b** seem to be most active and selective (entries 6 and 11). At this stage, we did not find out whether neutral or ionic catalytic systems had a specific influence. We explored the generality of the reaction in terminal and internal alkenes (Table 2) with precursor **6b**, because of the simplicity of its synthesis. Remarkably, the reaction continues to be completely chemoselective for diborane product formation and a slight increase in the reaction temperature was required for total conversion on the more hindered substrates.

As we mentioned above, previous theoretical studies[8,9] on Pd(0) phosphine model complexes concluded that oxidative addition of B–B cannot take place since it is an endothermic process with an extremely low reverse barrier. More recently, and in the framework of the diboration of styrene by means of Cu(I)–NHC, we reported a DFT study[15] suggesting that oxidative addition of B_2cat_2 to afford a Cu(III)–NHC–diboryl complex would be highly endothermic so that a Cu(I)–NHC–(σ-B_2cat_2) intermediate was formed instead. In that case, a mechanism involving transmetalation sequences was suggested.[15] Consequently, at this point we

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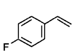
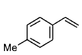
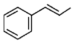
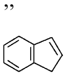
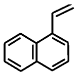
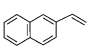
Table 1 Catalytic diboration of styrene with Pd(II)–NHC[a]

Entry	Catalytic system	B_2cat_2 (equiv.)	Base	Conv.[b] (%)	1,2-alkenyldiboronate[b] (%)
1	**5**	1.1	—	84	23
2	**6a**	”	—	89	25
3	**6b**	”	—	70	27
4	**6c**	”	—	83	30
5	**6b**	”	NaOAc	55	100
6	”	3	NaOAc	100	100
7	”	3	NaOH	77	100
8	”	”	NEt_3	98	76
9	”	”	K_2CO_3	28	100
10	**1**	”	NaOAc	100	92.5
11	**2**	”	NaOAc	100	100
12	**3a**	”	NaOAc	87	47
13	**3b**	”	NaOAc	74	44
14	**4a**	”	NaOAc	91	46
15	**4b**	”	NaOAc	90	61
16	**6c**	”	NaOAc	85	100

[a] Standard conditions: 5 mol% Pd–NHC, THF, 4 h, 25 °C. Base: 1.1 equiv. Diboron: bis(catecholato)diboron. [b] Determined by ^{1}H NMR (1,2-alkenyldiboronate) and GC (oxidised product).

Table 2 Catalytic diboration of alkenes with **6b**[a]

Entry	Substrate	T (°C)	Conv.[b] (%)	1,2-alkenyldiboronate[b] (%)
1		25	94	100
2		25	77	100
3	”	80	94	100
4		25	61	100
5	”	80	100	100
6		25	73	100
7	”	80	96	100
8		25	100	100
9		25	20	100
10	”	80	90	100

[a] Standard conditions: 5 mol% **6b**, substrate/diboron = 1/3, THF, 4 h, NaOAc (1.1 equiv.). Diboron: B_2cat_2. [b] Conversion and selectivity based on ^{1}H NMR.

wondered whether the observation that an excess of B_2cat_2 is required for total conversion of alkenes (Table 1, see entries 5 and 6) suggests an alternative mechanism. With the aim of gaining insight into the nature of the intermediates involved in the mechanism we carried out a DFT study considering compound **3a** in order to reduce conformational fluxionality.

Direct oxidative addition of B_2cat_2 to $[Pd(II)–NHC–Br]^+$ (**3a**) was first explored. As route **A** in Fig. 1 indicates, the oxidative addition of B_2cat_2 to the cationic complex **3a** is an endothermic process by 22.0 kcal mol^{-1}, while the barrier of the reverse process is extremely low. These results are in agreement with previous studies.[8,9] Note that the product of this process is a saturated hexacoordinated Pd(IV) complex which would require creation of a vacant site in order to enable the reaction to continue.

Decoordination of bromide followed by coordination of the substrate, alkene insertion and reductive elimination would follow the "classical" reaction pathway. Alternatively, reductive elimination of a B(cat)Br adduct would produce a $[Pd(II)–(NHC)–B(cat)]^+$ (**3a-B**) cationic complex intermediate which inserts the alkene into the Pd–B bond to form the Pd–alkylboronate species. We evaluated that the formation of **3a-B** is 3.4 kcal mol^{-1} above the reactants, as Fig. 1 shows. Another possible active species is conceivable which would result from preliminary decoordination of bromide to give a dicationic $[Pd(II)–NHC]^{2+}$ complex.

This intermediate could form a very stable sigma complex with B_2cat_2, **3a′-σB2**, shown in path **B** in Fig. 1, with 32.9 kcal mol^{-1} below the two isolated reagents. In contrast to the case of Cu(I)–NHC where the oxidative addition was discarded,[15] here the oxidative addition process is only slightly endothermic by 9.6 kcal mol^{-1} with a moderate energy barrier.[18] Since this product is coordinatively unsaturated, alkene coordination would follow the reaction. In view of these results, we do not rule out the possibility that Pd(IV) species participate in the mechanism, probably stabilised by the strong sigma donor NHC ligand. In this sense, when less basic ligands were used, the reaction did not proceed.

When the base is added, the mechanism could switch towards transmetalation, since this would also explain the increase in selectivity, but also in conversion when an excess of B_2cat_2 is used. The role of the base is thought to be the acceleration of the transmetalation rate, similar to the related cross-coupling reaction of organoboron compounds.[19] However, we cannot rule out the possibility that the base participates in the halide displacement at the palladium species favoring the transmetalation.[20] The treatment of (NHC)Pd(II)–Br, **6a**, with NaOAc and B_2cat_2 in d^8-THF favors the formation of a new signal at 13.6 ppm in ^{11}B NMR from the original 28 ppm of B_2cat_2. The shift of the ^{11}B signal to

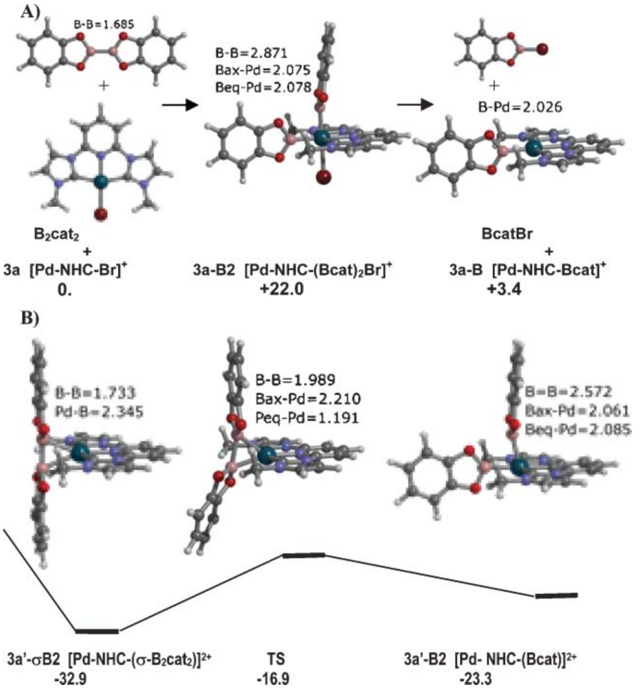


Fig. 1 Molecular structures, selected geometrical parameters (in Å) and reaction energies (in kcal mol^{-1}) for direct oxidative addition processes.

higher fields from the original B_2cat_2 could be explained by increasing the diboron nucleophilicity by the interaction with NaOAc. This idea is also supported by the fact that when the catalytic diboration was carried out in presence of **6a** and bis(pinacolato)diboron, (B_2pin_2), no diboronate ester was observed, in accordance with the absence of new signals in ^{11}B and ^1H NMR of the mixture of **6a** with NaOAc and B_2pin_2.

We also investigated the effect of the base when B_2cat_2 is coordinated to a palladium dicationic complex. The approach of the OH^- base to the sigma complex **3a′-σB2** was found to be highly dependent on the initial geometry, and led either to a new intermediate, or to the formation of the species BcatOH and the cationic complex **3a′-B**, which meant reconsidering the intermediates of the transmetalation process. In order to evaluate the thermodynamics of this transformation, we considered B_2cat_2 and $[Pd(II)–NHC–OH]^+$ as the starting point. In this way, the overall process is rather favorable by -39.7 kcal mol^{-1}. Note that this result contrasts with the bromide mediated transmetalation that was computed slightly endothermic by 3.4 kcal mol^{-1} as shown in Fig. 1. Therefore, the interaction of the base with the diboron reagent together with the strong exothermicity of the transmetalation step in presence of the base could be the driving force for completion of the reaction.

The remarkable advantages of a palladium-catalysed diboration reaction open perspectives towards a number of tandem sequences that may be useful for assembling targeted organic compounds, such as C–C bond formation through cross-coupling reaction of the alkyldiboronate ester.

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