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ARTICLE TYPE

## Selective Synthesis of *Cis*- and *Trans*-[(NHC<sup>Me</sup>)<sub>2</sub>PtCl<sub>2</sub>] and [NHC<sup>Me</sup>Pt(cod)Cl][NHC<sup>Me</sup>PtCl<sub>3</sub>] using NHC<sup>Me</sup>SiCl<sub>4</sub>

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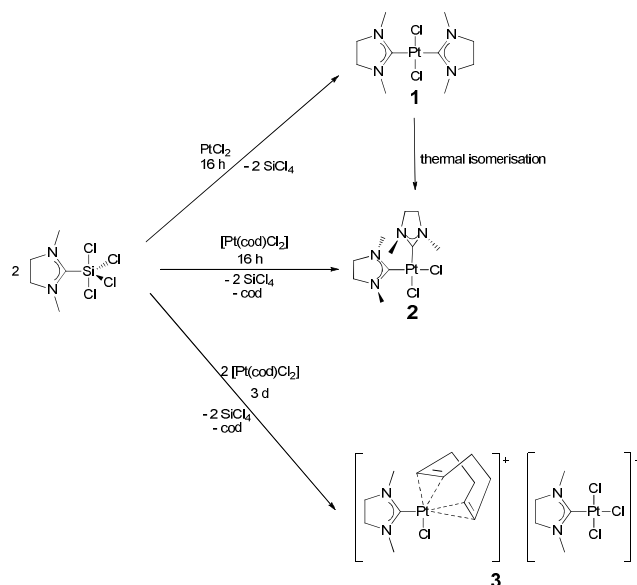
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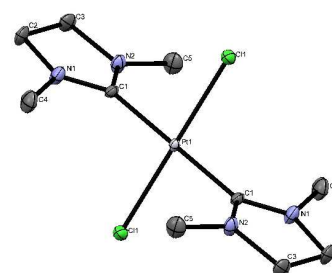
NHC<sup>Me</sup>SiCl<sub>4</sub>, (NHC<sup>Me</sup> = 1,3-dimethylimidazolidin-2-ylidene), was used to synthesise novel NHC<sup>Me</sup>-Pt(II) complexes. An atypical *trans-cis* isomerisation process has also been achieved for [(NHC<sup>Me</sup>)<sub>2</sub>PtCl<sub>2</sub>], while the synthesis of the unique double-complex salt, [(NHC<sup>Me</sup>)Pt(cod)Cl][NHC<sup>Me</sup>PtCl<sub>3</sub>] (NHC<sup>Me</sup> = 1,5-cyclooctadiene), revealed the first-ever N-heterocyclic carbene analogue of the Cossa's salt anion.

Metal complexes of N-heterocyclic carbenes (NHCs) have been established in organometallic chemistry and catalysis.<sup>1-4</sup> Another burgeoning field for such complexes is in medicine, where NHC complexes are finding valuable applications as antibiotic and anti-cancer agents.<sup>5-11</sup> The rational design, and synthesis, of metal-carbene complexes have benefited from several approaches.<sup>12, 13</sup> Among these, the use of NHC<sup>Me</sup>SiCl<sub>4</sub> shows huge efficacy for providing a low-cost, high-yielding, synthetic route to NHC-metal complexes when a saturated, non-bulky NHC is desired.<sup>14</sup> Our interest in NHC<sup>Me</sup>-Pt(II) complexes seeks primarily to provide promising candidates for testing in anti-cancer studies.

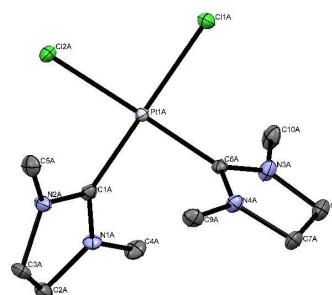
The facile reaction of PtCl<sub>2</sub> with 2 equivalents of NHC<sup>Me</sup>SiCl<sub>4</sub><sup>†</sup> (Scheme 1) gave exclusively *trans*-[(NHC<sup>Me</sup>)<sub>2</sub>PtCl<sub>2</sub>] (**1**) (Fig. 1)



Scheme 1 Reactions of NHC<sup>Me</sup>SiCl<sub>4</sub> with PtCl<sub>2</sub> and [Pt(cod)Cl<sub>2</sub>].



1



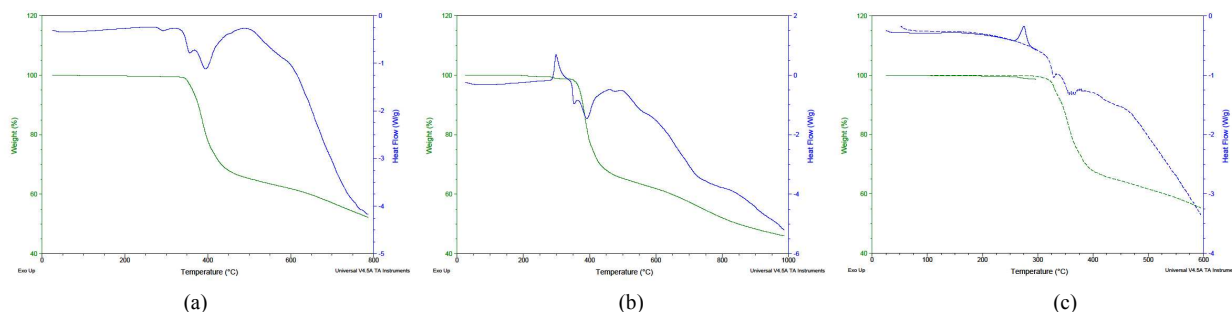
2

Fig. 1 Crystal structures for **1** and **2**, with ellipsoids set at 50% probability. All hydrogen atoms have been omitted for clarity.

Table 1 Selected bond lengths and angles

Selected bond lengths for <b>1</b> /Å		Selected angles for <b>1</b> /°	
Pt <sub>1</sub> -C <sub>1</sub>	2.027(2)	C <sub>1</sub> -Pt <sub>1</sub> -C <sub>1</sub>	180.0
Pt <sub>1</sub> -Cl <sub>1</sub>	2.3087(7)	Cl <sub>1</sub> -Pt <sub>1</sub> -Cl <sub>1</sub>	180.0
Selected bond lengths for <b>2</b> /Å		Selected angles for <b>2</b> /°	
Pt <sub>1A</sub> -C <sub>1A</sub>	1.967(3)	C <sub>1A</sub> -Pt <sub>1A</sub> -Cl <sub>1A</sub>	178.49(8)
Pt <sub>1A</sub> -C <sub>6A</sub>	1.971(3)	C <sub>6A</sub> -Pt <sub>1A</sub> -Cl <sub>2A</sub>	177.32(8)
Pt <sub>1A</sub> -Cl <sub>1A</sub>	2.3770(7)	Cl <sub>2A</sub> -Pt <sub>1A</sub> -Cl <sub>1A</sub>	91.75(2)
Pt <sub>1A</sub> -Cl <sub>2A</sub>	2.3734(7)	C <sub>1A</sub> -Pt <sub>1A</sub> -C <sub>6A</sub>	90.51(11)

as a pale yellow crystalline solid. This was in contrast to the product from the corresponding PdCl<sub>2</sub> reaction,<sup>14</sup> where the *cis* complex product was reported. *Cis*-complexes of platinum, in particular those with minimal steric hindrance,<sup>7, 8</sup> are regarded as the preferred configuration for the purpose of testing for anti-tumour properties. Considering that substitution reactions on a square-planar platinum(II) complex may preserve the original



**Figure 2** TGA/DSC Graphs for (a) **2**, (b) **1** and (c) Overlay of **1** heating up to 300 °C (solid) and cooled sample heating up to 600 °C (dashed).

5 geometry, the reaction of  $[\text{Pt}(\text{cod})\text{Cl}_2]$  with 2 equivalents of  $\text{NHC}^{\text{Me}}\text{SiCl}_4$ † (Scheme 1) was carried out, and this successfully yielded *cis*- $[(\text{NHC}^{\text{Me}})_2\text{PtCl}_2]$  (**2**) (Fig. 1) as the sole product. From NMR analysis, complexes **1** and **2** are distinguishable, in particular from  $^{195}\text{Pt}$  NMR, which showed a significant upfield

10 shift at -3730.20 ppm for the *cis* complex, **2**, compared to that for the *trans*-complex, **1**, at -3271.09 ppm. Both signals are in agreement with  $^{195}\text{Pt}$  NMR reported for other Pt(II)-NHCs.<sup>7, 15, 16</sup> Thermogravimetric Analysis (TGA) with Differential Scanning Calorimetry (DSC) was carried out for the two isomers

15 of  $[(\text{NHC}^{\text{Me}})_2\text{PtCl}_2]$  (Figure 2). The initial weight loss at decomposition, for both complexes, corresponds to the loss of the NHC ligands. In the TGA/DSC spectrum for **1** (Figure 2b), an exothermic process occurs before any significant loss of mass, and the final decomposition process at 320 °C. An irreversible

20 *trans-cis* isomerisation was suspected, and confirmed when the *trans* complex was heated to 300 °C (*i.e.* after the exothermic transition without loss of mass) and NMR spectra of the resulting material obtained. The  $^1\text{H}$  and  $^{195}\text{Pt}$  signals corresponded solely to the *cis*-complex. In addition, the TGA/DSC spectrum of the

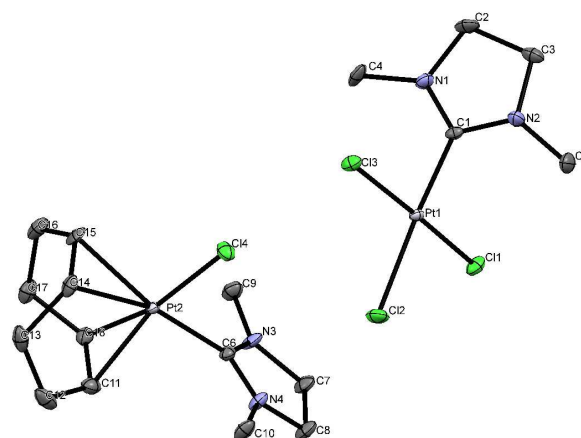
25 material obtained after an initial cycle of heating to 300 °C and cooling to room temperature (Figure 2c) showed the identical spectrum to that for **2** (Figure 2a). This is the first reported thermally induced *trans-cis* isomerisation for a bis-NHC platinum complex, which is in direct contrast to the *cis-trans* isomerisation

30 reported for similar bis-NHC-platinum(II) species.<sup>17</sup> Such non-typical *trans-cis* isomerisations of platinum coordination compounds were first reported for amino-<sup>18</sup> and bis-pentamethylsulfide-<sup>19</sup> platinum(II) derivatives, where it was suggested that increased stability may be related to crystal

35 structure effects. The NHC-platinum complex shows greater thermodynamic stability when the (sufficiently small)<sup>19</sup> NHC is in a *trans* position to the halide ligand. Such observations can also be made from earlier work on platinum-NHC coordination compounds by Lappert,<sup>20-22</sup> and even more recent reports.<sup>2, 23, 24</sup>

40 From the crystal structures, the conformation of the NHC ligands is oriented to minimise any steric hindrance.<sup>25</sup> Still, under appropriate conditions, **1** shows greater kinetic stability, similar to the complexes also reported by Lappert.<sup>20</sup>

45 During initial attempts to synthesise **2**, when  $\text{NHC}^{\text{Me}}\text{SiCl}_4$  was utilised as the limiting reagent, a second, easily-crystallisable, and visually distinguishable complex product was isolated. The bright yellow crystals were characterised by X-Ray crystallography (Figure 3) and shown to be a double complex



**Fig. 3** Crystal structure for **3** with ellipsoids set at 50% probability. All hydrogen atoms have been omitted for clarity.

**Table 2** Selected bond lengths and angles for **3**.

Selected bond lengths/Å	Selected angles/°
Pt <sub>1</sub> -C <sub>1</sub> 1.953(3)	C <sub>1</sub> -Pt <sub>1</sub> -Cl <sub>2</sub> 175.24(9)
Pt <sub>1</sub> -Cl <sub>1</sub> 2.3085(8)	Cl <sub>1</sub> -Pt <sub>1</sub> -Cl <sub>3</sub> 175.81(3)
Pt <sub>1</sub> -Cl <sub>2</sub> 2.3720(8)	
Pt <sub>1</sub> -Cl <sub>3</sub> 2.3222(8)	
Pt <sub>2</sub> -C <sub>6</sub> 2.003(3)	
Pt <sub>2</sub> -Cl <sub>4</sub> 2.3165(8)	
Pt <sub>2</sub> -C <sub>11</sub> 2.165(3)	
Pt <sub>2</sub> -C <sub>14</sub> 2.265(3)	
Pt <sub>2</sub> -C <sub>15</sub> 2.257(3)	
Pt <sub>2</sub> -C <sub>18</sub> 2.178(3)	

65 salt,  $[(\text{NHC}^{\text{Me}})\text{Pt}(\text{cod})\text{Cl}][(\text{NHC}^{\text{Me}})\text{PtCl}_3]$  (**3**). Subsequently, when the reaction of  $[\text{Pt}(\text{cod})\text{Cl}_2]$  with  $\text{NHC}^{\text{Me}}\text{SiCl}_4$  was carried out in a 1:1 ratio in a highly polar solvent† (to enhance the formation of an ionic salt), and prolonged heating, **3** was

70 selectively obtained (Scheme 1). The complex salt was further characterised by multi-nuclear and 2D NMR techniques.† The  $^{195}\text{Pt}$  NMR spectrum showed two signals; one at an upfield shift of -3542.34 ppm, thought to be the cationic complex component of **3**, and the other at -2930.61 ppm, for the anionic complex

75 component. While similar cationic platinum(II) complexes are known,<sup>26-28</sup> to the best of our knowledge,  $[\text{Pt}(\text{NHC}^{\text{Me}})\text{Cl}_3]^+$  is the first-reported N-heterocyclic carbene analogue of the Cossa's salt anion.<sup>29</sup> The *cis* and *trans* effects of ligands in  $[\text{PtLCl}_3]$

analogues can be easily compared,<sup>30</sup> particularly with respect to the chloride ligands, which have significance for anti-tumour agents.

Multi-nuclear platinum complexes offer further interest for potential electrochemical properties.<sup>31, 32</sup> The double-complex salt, **3**, poses a unique candidate, since both the cation and anion complexes contain an NHC ligand.

## Conclusions

Diverse forms of platinum(II)-NHC complexes have been readily prepared by the use of an inexpensive and efficient carbene transfer reagent, NHC<sup>Me</sup>SiCl<sub>4</sub>. In the literature, anti-tumour activity has been considered for neutral *cis*- and *trans*-platinum(II) complexes, as well as for cod-substituted platinum(II) complexes,<sup>33</sup> and even trichloro-platinum(II) complexes.<sup>34</sup> We expect our findings to contribute promising candidates for testing in anti-cancer studies, as well as to improve the rational design of complexes that are supported by a non-bulky NHC. While platinum(II)-NHC complexes are also useful in catalyst design, herein has also been shown the potential for NHC double-complex salts to be considered for materials with electrochemical properties.

## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: [details of experimental, XRD and TGA/DSC analysis are given]. See DOI: 10.1039/b000000x/

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# Selective Synthesis of *Cis*- and *Trans*- $[(\text{NHC}^{\text{Me}})_2\text{PtCl}_2]$ and $[\text{NHC}^{\text{Me}}\text{Pt}(\text{cod})\text{Cl}][\text{NHC}^{\text{Me}}\text{PtCl}_3]$ using $\text{NHC}^{\text{Me}}\text{SiCl}_4$

Lesley C. Lewis-Alleyne,\* Bassem S. Bassil, Tobias Böttcher and Gerd-Volker Röschenthaler\*

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$\text{NHC}^{\text{Me}}\text{SiCl}_4$  was used to selectively synthesise *cis* and *trans*- $[(\text{NHC}^{\text{Me}})_2\text{PtCl}_2]$ , as well as  $[\text{NHC}^{\text{Me}}\text{Pt}(\text{cod})\text{Cl}][\text{NHC}^{\text{Me}}\text{PtCl}_3]$ , which revealed the first ever N-heterocyclic carbene analogue of the Cossa's salt anion.

