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Catalytic Diboration of Unsaturated Molecules with Platinum(0)−NHC: Selective Synthesis of 1,2-Dihydroxysulfones

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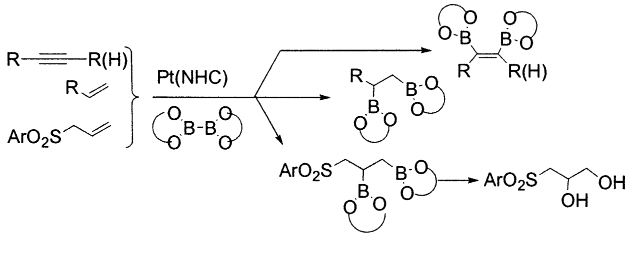
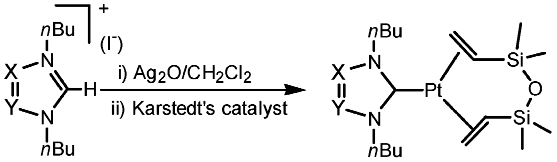
Summary: Readily available N-heterocyclic platinum complexes provide active catalytic species for 1,2-diboration and anticipate a wide range of applications in alkenes and alkynes. Unprecedented catalytic B−B addition of heteroatom-containing substrates provided high selectivity into organosulfur−diboronate esters. Their in situ basic oxidation afforded the desired 1,2-dihydroxysulfones in high yields.

The special electronic and steric properties induced by N-heterocyclic carbenes (NHCs) are affording new bases for the preparation of complexes with enhanced catalytic activity, which now have widespread applications in a large number of organic reactions.[1] In the field of catalyzed diboration reactions, the success of the process is based on the cleavage of the B−B bond by low-valent metal centers[2] and the kinetic lability of the resulting bis(boryl) complexes.[3] The combination of these two facts guarantees the activation of tetraalkoxy- and tetraaryloxydiboranes by oxidative addition, despite their relatively high B−B bond energy,[4] and also the B−C reductive elimination to afford synthetically suitable stereodefined organo-1,2-diborane compounds.[5] The acceptance of the advantageous metal-promoted 1,2-diboration versus the uncatalyzed reaction[6] has motivated researchers to find a suitable active catalytic system since Miyaura and Suzuki's first report.[7] Even the asymmetric version of the reaction has recently acquired special significance.[8] While all efforts have been focused on metal−phosphine complexes,[9] we recently described a series of NHC-based Ag(I) and Au(I) complexes that cleanly performed B−B addition to alkenes.[10] Our ongoing research in this field is now aimed at using a series of Pt(0)−NHC complexes in the 1,2-diboration of alkynes and alkenes. We point out the first example of B−B addition to aryl allylic sulfones to achieve, after oxidative workup, an alternative method for obtaining 1,2-dihydroxysulfones as valuable intermediates for functionalized cyclic ethers and lactones[11] (Scheme 1).

Scheme 1



Scheme 2



X= Y = C-Cl; **1**
X = N, Y = C-H, **2**
X = Y = C-H, **3**

The NHC−platinum compounds **1**−**3** were synthesized by transmetalation from the corresponding silver carbenes, as shown in Scheme 2. The three complexes were obtained to study how the electronic nature of the NHC ligand affects the catalytic performances. Complex **3** has already been reported,[12a] although we have changed the preparation procedure. To the best of our knowledge, this is the first example of a silver transmetalation to platinum(0). Complexes **1** and **2** were characterized by NMR

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Table 1. 1,2-Diboration of Alkynes with Pt(0)−NHC[a]

entry	Pt(0)−NHC	substrate	diboron	time (h)	conversion (%)[b]
1	**2**[c]	PhCCPh	$B_2(pin)_2$	24	4
2	**2**[d]	PhCCPh	$B_2(pin)_2$	24	39
3	**2**	PhCCPh	$B_2(pin)_2$	24	60
4	**1**	PhCCPh	$B_2(pin)_2$	24	41
5	**3**	PhCCPh	$B_2(pin)_2$	24	19
6	**2**	PhCCPh	$B_2(cat)_2$	5	>95
7	**2**	*p*-(CF_3)PhCCPh*p*(CF_3)	$B_2(cat)_2$	5	>95
8	**2**	*p*-(CF_3)PhCCPh*p*(OMe)	$B_2(cat)_2$	5	50
9	**2**	*p*-(OMe)PhCCPh	$B_2(cat)_2$	5	57
10	**2**	PhCCH	$B_2(pin)_2$	24	3
11	**2**	PhCCH	$B_2(cat)_2$	8	99
12	**2**	*p*(CF3)PhCCH	$B_2(cat)_2$	8	99
13	**2**	*p*(Cl)PhCCH	$B_2(cat)_2$	8	99
14	**2**	*p*(OMe)PhCCPh	$B_2(cat)_2$	8	99

[a] Standard conditions: 5 mol % of Pt(0)−NHC catalytic system, alkyne/diboron, 1:1.5, *T* 25 °C. [b]Conversion on *cis*-alkenyl bis(boronate) esters, based on ^{1}H NMR. Solvent: THF. [c]Solvent: CH_3CN. [d]Solvent: toluene.

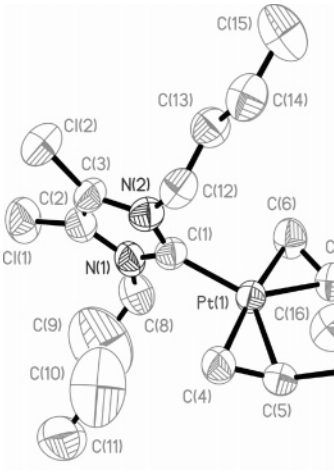

Figure 1. Molecular diagram of **1** (50% probability level, H atoms omitted). Selected bond lengths (Å) and angles (deg): Pt(1)−C(1) 2.037(6), Pt(1)−C(4) 2.093(7), Pt(1)−C(5) 2.129(6), Cl(1)−C(2) 1.689(7), Cl(2)−C(3) 1.682(7), C(2)−C(3) 1.354(10), C(4)−C(5) 1.407(9), C(6)−C(7) 1.418(9); C(4)−Pt(1)−C(1)−N(2) 78.6(6), C(6)−Pt(1)−C(1)−N(2) −102.1(6), α 80.3. α = angle between the imidazolium ring plane and the *xy* plane of the metal complex.

and elemental analysis. The most significant feature of the $^{13}C\{^1H\}$ NMR spectrum is the signal at δ 185.5 (**1**) and 183.5 (**2**), with coupling constants that confirm Pt binding ($^1J_{Pt-C}$ = 1392 Hz, **1**; $^1J_{Pt-C}$ = 1390 Hz, **2**).

Single crystals of **1** were obtained only by slow evaporation of a concentrated dichloromethane solution. The molecular diagram (Figure 1) shows that the coordination is trigonal planar at the Pt(0) center. The angle of the plane defined by the azole ring is almost perpendicular to the platinum coordination plane (α = 80.3°). The shortest interactions between both ligands arise from the pseudoaxial methyl groups of the dvtms and the wingtips of the NHC ligand. The platinum−carbene distance is in the expected range ($Pt-C_{carbene}$ = 2.037(6) Å). The C═C bond distance of the terminal vinyl groups provides a direct measurement of platinum back-bonding in the olefin delocalized π* orbital. Markó et al. have reported a series of similar complexes for which the C═C distances range from 1.42 to 1.49 Å, depending on the nature of the imidazolylidene ring.[12] In our case, compound **1** has a C═C bond length of 1.354 Å. This is in accordance with the fact that the electron-donating character of the carbene is lower than that of other NHC−Pt(0) complexes reported in the literature,[12] because of the introduction of the two chlorine substituents. In fact, the 4,5-dichloroimidazolylidene carbene can be considered to be topologically similar to other imidazolylidenes and electronically similar to phosphines, as has been observed for other chlorinated-NHC complexes.[13]

Table 2. 1,2-Diboration of Alkenes with Pt(0)−NHC and $B_2(cat)_2$[a]

Pt(0)−NHC	substrate	conv (%)[b]	bis(boryl) alkane (%)[b]
1	PhCH═CH_2	88	42
2	PhCH═CH_2	97	66
3	PhCH═CH_2	94	54
2[c]	PhCH═CH_2	85	58
2[d]	PhCH═CH_2		
2	*p*-(F)PhCH═CH_2	91	67
2	*p*-(MeO)PhCH═CH_2	85	62
2	vinylcyclohexene	100	21
2	3,3-dimethylbutene	100	11

[a] Standard conditions: 5 mol % of Pt(0)−NHC catalytic system; alkene/diboron, 1:1.1, *T* 25 °C reaction time 4 h, solvent THF. [b]Conversion and selectivity based on ^{1}H NMR. [c]Solvent: toluene. [d]Solvent: CH_3CN.

The Pt(0)−NHC complex **2** was initially tested in the diboration of alkynes using diphenylacetylene and phenylacetylene as model substrates for internal and terminal alkynes, respectively. As shown in Table 1, THF was the most suitable solvent for conducting (at room temperature) the clean addition of bis(pinacolato)diboron, $B_2(pin)_2$, to alkynes with the formation of the *cis*-alkene bis(boronate) esters (entries 1−3). However, conversion depends on the electronic properties of the NHC ligand, and the electron-releasing triazolylidene carbene ligand in complex **2** was the most suitable, as expected (entries 3−5). Thus, we selected complex **2** for further studies, and the use of the most reactive bis(catecholato)diboron, $B_2(cat)_2$, allowed quantitative conversions of diphenylacetylene in 5 h (entry 6).

When the significance of the electronic parameters in this process was reinforced, we observed that the less electron rich the diarylalkyne was, the higher the product yield (Table 1, entries 7−9). This is in agreement with Marder's observations.[14a] Remarkably, complex **2** performed a total conversion on diborated product, with the less reactive substrate, phenylacetylene, tolerating even electron-donating and electron-withdrawing moieties in the substrate (entries 10−14). Conversions were

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Table 3. 1,2-Diboration of Aryl Allylic Sulfones with Pt(0)−NHC[a]

Pt(0)−NHC	substrate	arylallylic sulfone/ diboron	conv (%)[b]	bis(boryl) alkane sulfone (%)[b]
1	$PhSO_2CH_2CH{=}CH_2$	1:1.1	90	75
2	$PhSO_2CH_2CH{=}CH_2$	1:1.1	69	71
3	$PhSO_2CH_2CH{=}CH_2$	1:1.1	87	85
1	$PhSO_2CH_2CH{=}CH_2$	1:2	100	90
1	*p*-(Me)$PhSO_2CH_2CH{=}CH_2$	1:2	100	91
1	*p*-(Cl)$PhSO_2CH_2CH{=}CH_2$	1:2	100	94

[a] Standard conditions: 5 mol % of Pt(0)−NHC catalytic system; diboron, bis(pinacolato)diboron ($B_2(pin)_2$); aryl allylic sulfone/diboron, 1:1.1, *T* 80 °C, reaction time 16 h, Solvent toluene. [b]Conversion and selectivity based on ^1H NMR.

calculated on the basis of the ^1H NMR. However, to test whether the substrate could be pumped off during the sample preparation, we carried out the same catalytic reaction under d_8-THF, and no changes in the conversion were detected. To broaden the scope of the catalytic performance of our Pt(0)−NHC complexes, we went on to study alkenes. Complex **2** was found to be an excellent catalyst precursor that allowed styrene to be diborated at room temperature within 4 h (Table 2), with THF being the solvent of choice. However, other alkylborane byproducts were observed, probably arising from β-H elimination pathways that compete with the diboration catalytic cycle.[9]

Electron-poor vinylarenes showed a slight decrease in bis(boryl)alkane formation. Extension to aliphatic alkenes was also possible, but greater percentages of byproducts were formed. Thus, platinum−carbene-catalyzed diboration improves the B−B addition with $Pt(PPh_3)_4$[15] and $[Pt(PPh_3)_2(C_2H_4)]$[16] and is an alternative to the more classical base-free platinum[17] and mono(phosphine)platinum complexes,[14] although the latter provided slightly faster performances.

The Pt−NHC-catalyzed 1,2-diboration reaction makes it possible for us to use our preliminary findings on alkynes and alkenes to generate a useful method for preparing bis(boryl)alkane sulfones that can be easily converted into 1,2-dihydroxysulfones through in situ oxidation with hydrogen peroxide in a basic medium. Heteroatom-containing substrates,[18] such as aryl allylic sulfones, have been hydroborated only in a symmetric[18b] and asymmetric[18c] catalytic way to provide, after in situ oxidation, the branched alcohol as a consequence of the directing effects of the sulfone functional group. This electron-attracting terminal group in the allylic system facilitated the simultaneous B−B catalytic addition to the C=C bond without any undesired byproduct formation due to the isomerization of the double bond. As shown in Table 3, $B_2(pin)_2$ was added quantitatively under optimized conditions (toluene, 80 °C, 16 h), in the presence of complexes **1**−**3**, and catalytic system **1** proved to be the most suitable for this transformation. However, small percentages of monoalkylboranes were observed as a subsequent β-H elimination competitive pathway. It is interesting to note that the aryl allylic sulfones could not be diborated with metal−phosphine catalytic systems based on rhodium or platinum complexes such as $[RhCl(PPh_3)_3]$, $[Rh(cod)(PPh_3)_3]BF_4$, or $Pt(PPh_3)_4$. An excess of diboron leads to total conversion, even with electron-donating or electron-withdrawing moieties in the substrate.

This study opens up new perspectives for future applications of metal-mediated synthesis toward chiral nonracemic 1,2-dihydroxysulfones when asymmetry can be induced through the chiral N-heterocyclic carbenes, as an alternative to the Sharpless asymmetric dihydroxylation method or the hydrolytic resolution of epoxysulfones with Jacobsen's catalyst. We are also studying the in situ intramolecular cyclization of bis(boryl)alkyl sulfones to provide suitable routes for preparing functionalized dihydrofurans.

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Supporting Information Available: Experimental procedures and crystallographic data are available free of charge via the Internet at http://pubs.acs.org.

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