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Journal Pre-proo

## New expanded-ring NHC platinum(0) complexes: synthesis, structure and highly efficient-diboration of terminal alkenes

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#### Journal Pre-proof Abstract

The synthesis and structural characterization of a series of novel platinum(0) complexes were reported. A number of (NHC)Pt(dvtms) (dvtms = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane) complexes were investigated in catalytic addition of  $B_2Pin_2$  to terminal alkenes. The novel expanded ring N-heterocyclic carbene complex (7-Dipp)Pt(dvtms) showed highest performance, turnover numbers up to 3800 were achieved. The scope of the reaction was illustrated by 20 examples with a variety of alkyl, alkoxy, halogen, ester, ketone and acetal substituents.

## **Graphical abstract**



Keywords

Platinum, N-heterocyclic carbenes, alkenes, diboration, catalysis

## Highlights

- A series of fourteen Pt(0) complexes with expanded-ring NHCs and 4,5-disubtituted NHCs were prepared.
- Structures of the novel complexes were described in solid state.
- The catalytic activity of the (NHC)Pt(dvtms) complexes was evaluated for the alkenes 1,2-diboration.

#### Iournal Pre-proof **1. Introduction**

Boronic acids and their derivatives proved to be useful reagents for a wide range of reactions, in particular, for the C-C, C-O and C-N bonds formation [1-5]. While aryl boronic acids and their derivatives have been well studied in organic synthesis, aliphatic boronic acids derivatives have received considerably less attention. Alkyl 1,2-bis(boronates) are of particular interest due to their feasibility toward synthesis of multi-functionalized compounds [6-16].

A number of catalysts have been proposed for the 1,2-diborylalkanes synthesis via 1,2diboration of alkenes. The most promising among them are platinum-based catalytic systems, such as Pt/TiO<sub>2</sub> [5], Pt(dba)<sub>2</sub> [17, 18], Pt(COD)<sub>2</sub>, Pt(NBE)<sub>3</sub>, [19], Pt(COD)Cl<sub>2</sub> [20] and Pt<sub>2</sub>(dba)<sub>3</sub>+taddolderived phosphonite ligands [21]. Transition metal complexes of N-heterocyclic carbenes (Ag, Au, Cu, Pd and Rh) are also shown to be active catalysts in alkenes 1,2-diboration [22-31]. Despite reported 1,2-diboration of alkenes catalyzed by (NHC)Pt(0) complexes [32], the influence of the NHC-ligand structure on the complexes activity was not shown.

We believe that expanded-ring (NHC)Pt(0) complexes may show enhanced catalytic performance in alkenes 1,2-diboration due to the unique steric and electronic-properties of expanded-ring NHCs. In the course of our ongoing studies on the development of new NHC-based metal complexes for the application in catalytic reactions under environmentally benign conditions [33-46], herein, we report our findings on diboration of terminal alkenes catalyzed by expanded-ring NHC platinum(0) complexes.

## 2. Experimental

#### Materials and methods

All reactions were carried out using standard Schlenk technique under argon atmosphere. Tetrahydrofuran and toluene were distilled over sodium-benzophenone under argon. All alkenes and Bis(pinacolato)diboron (B<sub>2</sub>Pin<sub>2</sub>) were purchased from Sigma-Aldrich. Chemicals and solvents were obtained from commercial sources and used without further purification. NMR spectra were obtained on a Bruker "Avance 600" (600 MHz <sup>1</sup>H, 151 MHz <sup>13</sup>C). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks. Coupling constants *J* are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as "s", "d", "t" or "m" for singlet, doublet, triplet or multiplet, respectively. The abbreviation "br" is given for broadened signals.

X-ray diffraction data were collected on a APEX II DUO CCD diffractometer using molybdenum radiation [ $\lambda$ (MoK $\alpha$ ) = 0.71072 Å,  $\omega$ -scans]. The substantial redundancy in data allowed empirical absorption correction to be applied with SADABS by multiple measurements of equivalent

reflections. The structures were solved by direct methods and refined by the full-matrix least-squares technique against  $F^2$  in the anisotropic-isotropic approximation. C-H hydrogen atoms in all structures were placed in calculated positions and refined within the riding model. All calculations were performed with the SHELXTL software package [47]. Crystal data and structure refinement parameters for complexes IPr<sup>Me</sup>Pt(dvtms) (2g, CCDC 1573639), IPr<sup>Cl</sup>Pt(dvtms) (2h, CCDC 1573640), IPr<sup>Br</sup>Pt(dvtms) (**2j**, CCDC 1573637) and (7-Dipp)Pt(dvtms) (**4d**, CCDC 1573638) are listed in supporting information (Table S1). Crystallographic data for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data via www.ccdc.cam.ac.uk/data\_request/cif.

All products were characterized using NMR, IR spectroscopy and HRMS and details are given in the supporting information.

#### Synthesis of azolium and cyclic amidinum salts

Imidazolium salt ICy·HBF<sub>4</sub> was synthesized via direct condensation of glyoxal, paraformaldehyde, appropriate amine and 48% aqueous HBF<sub>4</sub> in toluene solution. Imidazolium salts IPr·HCl and IMes·HCl were obtained via cyclization of *N*,*N*'-diarylethylenediimine under action of the paraformaldehyde and chlorotrimethylsilane in ethyl acetate solution [48]. The analogous corresponding bisimines cyclization under action of the paraformaldehyde solution in 4M HCl in 1,4-dioxane gave salts IPr<sup>Me</sup>·HBF<sub>4</sub> and IMes<sup>Me</sup>·HBF<sub>4</sub> [49]. Halogenated imidazolium salts IPr<sup>Cl</sup>·HCl and IPr<sup>Br</sup>·HCl were obtained by treatment of free NHC with CX<sub>4</sub> (X=Cl or Br) [50-52]. Imidazolinium salts SIPr·HCl and SIMes·HCl were prepared by cyclization of corresponding *N*,*N*'-diarylethylenediammonium dichlorides with triethyl orthoformate. Highly hindered imidazolium salts IPr\*·HCl and IPr<sup>OMe</sup>\*·HCl were obtained according to literature procedures [48, 53, 54]. Precursors of the expanded-ring NHC were synthesized via solvent-free alkylation of *N*,*N*'-diarylformamidines with 1,3-dibromopropane or 1,4-dibromobutane [55, 56].

#### General procedure for preparation of (NHC)Pt(dvtms)

A 10 ml Schlenk flask equipped with a magnetic stir bar was charged with 1.2 mmol (1.2 eq.) of corresponding azolium (or amidinium) salt and evacuated to 0.1-0.2 mmHg. The Schlenk flask was heated at 100 °C/0.1 mmHg for 1h. The flask was filled with argon and allowed to cool to room temperature followed by addition of 6 ml of dry THF. The reaction mixture was stirred for 5 min and 1.2 ml of a 1M NaHMDS in THF was added (2.4 ml for (7-Dipp)Pt(dvtms)). The reaction mixture was allowed to stir for 1 h at room temperature and 1.0 mmol of Pt<sub>2</sub>(dvtms)<sub>3</sub> in dvtms was added. The light yellow solution was stirred overnight, and then it was transferred to a 100 ml round-bottomed flask with dichloromethane and evaporated to dryness. The solids were triturated with 20 ml of

dichloromethane and filtered through a 1 cm pad of silica gel eluting with 3x20 ml of CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was evaporated to dryness; the solids were triturated with 3x1 ml of *n*-pentane to give a pure complex as white microcrystalline solid.

#### General procedure for alkene diboration.

A screw cap vial equipped with magnetic stir bar was charged with freshly distilled alkene (1 mmol) and  $B_2Pin_2$  (1.1 mmol) followed by 4 ml of heptane. (7-Dipp)Pt(dvtms) (4 mg) was added and the reaction mixture was allowed to stir at room temperature for 20 h. The reaction mixture was evaporated to dryness. The residue was purified by column chromatography (EtOAc/hexanes as eluent).

## 3. Results and discussion

A series of *N*-heterocyclic carbene platinum(0) complexes (NHC)Pt(dvtms) was synthesized for investigation diboration reaction of alkenes. Synthesis of imidazolium salts was performed according to previously reported techniques (see supplementary information) [48, 49, 53-56]. Platinum(0) complexes were obtained by direct interaction of Karstedt's catalyst  $Pt_2(dvtms)_3$  with free carbenes in THF solution (Scheme 1) [57].



Scheme 1. Synthesis of N-heterocyclic carbene platinum(0) complexes

Previously reported complexes bearing five-membered ring NHCs ICyPt(dvtms) (**2a**, 88%), IPrPt(dvtms) (**2b**, 47%), SIPrPt(dvtms) (**2c**, 50%), SIMesPt(dvtms) (**2d**, 87%) [58], IPr<sup>\*</sup>Pt(dvtms) (**2e**, 64%), IPr<sup>OMe\*</sup>Pt(dvtms) (**2f**, 70%) [59], as well as expanded six- and seven-membered ring NHCs 6-MesPt(dvtms) (**4a**, 42%), (6-Dipp)Pt(dvtms) (**4b**, 61%), and (7-Mes)Pt(dvtms) (**4c**, 51%) [60] were prepared (structures of ligands are shown on Scheme 2). We also performed synthesis of five new platinum NHC complexes: IPr<sup>Me</sup>Pt(dvtms) (**2g**, 88%), IPr<sup>Cl</sup>Pt(dvtms) (**2h**, 63%), IMes<sup>Me</sup>Pt(dvtms) (**2i**, 93%), IPr<sup>Br</sup>Pt(dvtms) (**2j**, 53%), (7-Dipp)Pt(dvtms) (**4d**, 59%).



Earlier, formation of air stable free carbenes  $IPr^{Cl}$  and  $IPr^{Br}$  upon halogenation of a free carbene with tetrahalomethane has been reported [50-52]. Introduction of halogen atoms (chlorine and bromine) at 4- and 5-positions of NHC leads to complex specific changes in the donor capability and steric properties of the carbene with respect to IPr. Therefore, we decided to study the effect of halogen atoms in NHCs on the catalytic properties of platinum complexes.

 $IPr^{Cl}Pt(dvtms)$  (**2h**) and  $IPr^{Br}Pt(dvtms)$  (**2j**) complexes were obtained similarly to techniques described previously (Scheme 3 and 4) [61]. *In situ* generated free carbenes were treated with CX<sub>4</sub> (X = Cl or Br) to obtain 4,5-dihalocarbenes. In case of  $IPr^{Cl}$ , solution of chlorinated carbene was treated with HCl solution in 1,4-dioxane to isolate  $IPr^{Cl}$ ·HCl. Then, platinum(0) complex was obtained

according to the above-mentioned technique using sodium bis(trimethylsilyl)amide and Karstedt's catalyst Pt<sub>2</sub>(dvtms)<sub>3</sub> (Scheme 3).



**Scheme 3.** Synthesis of the IPr<sup>Cl</sup>Pt(dvtms) (**2h**) complex.

In case of  $IPr^{Br}$ , formation of a mixture of mono-, di-, and tri-bromoderivatives  $IPr^{BrX}$ ·HCl takes place (see Supporting Information). Therefore, the technique was modified (Scheme 3): to the solution of a free carbene IPr, solution of 2.4 eq. of CBr<sub>4</sub> in THF was added dropwise and the mixture was stirred for 2 h. Then, Karstedt's catalyst  $Pt_2(dvtms)_3$  was added. The idea was to obtain a platinum complex that would differ from  $IPr^{Br3}$  (bromoiminium salt) by polarity. Monobromoderivative would be converted into target dibromide with small excess of CBr<sub>4</sub> and long-term aging of the reaction mixture.



Scheme 4. Synthesis of the IPr<sup>Br</sup>Pt(dvtms) (2j) complex.

All the obtained (NHC)Pt(dvtms) complexes are white powders stable in air. They were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. In <sup>13</sup>C NMR spectra, signals of ylidene carbon atoms appear in the region 179–212 ppm evidencing the platinum complex formation. Formation of the complexes was also indicated by the disappearance of the amidinium protons in <sup>1</sup>H NMR. Splitting of the SiMe<sub>2</sub> group signal into two distinct signals at –0.5 and 0.3 ppm, respectively, was

observed [58]. The obtained complexes were also characterized by elemental analysis and IR spectrometry.

We were unable to obtain signals corresponding to ylidene carbon atoms in <sup>13</sup>C NMR spectra of the complexes (7-Mes)Pt(dvtms) (**4c**) and (7-Dipp)Pt(dvtms) (**4d**) in CDCl<sub>3</sub>. However, it became possible when CDCl<sub>3</sub> was substituted with 1,2-dichlorobenzene-*d4* at 70°C. Signals of C<sub>NHC</sub> atoms appeared at 230.80 ppm for (7-Mes)Pt(dvtms) (**4c**), and 235.95 ppm for (7-Dipp)Pt(dvtms) (**4d**). We have also obtained <sup>1</sup>H-<sup>13</sup>C HMBC spectra of these compounds. Notably, coupling between ylidene carbon and <sup>195</sup>Pt was observed (<sup>1</sup>*J*<sub>Pt-C</sub> = 705 (**4c**) and 716 (**4d**) Hz).

Previously not reported complexes  $IPr^{Me}Pt(dvtms)$  (**2g**),  $IPr^{Cl}Pt(dvtms)$  (**2h**),  $IPr^{Br}Pt(dvtms)$  (**2j**), and (7-Dipp)Pt(dvtms) (**4d**) were characterized by X-ray crystallography (Figure 1). Crystals for X-ray crystallography were obtained by slow evaporation from  $CH_2Cl_2$ -pentane, 1:5. Structures of the complexes are presented in the figures below. The main geometric parameters of the complexes are presented in Table 1.



 $IPr^{Me}Pt(dvtms)$  (**2g**)



 $IPr^{Br}Pt(dvtms)$  (2j)



IPr<sup>Cl</sup>Pt(dvtms) (**2h**)



(7-Dipp)Pt(dvtms) (4d)

**Figure 1.** General view of IPr<sup>Me</sup>Pt(dvtms) (**2g**), IPr<sup>Cl</sup>Pt(dvtms) (**2h**), IPr<sup>Br</sup>Pt(dvtms) (**2j**), and (7-Dipp)Pt(dvtms) (**4d**) in representation of atoms by thermal ellipsoids (p=50%).

Complex	R(C <sub>NHC</sub> -Pt), Å	N-C <sub>NHC</sub> -N	Ref.
ICyPt(dvtms) (2a)	2.026	103.8°	[58]
IPrPt(dvtms) (2b)	2.068	103.9°	[58]
SIPrPt(dvtms) (2c)	2.053	107.0°	[58]
IPr <sup>Me</sup> Pt(dvtms) ( <b>2g</b> )	2.051	103.3°	this work
IPr <sup>*</sup> Pt(dvtms) ( <b>2e</b> )	2.054	104.1°	[59]
IPr <sup>*OMe</sup> Pt(dvtms) ( <b>2f</b> )	2.048	103.9°	[59]
IPr <sup>Cl</sup> Pt(dvtms) (2h)	2.042	104.2°	this work
IPr <sup>Br</sup> Pt(dvtms) ( <b>2j</b> )	2.052	103.9°	this work
(6-Mes)Pt(dvtms) (4a)	2.066	116.0°	[60]
(7-Mes)Pt(dvtms) ( <b>4c</b> )	2.070	117.1°	[60]
(7-Dipp)Pt(dvtms) (4d)	2.071	117.7°	this work
	Complex ICyPt(dvtms) ( <b>2a</b> ) IPrPt(dvtms) ( <b>2b</b> ) SIPrPt(dvtms) ( <b>2c</b> ) IPr <sup>Me</sup> Pt(dvtms) ( <b>2g</b> ) IPr <sup>*</sup> Pt(dvtms) ( <b>2g</b> ) IPr <sup>*OMe</sup> Pt(dvtms) ( <b>2f</b> ) IPr <sup>CI</sup> Pt(dvtms) ( <b>2f</b> ) IPr <sup>CI</sup> Pt(dvtms) ( <b>2f</b> ) (6-Mes)Pt(dvtms) ( <b>4</b> ) (7-Mes)Pt(dvtms) ( <b>4</b> )	Complex         R(C <sub>NHC</sub> -Pt), Å           ICyPt(dvtms) (2a)         2.026           IPrPt(dvtms) (2b)         2.068           SIPrPt(dvtms) (2c)         2.053           IPr <sup>Me</sup> Pt(dvtms) (2g)         2.051           IPr*Pt(dvtms) (2e)         2.054           IPr*Pt(dvtms) (2f)         2.048           IPr <sup>CI</sup> Pt(dvtms) (2h)         2.042           IPr <sup>CI</sup> Pt(dvtms) (2h)         2.042           IPr <sup>Br</sup> Pt(dvtms) (2j)         2.052           (6-Mes)Pt(dvtms) (4a)         2.066           (7-Mes)Pt(dvtms) (4c)         2.070           (7-Dipp)Pt(dvtms) (4d)         2.071	ComplexR(C <sub>NHC</sub> -Pt), ÅN-C <sub>NHC</sub> -NICyPt(dvtms) (2a)2.026103.8°IPrPt(dvtms) (2b)2.068103.9°SIPrPt(dvtms) (2c)2.053107.0°IPr <sup>Me</sup> Pt(dvtms) (2g)2.051103.3°IPr*Pt(dvtms) (2e)2.054104.1°IPr*OMePt(dvtms) (2f)2.048103.9°IPr <sup>Cl</sup> Pt(dvtms) (2h)2.042104.2°IPr <sup>Br</sup> Pt(dvtms) (2j)2.052103.9°(6-Mes)Pt(dvtms) (4a)2.066116.0°(7-Mes)Pt(dvtms) (4c)2.070117.1°

**Table 1.** Main geometric parameters of the Pt(0) NHC complexes.

The N– $C_{NHC}$ –N angle in the NHC ligand increases when transferring from five- to sevenmembered cyclic salts. Values of the parameter for platinum(0) complexes with five-membered carbenes are practically the same independently of the presence of substituents. The table also evidences that Pt– $C_{NHC}$  bond lengths in platinum(0) complexes with five-, six-, and seven-membered carbenes are close to each other and lie within the range of 2.042–2.071 Å.

Our preliminary studies showed that (NHC)Pt(dvtms), bis(pinacolato)diboron, starting substances and products are stable towards air, thus all catalytic reactions were performed under ambient atmosphere. Aliphatic solvents, such as hexane, heptane and cyclohexane are among the most favorable solvents for industrial applications due to their properties such as cost, stability, toxicity, corrosivity, and environmental hazard [44, 45, 62, 63]. In this regard, heptane was chosen as reaction solvent. The reactions were performed in air by using 1 mol% of platinum catalyst loading, styrene as substrate and heptane as solvent (Table 2).

Table 2. Diboration of styrene catalyzed by (NHC)Pt(dvtms).

Journal Pre-proof							
		1 mol%	PPin				
	<b>)</b> +	B <sub>2</sub> Pin <sub>2</sub>					
		room temp. air.	20h 🗍 🚶				
		• *					
	No.	Complex	Yield, %				
	1	ICvPt(dvtms) ( <b>2a</b> )	34				
	3	IPrPt(dvtms) ( <b>2b</b> )	0				
	4	SIPrPt(dvtms) (2c)	38				
	5	SIMesPt(dvtms) (2d)	traces				
	6	IPr <sup>Me</sup> Pt(dvtms) ( <b>2g</b> )	43				
	7	IPr*Pt(dvtms) (2e)	0				
	8	$IPr^{*OMe}Pt(dvtms)$ ( <b>2f</b> )	0				
	9	IPr <sup>Cl</sup> Pt(dvtms) ( <b>2h</b> )	75				
	10	IMes <sup>Me</sup> Pt(dvtms) ( <b>2i</b> )	0				
	11	IPr <sup>Br</sup> Pt(dvtms) ( <b>2j</b> )	72				
	12	(6-Mes)Pt(dvtms) ( <b>4a</b> )	83				
	13	(6-Dipp)Pt(dvtms) (4b)	>99				
	14	(7-Mes)Pt(dvtms) (4c)	63				
	15	(7-Dipp)Pt(dytms) (4d)	>99				

Reagents and conditions: styrene (1 equiv.), B<sub>2</sub>Pin<sub>2</sub> (1.1 equiv.), catalyst (1 mol%). Yields by <sup>1</sup>H NMR spectroscopy with BHT as Internal Standard.

Catalyst screening showed that structure of NHC-ligand strongly affects yield of diboration product. Catalytic activity of corresponding platinum(0) complexes seems to related with several factors, such as electronic and steric effects of NHC carbene ligand. Our experiments have shown that catalytic activity increases primarily due to expansion of carbene cycle in order: SIPrPt(dvtms) (**2c**) < (6-Dipp)Pt(dvtms) (**4b**)  $\leq$  (7-Dipp)Pt(dvtms) (**4d**). We suppose that observed increase in activity related with N–C<sub>NHC</sub>–N angle expansion and increase of ligand steric bulk (Table 1). Among the expanded ring complexes the highest activities were found for six- and seven- membered ligands decorated with bulky 2,6-diisopropylphenyl-substituents (7-Dipp)Pt(dvtms) (**4b**) and (6-Dipp)Pt(dvtms) (**4d**). In comparison with them complexes (6-Mes)Pt(dvtms) (**4a**) and (7-Mes)Pt(dvtms) (**4c**) with less-bulky mesityl- substituents demonstrated decreased activity. The same trend was observed for SIPrPt(dvtms) (**2c**) and SIMesPt(dvtms) (**2d**) couple (Table 2).

Five-membered imidazol-2-ylidene complexes were generally less active in diboration of styrene. Whereas the IMes and backbone-substituted IMes<sup>Me</sup> complexes were inactive, IPr-based complexes showed moderate to good activity; catalytic activity increased in order: H (**2b**) << CH<sub>3</sub> (**2g**) < Br (**2j**)  $\approx$ Cl (**2h**). Such effect may be attributed to the increase in  $\% V_{bur}$  for IPr-ligands bearing substituents at C4 and C5 atoms of imidazole ring [49], larger steric bulk on NHC ligand resulted in higher activity. Interestingly, further increase of NHC steric bulk in complexes **2e** and **2f** resulted in the loss of catalytic activity.

Next, we evaluated activities of (7-Dipp)Pt(dvtms) (**4b**) and (6-Dipp)Pt(dvtms) (**4d**) under low loadings (Table 3). To our delight, decreasing the catalyst loading from 1 to 0.1 mol% did not significantly affect the yields of the desired product for both catalysts. However, when the catalyst loading was further decreased to 0.025 mol%, much lower product yield (67%) was obtained with (6-Dipp)Pt(dvtms) (**4b**), whereas 0.025 mol% of (7-Dipp)Pt(dvtms) (**4d**) afforded product in nearquantitative yield (TON = 3800). Thus, these conditions were selected as the standard conditions for the substrate screening.

	+ B <sub>2</sub> Pin <sub>2</sub> -	catalyst x mol% heptane r.t., air, 20h	BPin Bpin
No.	Catalyst	Catalyst loading, mol9	% Yield, %
	(7-Dipp)Pt(dvtms) ( <b>4d</b> )	1	>99
		0.5	>99
1		( <b>4d</b> ) 0.1	98
		0.025	95
		0.005	20.5
	(6-Dipp)Pt(dvtms) ( <b>4b</b> )	1	>99
r		( <b>4b</b> ) 0.5	>99
2		(40) 0.1	97
		0.025	67
<b>D</b>			

Table 3. Detailed comparison of 4b and 4d activity

Reagents and conditions: styrene (1 equiv.), B<sub>2</sub>Pin<sub>2</sub> (1.1 equiv.), catalyst (x mol%).

Next, we evaluated performance of catalyst **4d** in diboration of terminal alkenes (Table 4). The elaborated catalyst allowed diboration of styrenes bearing alkyl- and alkoxy- substituents and gave products **5b-e** in near quantitative yields. Halogen-substituted styrenes were also suitable substrates, products **5f-g** were obtained with 98-99% yields.



Table 4. (NHC)Platinum(0)-catalyzed diboration of terminal alkenes

Reagents and conditions: alkene 1 equiv., B2Pin2 1.1 equiv., catalyst 0.5 % mol, r.t., 20h.

*Ortho*-substituents on the styrene core were also tolerated; products **5h** and **5i** were isolated in yields of 95 and 98%, respectively. Diboration of allylbenzene, 1-allylnaphtalene and THP-protected

2-allylphenol gave products **5j** (86%), **5k** (82%) and **5l** (90%), respectively. Allyloxybenzenes were diborated in 97-99% yields (Table 4, **5m-o**).

Addition of  $B_2Pin_2$  to alkenes, bearing ester, ketone and acetal groups were efficient, products were obtained in 87-95% yields (Table 4, **5p-r**). Simple aliphatic alkenes were tested under reaction conditions; 1-hexene gave product in 89% yield, whereas 1-vinylcyclohexene was diborated in 92% yield (Table 4, **5s** and **5t** respectively).

### Conclusions

In conclusion, a series of fourteen (NHC)Pt(dvtms) complexes was prepared. Five complexes were reported for the first time: IPr<sup>Me</sup>Pt(dvtms) (**2g**), IPr<sup>Cl</sup>Pt(dvtms) (**2h**), IPr<sup>Br</sup>Pt(dvtms) (**2j**), IMes<sup>Me</sup>Pt(dvtms) (**2i**), (7-Dipp)Pt(dvtms) (**4d**); four of which (**2g**, **2h**, **2j**, and **4d**) were characterized structurally in the solid state using XRD.

Catalytic activities of complexes in diboration of terminal alkenes were evaluated. High catalytic activity of novel expanded-ring seven-membered NHC complex (7-Dipp)Pt(dvtms) (4d) was found. Scope and limitations of elaborated catalyst were examined on 20 examples. Combination of using non-toxic and recoverable alkane solvents, ambient conditions and low loading of catalyst leading to near-quantitative yields of corresponding products seems to us as highly effective and atom-economical method of obtaining valuable 1,2-diborylalkanes.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at

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## **Highlights**

- A series of fourteen Pt(0) complexes with expanded-ring NHCs and 4,5-• disubtituted NHCs were prepared.
- Structures of the novel complexes were described in solid state. ٠
- The catalytic activity of the (NHC)Pt(dvtms) complexes was evaluated for the • alkenes 1,2-diboration.

#### **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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