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A general protocol for the synthesis of Pt-NHC (NHC = N-heterocyclic carbene) hydrosilylation catalysts†

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A general, user-friendly synthetic route to [Pt(NHC)(L)Cl_2] and [Pt(NHC)(dvtms)] (L = DMS, Py; DMS = dimethyl sulfide, dvtms = divinyltetramethylsiloxane, Py = pyridine) complexes has been developed. The procedure is applicable to a wide range of ligands and enables facile synthetic access to key Pt(0)- and Pt(II)-NHC complexes used in hydrosilylation catalysis.

Introduction

The use of N-heterocyclic carbenes (NHCs) as ligands for platinum coordination compounds, as with the other Late Transition-Metals (LTM), has provided key breakthroughs in many research areas over the last two decades.[1] Despite the great success of Pt-NHC complexes, prominent as hydrosilylation catalysts,[2] anticancer drugs[3] or luminescent materials,[4] a general and convenient synthetic protocol to such complexes has yet to be established.[5]

The initial synthetic approach to Pt-NHC complexes, one that has also been used for numerous LTM-NHC complexes, is the one relying on a ligand substitution involving the free carbene and requiring strictly anhydrous conditions. Markó and co-workers employed this methodology to isolate [Pt(NHC)(dvtms)] complexes that act as efficient catalysts in the hydrosilylation of olefins.[2a] In Markó's later work, an improved synthetic route was developed, involving free carbenes generated *in situ* by deprotonation of imidazolium, imidazolidinium and benzimidazolium salts using a strong base (KO^tBu) in tetrahydrofuran (THF).[6] Other common synthetic methods, such as reacting azolium salts with base-containing platinum precursors (*e.g.* [Pt(acac)$_2$])[7] or silver-platinum transmetallation[8,9] have also been employed to yield Pt-NHC complexes. These synthetic routes are multistep or require the pre-installation of a built-in base onto the platinum center. The generation of the free NHC, whether isolated or generated *in situ* also has practical limitations. Another method is oxidative addition of C_2-halogenated azolium cations to platinum (0) species, however its utility is restricted to Pt(II)- and Pt(IV)-NHC complexes.[10]

One of the recent advances in facilitating access to metal-NHC complexes is the development of the weak base route, where a metal precursor reacts with an azolium salt in the presence of a weak base. A significant advantage of this method is the use of cheap and environmentally-friendly reagents and solvents, typically K_2CO_3 and technical grade acetone (or green acetone).[11] Furthermore, the reaction proceeds smoothly under mild, open-to-air conditions and the entire synthesis, including subsequent work-up, is operationally simple.[12] There are now a number of examples of the weak base approach for the preparation of NHC complexes of gold,[12] copper,[13] palladium,[14] rhodium and iridium[15] but its utility for platinum compounds remains largely unexplored.

Although the use of NaOAc in the synthesis of Pt-NHC complexes has been described as early as in 2002,[16a] only a handful of synthetic reports utilizing a weak base have been disclosed so far.[16,17] The existing procedures typically make use of less sustainable approaches of carrying out the reaction in pyridine (and its derivatives)[17] or employ high-boiling DMSO as a solvent[16] and to the best of our knowledge the weak base route has not yet been used with any imidazolium or imidazolidinium salts to yield Pt(0)-NHC complexes.

In the present study, we report on the reactivity of readily available platinum(0) and platinum(II) precursors with imidazolium and imidazolidinium chlorides in the presence of a weak base in sustainable solvents leading to Pt-NHC complexes relevant to, among others, hydrosilylation catalysis.

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†Electronic supplementary information (ESI) available: Copies of NMR spectra. CCDC 2015489–2015494, compounds **2**, **3a**, **3b**, **3c**, **3d** and **3e**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0dt03480k

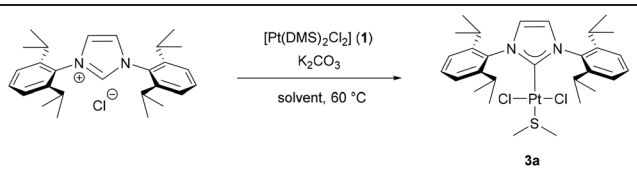
Results and discussion

Optimisation of the protocol

We first investigated the reaction of $[Pt(DMS)_2Cl_2]$ (**1**), a readily available[18] platinum complex, with IPr·HCl (IPr = *N*,*N*′-bis[2,6-(diisopropyl)phenyl]imidazol-2-ylidene)[19] as a model imidazolium salt. When NEt_3 was used as the base in the same manner as in our previous works,[12b] only 17% conversion to the desired complex was achieved, and thus we deemed the carbonate base a more viable option. We examined the impact of the amount of added base and tested both acetone and ethyl acetate, as an even greener alternative to acetone[20] (Table 1). The progress, leading to well-defined Pt-NHC complexes, was simply monitored by ^{1}H NMR spectroscopy. We were pleased to see that all reactions proceeded smoothly to afford the desired $[Pt(IPr)(DMS)Cl_2]$ (**3a**) complex in very good yields. Moreover, ethyl acetate does prove a suitable and attractive alternative to acetone. In view of its lower toxicity[20] and higher boiling point, allowing synthesis at higher temperatures if needed, it may in the future become the solvent of choice for the synthesis of M-NHC complexes. Note here that the amount of K_2CO_3 has a considerable impact on the kinetics of the reaction (Fig. 1). A side-by-side comparison of reactions carried out with 2.0, 4.0 and 8.0 eq. of base showed significant difference in the conversion of IPr·HCl after 1 hour (Table 1, entries 5–7). In fact, with 8.0 eq. the reaction is complete after 1 hour (entry 7). The reaction rate also varies for different NHC salts and is much slower with more sterically demanding NHCs (Fig. 2). For operational simplicity, and since no decomposition was observed even after extended reaction times, the 20-hour period was adopted as standard operating time.

To highlight the ease and efficacy of the weak base route, a gram-scale reaction (2.6 mmol) was performed targeting **3a**. The reaction illustrated in Scheme 1 was simply carried out in air in a scintillation vial.

Table 1 Optimisation of the protocol for model reagents



Entry[a]	Solvent	K_2CO_3 [eq.]	Yield (%)
1	Acetone	2.0	89
2	Acetone	3.0	90
3	Acetone	4.0	91
4	Ethyl acetate	4.0	91
5[b]	Acetone	2.0	69[c]
6[b]	Acetone	4.0	90[c]
7[b]	Acetone	8.0	>99[c]

[a] Reaction conditions: 0.13 mmol of $[Pt(DMS)_2Cl_2]$, 0.13 mmol of IPr·HCl, 1.0 mL of solvent, 60 °C, 20 h. [b] Reaction conditions: 0.064 mmol of $[Pt(DMS)_2Cl_2]$, 0.064 mmol of IPr·HCl, 1.0 mL of acetone, 60 °C, 1 h. [c] Conversion of IPr·HCl after 1 h.

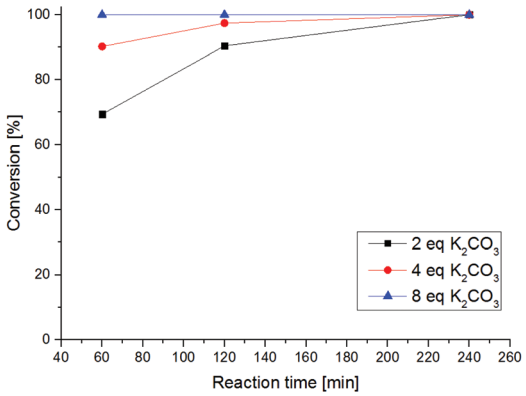


Fig. 1 Time-conversion relations for various amount of base. Reaction conditions: 0.064 mmol of $[Pt(DMS)_2Cl_2]$, 0.064 mmol of IPr·HCl, 1.0 mL of acetone, 60 °C.

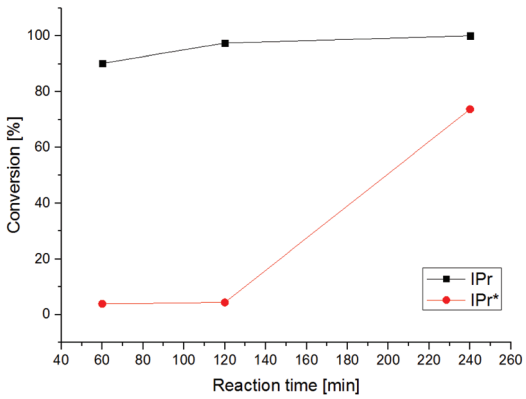
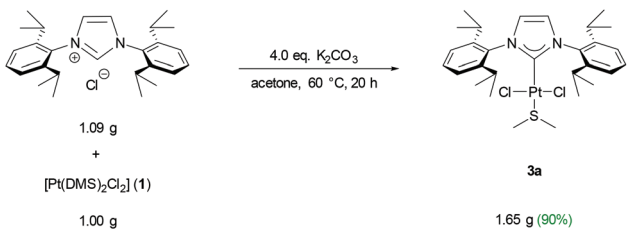


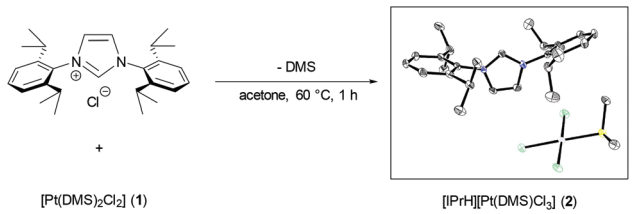
Fig. 2 Time-conversion relations for different NHC salts. Reaction conditions: 0.064 mmol of $[Pt(DMS)_2Cl_2]$, 0.064 mmol of NHC·HCl, 1.0 mL of acetone, 60 °C.



Scheme 1 Large scale synthesis of $[Pt(IPr)(DMS)Cl_2]$ (**3a**).

Identification of the reaction intermediate

An experiment without base was also carried out to confirm the formation of a platinate(II) complex, [IPrH][Pt(DMS)Cl_3] (**2**), as an intermediate (Scheme 2). The identity of **2** was unambiguously confirmed by single-crystal X-ray diffraction analysis on a crystal grown by slow diffusion of *n*-pentane into a saturated acetone solution of **2**. Complex **2** is an air- and moisture-stable complex. The formation of such an intermediate has also been encountered in prior synthetic methods developed



Scheme 2 Synthesis and molecular structure of the platinate(II) complex, [IPrH][Pt(DMS)Cl_3] (**2**).

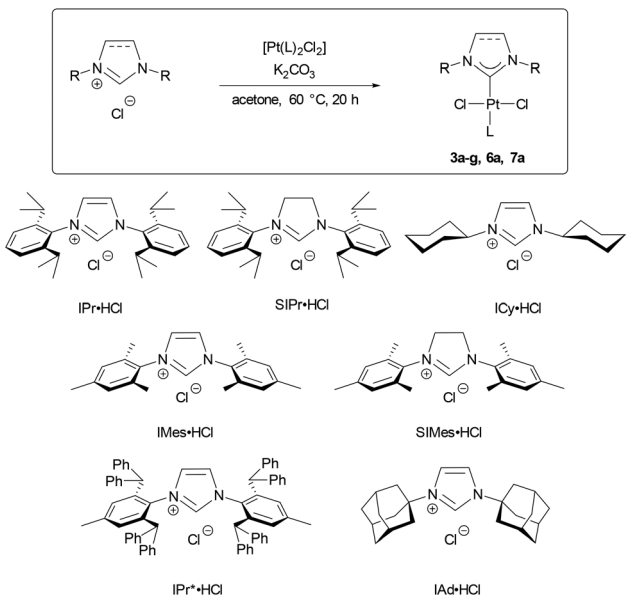
for Au-, Cu- and Pd-NHC systems.[12–14] When **2** is reacted with K_2CO_3 in acetone, complete conversion into **3a** was observed, illustrating the role of **2** as an intermediate along the reaction pathway to **3a**.

Synthesis of novel [Pt(NHC)(DMS)Cl_2] complexes

We next examined if the operationally simple conditions for IPr·HCl could be extended to other [Pt(NHC)(DMS)Cl_2] complexes (**3a–g**) bearing various NHC ligands (Table 2). Our protocol proved successful for most of the tested azolium salts, allowing facile access to the Pt-DMS complexes (**3a–e**) bearing both saturated and unsaturated NHC ligands. A number of these compounds were unambiguously characterised by single-crystal X-ray diffraction technique (Fig. 3). The molecular structure of **3e** is noteworthy, as the two chlorides adopt a mutually *cis* arrangement whereas the presence of larger NHCs (IMes, IPr, IPr* and SIPr) favours the sterically less congested *trans* arrangement around Pt.

Some limitations were encountered as we were unable to obtain [Pt(SIMes)(DMS)Cl_2] (**3f**) and [Pt(IAd)(DMS)Cl_2] (**3g**). An additional reaction with a related platinum precursor, [Pt(DMSO)$_2$$Cl_2$] (**4**), also did not prove successful.

Table 2 Synthesis of [Pt(NHC)(L)Cl_2] complexes



Entry[a]	L	NHC	Product	Yield (%)
1	DMS	IPr	**3a**	91
2	DMS	SIPr	**3b**	60
3	DMS	IPr*	**3c**	79
4	DMS	IMes	**3d**	80
5	DMS	ICy	**3e**	66
6	DMS	SIMes	**3f**	—
7	DMS	IAd	**3g**	—
8[b]	DMSO	IPr	**6a**	—
9[c]	Py	IPr	**7a**	—

[a] Reaction conditions: 0.13 mmol of [Pt(DMS)$_2$$Cl_2$], 0.13 mmol of NHC·HCl, 0.52 mmol of K_2CO_3 (4.0 eq.), 1.0 mL of acetone, 60 °C, 20 h. [b] 0.12 mmol of [Pt(DMSO)$_2$$Cl_2$] and 0.12 mmol of NHC·HCl was used. [c] 0.12 mmol of [Pt(Py)$_2$$Cl_2$] and 0.12 mmol of NHC·HCl was used.

Synthesis of a Pt-PEPPSI-type complex

To further examine the scope of the ligands applicable in our protocol, we attempted the synthesis of PEPPSI-type [Pt(IPr)(Py)Cl_2] (**7a**) complex (PEPPSI = **P**yridine-**E**nhanced **P**recatalyst **P**reparation, **S**tabilization and **I**nitiation). Palladium PEPPSI complexes were developed by Organ and co-workers[21] and their Pt-PEPPSI analogues also appear to be promising pre-catalysts.[17b] As we have shown in our recent studies on the synthetic routes to Pd-PEPPSI complexes[22] the main issue with the commonly employed approach is the use of pyridine as a solvent for the reaction. As a consequence, the reaction requires high temperatures and generates unnecessary pyridine waste. In our previous work, we proposed an improved synthetic protocol utilizing [Pd(Py)$_2$$Cl_2$] instead of [PdCl$_2$] and now the same strategy is employed for the synthesis of a platinum Pt-PEPPSI analogue, [Pt(IPr)(Py)Cl_2] (**7a**). Unfortunately, similar to the case of [Pt(DMSO)$_2$$Cl_2$], the reaction of [Pt(Py)$_2$$Cl_2$] (**5**) and IPr·HCl did not proceed cleanly, but resulted in the formation of multiple products, none of which being

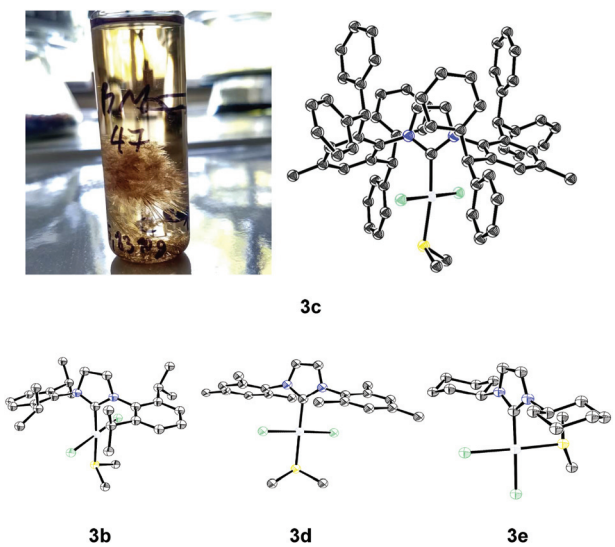
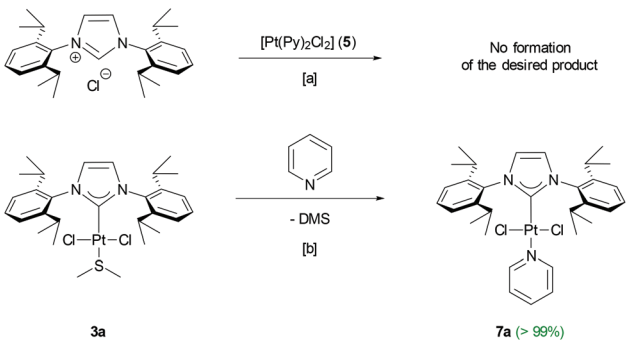


Fig. 3 Crystals of [Pt(IPr*)(DMS)Cl_2] (**3c**) in *n*-pentane and molecular structures of [Pt(NHC)(DMS)Cl_2] (NHC = SIPr (**3b**), IPr* (**3c**), IMes (**3d**), ICy (**3e**)) showing thermal displacement ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

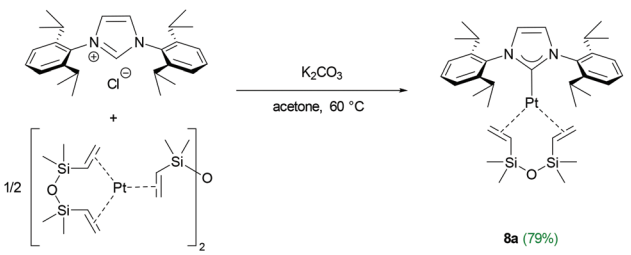
the targeted [Pt(IPr)(Py)Cl_2] (Table 2). In search of an alternative route, we thought of a simple ligand-exchange reaction by substituting the labile DMS ligand in **3a** with pyridine. Gratifyingly, when [Pt(IPr)(DMS)Cl_2] was reacted with 4.0 eq. of pyridine in acetone at 60 °C the desired complex **7a** was formed in nearly quantitative yield (Scheme 3). It should be noted that an analogous reaction with DMSO instead of pyridine did not lead to the desired [Pt(IPr)(DMSO)Cl_2].

Synthesis of a Pt(0)-NHC complex

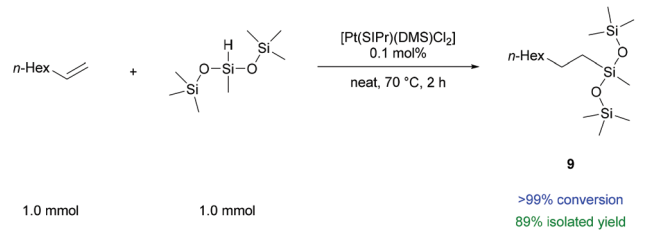
To test the extent of the methodology, a Pt(0) complex, [Pt(IPr)(dvtms)], was targeted (Scheme 4). This class of catalysts has facilitated major breakthroughs in catalytic hydrosilylation due to their unprecedented selectivity and stability.[2a] Some of the complexes of this family are commercially available,[23] yet, to the best of our knowledge, their synthesis relies on *in situ* generated carbene formation followed by metalation. Applying the weak base approach for this family of compounds would be again, a major improvement. To test the viability and practicality of the method to Pt(0) synthons, we examined the reaction of [Pt_2(dvtms)$_3$] (Karstedt's catalyst)[24] with IPr·HCl in the presence of K_2CO_3 and were able to obtain the targeted [Pt(IPr)(dvtms)] complex (**8a**) in very good yield (Scheme 4).



Scheme 3 Synthetic routes to [Pt(IPr)(Py)Cl_2] (**7a**). Reaction conditions: 0.13 mmol of [Pt(py)$_2Cl_2$], 0.13 mmol of IPr·HCl, 0.52 mmol of K_2CO_3 (4.0 eq.), 1.0 mL of acetone, 60 °C, 20 h. [b]Reaction conditions: 0.13 mmol of [Pt(IPr)(DMS)Cl_2], 0.52 mmol of pyridine (4.0 eq.), 1.0 mL of acetone, 60 °C, 20 h.



Scheme 4 Synthesis of [Pt(IPr)(dvtms)] (**8a**). Reaction conditions: 0.13 mmol of [Pt_2(dvtms)$_3$], 0.26 mmol of IPr·HCl, 1.04 mmol of K_2CO_3 (4.0 eq.), 1.0 mL of acetone, 60 °C, 20 h.



Scheme 5 Hydrosilylation of 1-octene.

Catalytic test

In order to showcase the catalytic activity of the new [Pt(NHC)(DMS)Cl_2] complexes in olefin hydrosilylation, a solventless and open-to-air reaction between 1-octene and 1,1,1,3,5,5,5-heptamethyltrisiloxane using 0.1 mol% of [Pt(SIPr)(DMS)Cl_2] (**3b**) was carried out (Scheme 5). The reaction proceeded as expected and permitted the isolation of the desired 1,1,1,3,5,5,5-heptamethyl-3-octyltrisiloxane (**9**) in high yield (see Experimental section for the details).

Experimental

Materials and methods

All reactions were performed in glass vials under air. Solvents and reagents were used as received without any additional purification. Elemental analyses were performed at London Metropolitan University, 166–220 Holloway Road, London, N7 8DB and Université de Namur, Rue de Bruxelles 55, B-5000 Namur, Belgium. ^{1}H and ^{13}C–{^{1}H} NMR spectra were recorded in $CDCl_3$ using a Bruker 300 MHz spectrometer. All chemical shifts are quoted in parts per million relative to the $CHCl_3$ solvent residue (δ 7.26 ppm). ^{1}H NMR splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), triplet of triplets (tt), heptet (hept), multiplet (m). [Pt_2(dvtms)$_3$] was obtained from Umicore (HS220) and [Pt(DMS)$_2Cl_2$] (**1**) was synthesized following the procedure described in the literature.[18] The reported yields correspond to isolated products and have been reproduced at least two times for each case.

Synthesis of the platinate [IPr·H][Pt(DMS)Cl_3] (2) intermediate

A vial was charged with [Pt(DMS)$_2Cl_2$] (**1**) (50 mg, 0.13 mmol, 1.0 eq.), IPr·HCl (54 mg, 0.13 mmol, 1.0 eq.) and acetone (0.6 mL). The reaction mixture was stirred at 60 °C for 1 h. After this time, the reaction volatiles were removed under vacuum, affording 104 mg of an orange microcrystalline solid (**2**). The [Pt(DMS)Cl_3]$^-$ anion was found to be in an equilibrium with [Pt(DMS)$_2Cl_2$] (see ESI† for the copy of ^{1}H NMR). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 9.53 (t, J = 1.4 Hz, 1H; N–C**H**–N), 8.06 (d, J = 1.4 Hz, 2H; NC**H**=C**H**N), 7.55 (t, J = 8.1, 7.6 Hz, 2H; C**H**$_{Ar}$), 7.33 (d, J = 7.8 Hz, 4H; C**H**$_{Ar}$), 2.52 (s, 6H; S(C**H**$_3$)$_2$), 2.44 (hept, J = 6.8 Hz, 4H; C**H**(CH$_3$)$_2$), 1.27 (d, J = 6.8 Hz, 12H; CH(C**H**$_3$)$_2$), 1.23 (d, J = 6.9 Hz, 12H; CH(C**H**$_3$)$_2$).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 145.2 ($\mathbf{C}^{IV}_{Ar}$), 137.9 (N–**C**–N), 132.2 ($\mathbf{C}H_{Ar}$), 130.0 ($\mathbf{C}^{IV}_{Ar}$), 127.0 (N**C**H=**C**HN), 124.8 ($\mathbf{C}H_{Ar}$), 29.2 ($\mathbf{C}H(CH_3)_2$), 24.7 ($CH(\mathbf{C}H_3)_2$), 24.1 ($CH(\mathbf{C}H_3)_2$), 23.1 ($S(\mathbf{C}H_3)_2$).

Synthesis of [Pt(NHC)(DMS)Cl_2] (3a–e) complexes

General procedure. A vial was charged with [Pt$(DMS)_2Cl_2$] (**1**) (50 mg, 0.13 mmol, 1.0 eq.), NHC·HCl (0.13 mmol, 1.0 eq.), freshly dried and crushed K_2CO_3 (72 mg, 0.52 mmol, 4.0 eq.) and acetone (1.0 mL). The reaction mixture was stirred at 60 °C for 20 h. After this time, the reaction volatiles were removed under vacuum, 1.0 mL of CH_2Cl_2 was added and the resulting mixture was filtered through a 2 cm layer of silica gel in a Pasteur pipette. The silica gel was washed with 5.0 mL of CH_2Cl_2 and the solvent was then evaporated to dryness to yield a solid, which was then precipitated from a concentrated solution in CH_2Cl_2 using cold *n*-pentane and dried overnight in a vacuum oven at room temperature.

Synthesis of [Pt(IPr)(DMS)Cl_2] (3a)

According to the general procedure, **3a** was obtained as an off-white microcrystalline solid (84 mg, 91%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.48 (t, J = 8.0 Hz, 2H; $\mathbf{C}H_{Ar}$), 7.31 (d, J = 7.5 Hz, 4H; $\mathbf{C}H_{Ar}$), 7.09 (s, 2H; NC**H**=C**H**N), 3.11 (hept, J = 6.8 Hz, 4H; $\mathbf{C}H(CH_3)_2$), 2.03 (s, 6H; $S(\mathbf{C}H_3)_2$), 1.42 (d, J = 6.6 Hz, 12H; $CH(\mathbf{C}H_3)_2$), 1.11 (d, J = 6.9 Hz, 12H; $CH(\mathbf{C}H_3)_2$). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 152.4 (N–**C**–N), 146.6 ($\mathbf{C}^{IV}_{Ar}$), 135.3 ($\mathbf{C}^{IV}_{Ar}$), 130.1 ($\mathbf{C}H_{Ar}$), 124.2 (N**C**H=**C**HN), 123.9 ($\mathbf{C}H_{Ar}$), 28.7 ($\mathbf{C}H(CH_3)_2$), 26.3 ($CH(\mathbf{C}H_3)_2$), 23.1 ($CH(\mathbf{C}H_3)_2$), 20.1 ($S(\mathbf{C}H_3)_2$). **Elemental analysis**: expected [%]: C 48.60, H 5.91, N 3.91. Found: C 48.21, H 5.93, N 3.73.

Synthesis of [Pt(SIPr)(DMS)Cl_2] (3b)

According to the general procedure, **3b** was obtained as an off-white microcrystalline solid (55 mg, 60%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.39 (t, J = 7.6 Hz, 2H; $\mathbf{C}H_{Ar}$), 7.25 (d, J = 7.6 Hz, 4H; $\mathbf{C}H_{Ar}$), 4.05 (s, 4H; $\mathbf{C}H_2$–$\mathbf{C}H_2$), 3.50 (hept, J = 6.5 Hz, 4H; $\mathbf{C}H(CH_3)_2$), 1.98 (s, 6H; $S(\mathbf{C}H_3)_2$), 1.48 (d, J = 6.6 Hz, 12H; $CH(\mathbf{C}H_3)_2$), 1.25 (d, J = 6.9 Hz, 12H; $CH(\mathbf{C}H_3)_2$). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 179.7 (N–**C**–N), 147.5 ($\mathbf{C}^{IV}_{Ar}$), 135.7 ($\mathbf{C}^{IV}_{Ar}$), 129.2 ($\mathbf{C}H_{Ar}$), 124.3 ($\mathbf{C}H_{Ar}$), 54.0 (N$\mathbf{C}H_2$–$\mathbf{C}H_2$N), 28.8 ($\mathbf{C}H(CH_3)_2$), 26.9 ($CH(\mathbf{C}H_3)_2$), 24.0 ($CH(\mathbf{C}H_3)_2$), 20.0 ($S(\mathbf{C}H_3)_2$). **Elemental analysis**: expected [%]: C 48.46, H 6.17, N 3.90. Found: C 48.38, H 5.89, N 3.63.

Synthesis of [Pt(IPr*)(DMS)Cl_2] (3c)

According to the general procedure, **3c** was obtained as an off-white microcrystalline solid (126 mg, 79%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.47–7.36 (m, 8H; $\mathbf{C}H_{Ar}$), 7.30–7.13 (m, 12H; $\mathbf{C}H_{Ar}$), 7.10–6.92 (m, 12H; $\mathbf{C}H_{Ar}$), 6.78–6.60 (m, 12H; $\mathbf{C}H_{Ar}$), 6.20 (s, 4H; $\mathbf{C}H(Ph)_2$), 4.81 (s, 2H; NC**H**=C**H**N), 2.38 (s, 6H; $S(\mathbf{C}H_3)_2$), 2.19 (s, 6H; $\mathbf{C}H_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 148.9 (N–**C**–N), 144.6 ($\mathbf{C}^{IV}_{Ar}$), 144.5 ($\mathbf{C}^{IV}_{Ar}$), 141.7 ($\mathbf{C}^{IV}_{Ar}$), 138.3 ($\mathbf{C}^{IV}_{Ar}$), 135.2 ($\mathbf{C}^{IV}_{Ar}$), 130.6 ($\mathbf{C}H_{Ar}$), 130.6 ($\mathbf{C}H_{Ar}$), 129.5 ($\mathbf{C}H_{Ar}$), 128.2 ($\mathbf{C}H_{Ar}$), 128.0 ($\mathbf{C}H_{Ar}$), 126.2 ($\mathbf{C}H_{Ar}$), 126.1 ($\mathbf{C}H_{Ar}$), 123.0 (N**C**H=**C**HN), 50.9 ($CH(Ph)_2$), 22.0 ($\mathbf{C}H_3$), 20.5 ($S(\mathbf{C}H_3)_2$). **Elemental analysis**: expected [%]: C 68.70, H 5.03, N 2.26. Found: C 68.64, H 4.67, N 0.46.

Synthesis of [Pt(IMes)(DMS)Cl_2] (3d)

According to the general procedure, **3d** was obtained as an off-white microcrystalline solid (65 mg, 80%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.02 (s, 2H; NC**H**=C**H**N), 7.00 (s, 4H; $\mathbf{C}H_{Ar}$), 2.35 (s, 6H; $\mathbf{C}H_3$), 2.31 (s, 12H; $\mathbf{C}H_3$), 2.03 (s, 6H; $S(\mathbf{C}H_3)_2$). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 151.0 (N–**C**–N), 139.0 ($\mathbf{C}^{IV}_{Ar}$), 136.2 ($\mathbf{C}^{IV}_{Ar}$), 135.5 ($\mathbf{C}^{IV}_{Ar}$), 129.1 ($\mathbf{C}H_{Ar}$), 123.2 (N**C**H=**C**HN), 21.3 ($\mathbf{C}H_3$), 20.1 ($S(\mathbf{C}H_3)_2$), 19.0 ($\mathbf{C}H_3$). **Elemental analysis**: expected [%]: C 43.67, H 4.78, N 4.43. Found: C 43.87, H 4.53, N 3.62.

Synthesis of [Pt(ICy)(DMS)Cl_2] (3e)

According to the general procedure, **3e** was obtained as an off-white microcrystalline solid (47 mg, 66%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 6.96 (s, 2H; NC**H**=C**H**N), 5.28–5.12 (m, 2H, NC**H**), 2.54 (s, 6H; $S(\mathbf{C}H_3)_2$), 2.37–2.23 (m, 2H; $\mathbf{C}H_2$), 1.97–1.70 (m, 8H; $\mathbf{C}H_2$), 1.66–1.34 (m, 8H; $\mathbf{C}H_2$), 1.22 (tt, J = 12.8, 3.4 Hz, 2H; $\mathbf{C}H_2$). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 141.7 (N–**C**–N), 117.9 (N$\mathbf{C}H_2$=$\mathbf{C}H_2$N), 59.9 (N**C**H), 34.3 ($\mathbf{C}H_2$), 33.7 ($\mathbf{C}H_2$), 25.7 ($\mathbf{C}H_2$), 25.3 ($\mathbf{C}H_2$), 23.8 ($S(\mathbf{C}H_3)_2$). **Elemental analysis**: expected [%]: C 36.43, H 5.40, N 5.00. Found: C 36.42, H 5.15, N 4.89.

Synthesis of [Pt(IPr)(Py)Cl_2] (7a)

A vial was charged with [Pt(IPr)(DMS)Cl_2] (**3a**) (50 mg, 0.07 mmol, 1.0 eq.), pyridine (22 µl, 0.28 mmol, 4.0 eq.) and acetone (1.0 mL). The reaction mixture was stirred at 60 °C for 20 h. After this time, the volatiles were evaporated under reduced pressure and the obtained solid was dried overnight in a vacuum oven at room temperature, affording the desired complex **7a** as an off-white microcrystalline solid (51 mg, 99%). NMR analysis is in accordance with the literature data.[25] **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.57 (dt, J = 5.2, 1.6 Hz, 2H), 7.56 (tt, J = 7.6, 1.7 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.32 (d, J = 7.5 Hz, 4H), 7.17–7.08 (m, 2H), 7.09 (s, 2H), 3.19 (hept, J = 6.7 Hz, 4H), 1.47 (d, J = 6.6 Hz, 12H), 1.14 (d, J = 6.9 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 151.5, 146.7, 137.4, 135.5, 130.1, 124.5, 124.2, 124.0, 28.8, 26.3, 23.2.

Synthesis of [Pt(IPr)(dvtms)Cl_2] (8a)

A vial was charged with [Pt_2(dvtms)$_3$] (123 mg, 0.13 mmol, 0.5 eq. (1.0 eq. Pt)), IPr·HCl (109 mg, 0.26 mmol, 1.0 eq.), freshly dried and crushed K_2CO_3 (288 mg, 1.04 mmol, 4.0 eq.) and acetone (1.0 mL). The reaction mixture was stirred at 60 °C for 20 h. After this time, the reaction volatiles were removed under vacuum, 1.0 mL of CH_2Cl_2 was added and the resulting mixture was filtered through a 2 cm layer of silica gel in a Pasteur pipette. The silica gel was washed with 5.0 mL of CH_2Cl_2, the solvent was then evaporated to dryness and the obtained solid was recrystallized from a minimal amount of hot 2-propanol, affording the desired complex **8a** as a colorless microcrystalline solid (158 mg, 79%). NMR analysis is in

accordance with the literature data.[26] **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.35 (t, J = 7.8 Hz, 2H), 7.20 (s, 2H), 7.17 (d, J = 7.7 Hz, 4H), 2.98 (hept, J = 6.7 Hz, 4H), 1.69 (d, J = 11.3 Hz, 2H), 1.53–1.33 (m, 4H), 1.24 (d, J = 6.8 Hz, 12H), 1.13 (d, J = 6.8 Hz, 12H), 0.13 (s, 6H), −0.76 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 186.1, 145.9, 136.8, 129.5, 124.0, 123.7, 41.9, 35.6, 28.5, 26.0, 22.6, 1.7, −2.2.

Hydrosilylation of 1-octene

A vial was charged with [Pt(IPr)(DMS)Cl_2] (**3b**) (0.1 ml of 0.01 mmol mL^{-1} solution in toluene, 0.1 mol%), toluene was removed under vacuum and 1,1,1,3,5,5,5-heptamethyltrisiloxane (222 mg, 1.0 mmol, 1.0 eq.) was added. The mixture was stirred at 70 °C for 60 min. After this time, 1-octene (112 mg, 1.0 mmol, 1.0 eq.) was added dropwise over the course of 5 min. The resulted mixture was stirred at 70 °C for 120 min. The colorless solution was then cooled to room temperature, filtered through a pad of silica gel/Celite/$MgSO_4$ (v/v/v 1 : 1 : 1), using 10.0 mL of *n*-hexane and the volatiles were removed under vacuum affording 297 mg (89%) of the desired 1,1,1,3,5,5,5-heptamethyl-3-octyltrisiloxane (**9**) as a colorless liquid. NMR analysis is in accordance with the literature data.[27] **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 1.38–1.17 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H), 0.45 (t, J = 7.7 Hz, 2H), 0.09 (s, 18H), 0.01 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 33.4, 32.1, 29.5, 29.4, 23.2, 22.8, 17.8, 14.3, 2.0, −0.1.

Conclusions

In summary, a new,[28] convenient protocol for the synthesis of Pt(0) and Pt(II) N-heterocyclic carbene complexes has been developed. The platinate, an intermediate along the reaction pathway, has been isolated and its molecular structure was determined. Five new well-defined pre-catalysts of the formula [Pt(NHC)(DMS)Cl_2] have been synthesized and fully characterised. The established protocol was tested in the synthesis of commercially available [Pt(IPr)(dvtms)] (**8a**) and proven to be an excellent alternative to the previously reported synthetic methods. One of the new complexes, [Pt(SIPr)(DMS)Cl_2], has been tested in the hydrosilylation of 1-octene and proved to be an efficient pre-catalyst. Ongoing studies are aimed at the optimisation of the reaction conditions and structure-activity relationship of the novel [Pt(NHC)(DMS)Cl_2] complexes in hydrosilylation of olefins.

Conflicts of interest

There are no conflicts to declare.

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