

## Synthesis of electron-rich platinum centers: Platinum<sup>0</sup>(carbene)(alkene)<sub>2</sub> complexes

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### Abstract

The synthesis and molecular structure of the zero-valent platinum-mono-carbene-bis-alkene complexes [Pt<sup>0</sup>(NHC)(dimethyl fumarate)<sub>2</sub>] (NHC = 1,3-dimesityl-imidazol-2-ylidene (**1a**); 1,3-dimesityl-dihydroimidazol-2-ylidene (**2a**); diphenyl-dihydroimidazol-2-ylidene (**2b**)) are described. Two routes have been evaluated for the synthesis of **1a** and **2a**, involving reaction of a zero-valent platinum compound either with an isolated carbene ligand, or with an in situ generated carbene ligand. The in situ method proved to be easier and gave similar yields of about 50% after crystallization. Attempts have been made to synthesize similar compounds with *N*-phenyl and *N*-alkyl groups, of which the latter met with little success. However, (1,3-diphenyl-dihydroimidazol-2-ylidene)-bis(η<sup>2</sup>-dimethyl fumarate) platinum(0) (**2b**) could be obtained in 49% yield, after crystallization, from the appropriate *Wanzlick* dimer.

Compound **1a** reacts with H<sub>2</sub> and D<sub>2</sub> in sequences of oxidative addition, migration–insertion involving dimethyl fumarate, and reductive elimination to form neutral hydrido platinum (II) carbene complexes, probably containing a metallacyclic (R)–C=O...Pt unit.

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**Keywords:** N-Heterocyclic carbene; Alkene; Low-valent; Insertion; Addition; C–H activation

### 1. Introduction

N-Heterocyclic carbenes (NHCs) are being applied more and more frequently as ligands in metal-mediated synthesis and homogeneous catalysis [1,2]. For almost all d<sup>10</sup>-metals, complexes with NHC ligands have been reported, which are able to catalyze reactions, such as Heck and Suzuki coupling (Pd, Ni) [3–7], aryl amination (Pd, Ni) [8,9], hydrosilylation (Pt) [10,11], Grignard cross-coupling (Ni) [12] and Stille coupling (Pd) [13]. These transition-metal-NHC-catalysts have several

advantages and potential for catalysis [4]. Promising features are, apart from generally good to high turnover numbers and high rates, the excellent catalyst stability, due to high thermal and hydrolytic durability resulting from exceptionally stable M–C bonds, i.e., long shelf-life and stability to oxidation. Fortunately, many NHC and their metal complexes are readily accessible, requiring only stoichiometric amounts of the free ligand; there is generally no need to employ an excess of the NHC.

Despite the increasing interest in this class of NHC d<sup>10</sup>-metal complexes, relatively few examples of isolated and well-characterized nickel(0)-, palladium(0)- or platinum(0)-carbene complexes are known [10–19]. One of these compounds (Fig. 1, left) is a highly efficient catalyst for telomerization of 1,3-dienes with alcohols

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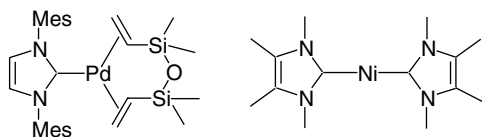


Fig. 1. Pd(0)- and Ni(0)-NHC complexes reported by Beller [14] and Cavell [15].

(TON =  $2.67 \times 10^5$ ) [14]. Concerning platinum (0) complexes with NHCs, apart from the seminal report by Arduengo et al. describing the synthesis of a platinum (0) biscarbene compound [19], only recently several isolated complexes (Fig. 2) have been reported by Markó and by our group, that are active in hydrosilylation [10,11]. Although the Arduengo complex is formally a 14-electron species, it is thermally rather stable, which is probably due to the large mesityl-substituents on the N-atoms of the imidazolium-based carbene. In this way the platinum center is shielded by these large ligands and thereby very difficult to approach by other ligands or reagents. Since the  $\text{Pt}^0(\text{IMes})_2$  complex lacks reactivity, we reasoned that one of its carbene ligands should be replaced by one or two more labile ligands, thereby facilitating dissociative routes into active platinum complexes for, for instance, oxidative addition and catalysis.

As an approach to compounds having an electron-rich platinum center, we endeavored to synthesize a new class of platinum (0) complexes containing one carbene ligand and two alkenes. The carbene ligand is deemed to endow a rather high electron density on the metal center, which may have an accelerating effect on oxidative addition of C–X, C–H and H–H bonds to such compounds. The alkene should dissipate some of the electron density and provide reasonable thermal stability, yet be an easily (relative to the NHC) dissociating ligand.

Previously, the efficient synthesis of a number of zero-valent  $[\text{Pt}^0(\text{L})_2(\text{fumarate})]$  and  $[\text{Pt}^0(\text{L})(\text{fumarate})_2]$  complexes has been detailed [20]. We reasoned that, although the fumarate will – due to  $\pi$ -backdonation from the metal center – be relatively strongly bonded in many  $[\text{Pt}^0(\text{L})_2(\text{fumarate})]$  and  $[\text{Pt}^0(\text{L})(\text{fumarate})_2]$  compounds, it will probably be less strongly bonded than an NHC type carbene ligand in  $[\text{Pt}^0(\text{NHC})(\text{fumarate})_2]$ . So, although such compounds would be

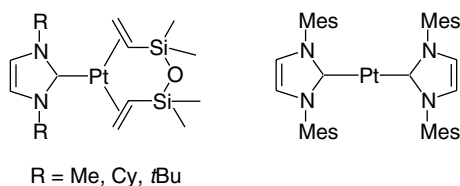


Fig. 2. Pt(0) NHC-complexes reported by Markó [10] and Arduengo [19].

thermally stable, they could yet be prone to fumarate dissociation, opening pathways to activity in catalysis.

The pre-eminent method for the synthesis of these platinum complexes in our hands started from  $\text{Pt}(\text{nbe})_3$  (nbe = norbornene) or  $\text{Pt}(\text{cod})_2$  (cod = 1,5-cyclooctadiene). In this paper, we describe the synthesis of novel compounds  $[\text{Pt}^0(\text{NHC})(\text{dmfu})_2]$ , which were prepared by this approach [21]. Furthermore, the reactivity of these novel compounds towards dihydrogen will be reported.

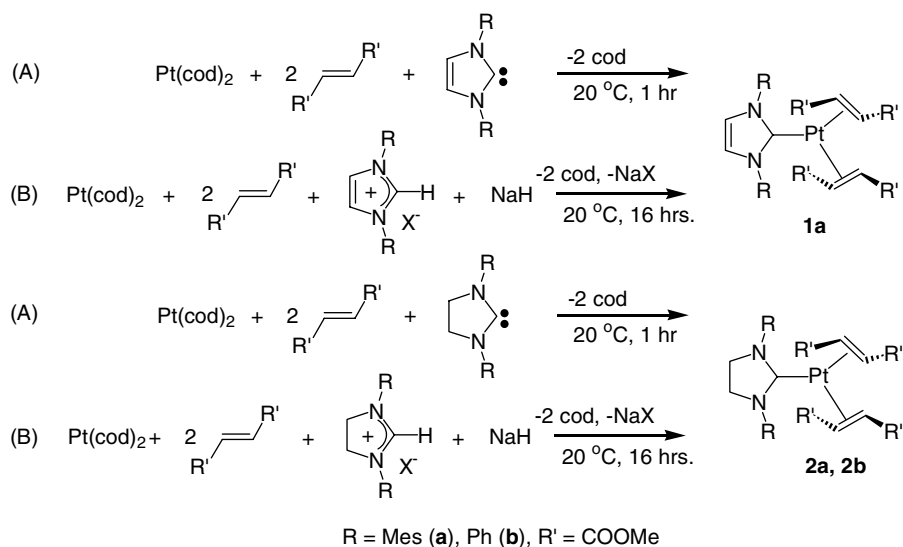
## 2. Results and discussion

### 2.1. Synthesis of $[\text{Pt}(\text{IMes})(\text{dmfu})_2]$ and $[\text{Pt}(\text{SIMes})(\text{dmfu})_2]$

These zero-valent platinum(NHC)bis(dimethyl fumarate) compounds were prepared via two methods. The first method (A, see Scheme 1) consists of two steps: First, the free carbene, 1,3-dimesitylimidazol-2-ylidene (IMes) or 1,3-dimesityldihydroimidazol-2-ylidene (SIMes) has been prepared [22]. Second, one equivalent of  $[\text{Pt}(\text{cod})_2]$  (cod = 1,5-dicyclo-octadiene) and two equivalents of the alkene, dimethyl fumarate (dmfu), were added to the free carbene in THF at room temperature. Immediate reaction resulted in the formation of thermally stable, white products in good yields (55–73%).

The second method (B, see Scheme 1) concerns the reaction of  $\text{Pt}(\text{cod})_2$  with two equivalents of dmfu, one equivalent of a imidazolium salt (IMesHCl) or imidazolium salt (SIMesHCl) and sodium hydride. The latter is used as a base for deprotonation of (S)IMesHCl, providing the free carbene in situ. This method is somewhat more time consuming than the first one, but obviates the additional step of isolating the free carbene; overall this method benefits from easier workup.  $\text{Pt}(\text{nbe})_3$  can be used as the starting material instead of  $[\text{Pt}(\text{cod})_2]$ . However, according to  $^1\text{H}$  NMR spectroscopy, overnight stirring yields a mixture of  $[\text{Pt}(\text{carbene})(\text{dmfu})(\text{nbe})]$  and  $\text{Pt}(\text{carbene})(\text{dmfu})_2$ . So, the substitution of the last nbe from  $\text{Pt}(\text{carbene})(\text{dmfu})(\text{nbe})$  to  $\text{Pt}(\text{carbene})(\text{dmfu})_2$  is not complete at room temperature. It appeared to be necessary to add more dmfu, as well as to stir the reaction mixture at elevated temperature (40–50 °C). In situ preparation of  $\text{Pt}(\text{cod})_2$  by addition of cod to  $\text{Pt}(\text{nbe})_3$  [23] before adding the other reagents, can overcome this problem. However, employing  $\text{Pt}(\text{cod})_2$  is to be preferred, and leads to overall exhaustive displacement of cod by using two equivalents of dimethyl fumarate.

The  $[\text{Pt}(\text{carbene})(\eta^2\text{-alkene})_2]$  complexes  $[\text{Pt}(\text{IMes})(\text{dmfu})_2]$ , (**1a**, IMes = 1,3-dimesitylimidazol-2-ylidene) and  $[\text{Pt}(\text{SIMes})(\text{dmfu})_2]$ , (**2a**, SIMes = 1,3-dimesityldihydroimidazol-2-ylidene) can be handled in air without significant decomposition and are stable for

Scheme 1. Synthesis of platinum(carbene)( $\eta^2$ -alkene)<sub>2</sub> complexes.

extended periods of time in solution, even in refluxing acetone. Their stability is surprising, taking into account that similar complexes are known to easily undergo alkene dissociation [11,20,21].

## 2.2. Decreasing the size of the carbene ligands and synthesis of Pt(SIPh)(dmfu)<sub>2</sub>

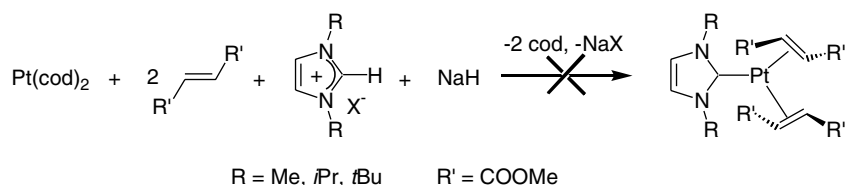
In order to evaluate the influence on C–H activation reactions, we would also like to decrease the steric bulk on the N-atom of the carbenes. Therefore, we used several imidazolium salts like 1,3-dimethyl-imidazolium iodide (IMeHI), 1,3-diisopropyl-imidazolium chloride (I*i*PrHCl) and 1,3-(di(*t*-butyl)-imidazolium chloride (I*t*BuHCl) as starting salt. We used method B (in situ method) for making the (IR)Pt(dmfu)<sub>2</sub>-complexes (Scheme 2). All reactions resulted in off-white solids, but products containing a carbene ligand were not found for R = *i*Pr, *t*Bu. In the case of R = Me, a carbene-containing product was formed according to <sup>1</sup>H NMR spectroscopy. However, washing and crystallization did not yield pure products.

Apparently, contrary to the *N*-mesityl analogues, *N*-alkyl NHCs did not result in Pt(carbene) complexes using method B. We then decided to synthesize phenyl-substituted imidazolium and imidazolium salts, which were synthesized from the corresponding  $\alpha$ -di-

imines (Ar–N=CH–)<sub>2</sub>. Under normal conditions, the condensation of glyoxal with two equivalents of aniline in methanol, did not result in phenyl-DAB. The <sup>1</sup>H NMR of the resulting tar shows that this method is not suitable for the synthesis of the phenyl-substituted imidazolium salt, hence the corresponding platinum complex Pt(IPh)(dmfu)<sub>2</sub> (**1b**, IPh = 1,3-diphenyl-imidazol-2-ylidene), cannot be obtained by this route.

An early method for synthesizing saturated N-heterocyclic carbenes had been discovered by Wanzlick and co-workers [24]. Recently, the equilibrium between monomer and dimer proposed by Wanzlick [25] has indeed been observed by Hahn et al. and Lemal et al. [26–28]. These authors were actually able to observe a mixture of the dimer and monomer by <sup>1</sup>H NMR spectroscopy, by using sterically larger aromatic N-substituents. We used this approach for the synthesis of the saturated phenyl-NHC and its corresponding platinum complex [Pt(SIPh)(dmfu)<sub>2</sub>] (**2b**, SIPh = 1,3-diphenyl-dihydroimidazol-2-ylidene). Various metal-carbene complexes have already been prepared by this method [29]. 1,3-Diphenyl-2-trichloromethyl-imidazoline (**3**; see Section 4) has been used for the straightforward synthesis of the “Wanzlick-dimer” **4** by a slightly modified literature method [24].

When the dimer **4** is treated with Pt(cod)<sub>2</sub> and two equivalents of dmfu, no platinum(carbene) complex

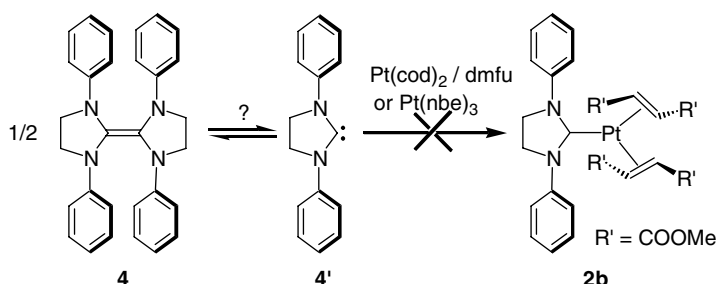
Scheme 2. Attempted synthesis of (*N*-alkyl-NHC)Pt(dmfu)<sub>2</sub> complexes.

was obtained, even gentle heating did not result in the formation of **2b** (Scheme 3). Using  $\text{Pt}(\text{nbe})_3$  instead of  $\text{Pt}(\text{cod})_2/\text{dmfu}$ , i.e., a more labile alkene, did not result in a platinum(carbene) complex either. Apparently, the Wanzlick-dimer is either too stable in this case (no formation of **4'**), or the in situ formed  $\text{Pt}(\text{cod})(\text{dmfu})$  (or  $\text{Pt}(\text{nbe})_2(\text{dmfu})$ ) is not reactive enough towards the free carbene **4'**. From the observed failure to form **2b** according to Scheme 3, it can be concluded that for saturated carbenes, the Wanzlick-dimer **4** either does not dissociate at all to give **4'**, or that the Wanzlick equilibrium as shown in Scheme 3 lies extremely far to the left. The alternative, that the carbene **4'** does form but cannot substitute an alkene from the  $\text{Pt}^0(\text{alkene})_n$  precursor can be excluded. It is known and has amply been demonstrated that NHCs can substitute all kinds of ligands and certainly one alkene [2].

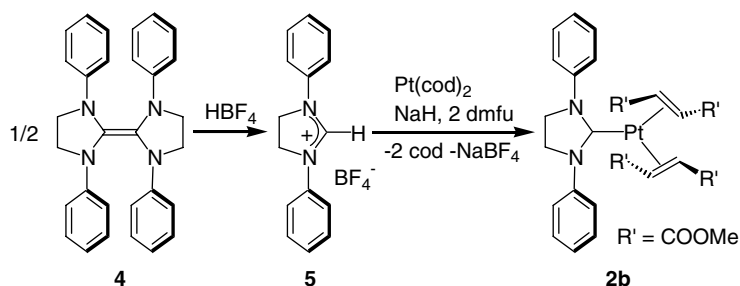
As the direct synthesis of **2b** was not possible starting from the dimer **4**, we treated **4** with  $\text{HBF}_4$  in ether under

dry conditions. Adding this strong acid in THF resulted in the fast precipitation of imidazolium salt **5**. In a slow reaction, the addition of  $\text{NaH}$ ,  $\text{Pt}(\text{cod})_2$  and two equivalents of  $\text{dmfu}$  to the imidazolium salt **5** indeed gave **2b**, c.f. Scheme 4 [30].

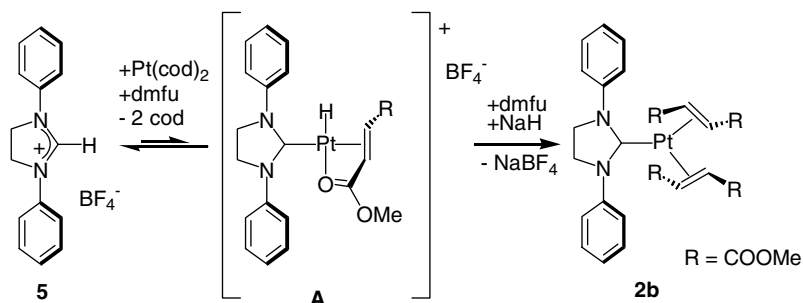
This successful formation of **2b** according to Scheme 4 may have two reasons. The first possibility is, that  $\text{NaH}$  slowly deprotonates **5** to give the free carbene **4'**, which then immediately reacts with  $\text{Pt}^0(\text{alkene})_n$ . However, we doubt that this explanation is correct. Wanzlick [31] noted already 40 years ago, and Denk et al. [32] recently confirmed, that the free carbene **4'** dimerizes in a very fast reaction to the unreactive dimer **4**. So, the following alternative seems more likely. According to Scheme 5, the  $\text{Pt}^0(\text{alkene})_n$  precursor may react with the imidazolium salt **5** by C–H activation at the 2-position, giving the probably unstable hydrido $\text{Pt}^{\text{II}}$ (carbene) complex **A**, which is subsequently deprotonated by  $\text{NaH}$  to form **2b** and dihydrogen.



Scheme 3. First approach to the synthesis of **2b** via the “Wanzlick dimer” **4**.



Scheme 4. Synthesis of **2b** via an imidazolium salt.



Scheme 5. Proposed intermediate **A**.

### 2.3. $^1\text{H}$ NMR spectroscopy

In agreement with the  $\text{C}_2$ -symmetry of complexes **1a**, **2a** and **2b**, the  $^1\text{H}$  NMR spectra of the zero-valent platinum compounds show two different signals for the anisochronous alkene-protons (Table 1). Two of the protons of the alkenes are pointing toward the aromatic part of the carbene-ligand, these are found at lower frequency due to the anisotropic shielding of the aryl ring. The other two protons of the alkenes are pointed away from the aromatic part of the carbene-ligand and are found at normal frequencies for coordinated alkenes [20] (see Fig. 3).

The saturated carbene is a stronger  $\sigma$ -donor than the unsaturated carbene [33,34], which leads to more  $\pi$ -backbonding to the dmfu in **2a** as compared to **1a**, and hence lower bond order and smaller  $^2J_{\text{PtH}}$  for **2a**. Furthermore the Ph-carbene **b** is a better acceptor than carbene **a** because of the fact that the unsubstituted phenyl-group has significantly more  $\pi$ -overlap with the NHC frame, thereby increasing the alkene C–C double bond character leading to higher values for  $^2J_{\text{PtH}}$  in case of **2b**.

### 2.4. $^{195}\text{Pt}$ NMR spectroscopy

More information on the chemical properties of the metal center was sought by means of  $^{195}\text{Pt}$  NMR. The  $^{195}\text{Pt}$  chemical shift is very sensitive to the ligands present in the coordination sphere in the Pt-compound and is therefore a useful probe of the electronic environment of the metal [35,36]. In the  $^{195}\text{Pt}$  NMR spectra the chemical shifts are found at  $-5184$  and  $-5200$  ppm for **1a** and **2a**, respectively; for **2b** the value is  $-5129$  ppm. Since the chemical shift differences are only small and

the coordination angles as well as the donor/acceptor properties of the ligands have a large influence on the chemical shift in  $^{195}\text{Pt}$  NMR, we refrain from discussing the differences between these shifts. However, concerning the range of the  $^{195}\text{Pt}$  chemical shifts, comparison to another, recently published, Pt(0)-monocarbene complex with alkene with a chemical shift of  $-5343$  ppm and with  $\text{Pt}^0(\text{IMes})_2$  (Fig. 2) [19], shows that such low shifts are not uncommon for this type of compounds [10] and that the electron density on the platinum centers of these molecules is quite similar. Other tris-coordinated platinum(0) complexes, like the  $[\text{Pt}^0(\text{NN})(\text{alkene})]$  complexes, have  $^{195}\text{Pt}$  chemical shifts around  $-4000$  ppm [20]. Compared to the latter, the present [platinum(carbene)bis(alkene)] compounds **1a**, **2a**, **2b** have their  $^{195}\text{Pt}$  resonances at much lower frequencies, which must be attributed to the fact that carbenes are carbon donor ligands, which cause larger ligand fields than chelating didentate nitrogen ligands, hence lower  $^{195}\text{Pt}$  chemical shifts [35,36].

### 2.5. Variable temperature NMR spectroscopy of **2a** and **2b**

When investigating the chemical and physical properties of **2b**, line-broadening of the alkene hydrogen atoms was observed in the  $^1\text{H}$  NMR spectrum of **2b** in benzene- $d_6$  slightly above room temperature (303 K). In order to probe the fluxional process, we measured the  $^1\text{H}$  NMR spectra of **2b** and **2a** in toluene- $d_8$  in the temperature range from 298 to 378 K. At 298 K two doublets are seen for the alkene protons of the dmfu ligands in **2b** around 4.1 and 3.6 ppm with  $^2J\{^1\text{H}, ^{195}\text{Pt}\}$ -couplings superimposed (see Fig. 4). A gradual increase of the temperature leads to broadening of the signals (at 308 K), coalescence and disappearing of the signals in the base line (318 K). No average signals for the alkene-protons between the former alkene-resonances (at 298 K) were observed when the temperature was further increased up to 378 K. After cooling down to room temperature the starting spectrum was found, but also some depletion of platinum metal was found. The same experiments were also carried out with a solution of **2a** in toluene- $d_8$ . For **2a**

Table 1  
 $^1\text{H}$  NMR spectroscopic data of the alkene-protons

Compound	$\delta(\text{H}_A)$ (ppm) [ $^2J_{\text{HPt}}$ (Hz)]	$\delta(\text{H}_B)$ (ppm) [ $^2J_{\text{HPt}}$ (Hz)]
Pt(IMes)(dmfu) $_2$ ( <b>1a</b> )	3.92 [46.0]	3.13 [63.0]
Pt(SIMes)(dmfu) $_2$ ( <b>2a</b> )	3.89 [43.2]	3.17 [52.8]
Pt(SIPh)(dmfu) $_2$ ( <b>2b</b> )	3.49 [57.0]	3.10 [60.6]

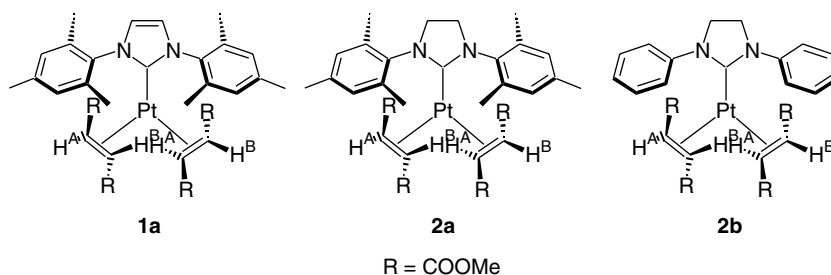


Fig. 3. Prepared Pt(carbene)(dmfu) $_2$  complexes.

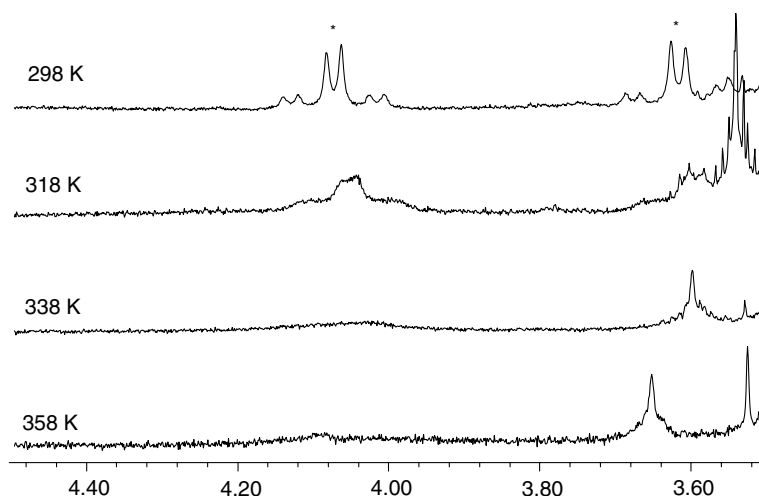


Fig. 4. VT  $^1\text{H}$  NMR spectra of **2b** (\* alkene protons region).

the signals of the alkene-protons remain sharp over the whole temperature range (298–378 K).

The most plausible explanation for the absence of an average signal for the alkene-protons at higher temperatures is an exchange of free dmfu and coordinated dmfu at higher temperatures for **2b**. The reason why this is not observed for a solution of **2a** may be that the SIMes-carbene is the better  $\sigma$ -donor relative to IMes, resulting in more  $\pi$ -backbonding to the dmfu's in case of the former and, as a result, stronger coordination of the dmfu's in **2a**. Moreover, in contrast to the situation for the SIMes-carbene, the phenyl-group of the SIPh-carbene is in plane of the imidazol-2-ylidene, resulting in better  $\pi$ -accepting properties and less  $\pi$ -donation for this carbene-ligand. This feature causes weaker coordination of dmfu.

## 2.6. X-ray crystal structure determination of **1a**

The molecular structure of [Pt(IMes)bis(dimethyl fumarate)], **1a**, was unambiguously proven by a single crystal X-ray structure analysis, which is depicted in Fig. 5. Selected bond lengths and angles are given in Table 2.

Compound **1a** is monoclinic, space group  $P2_1/c$ . The platinum has a distorted square-planar environment with a sum of *cis* angles of  $360.4^\circ$ . The compound is approximately  $C_{2v}$  symmetric. The C=C bonds of the coordinated dmfu's (1.422(4) and 1.427(4) Å) are elongated compared to free dmfu (1.318(2) Å) [37] caused by the donation of electron density from platinum into the  $\pi^*$ -orbitals of the dimethyl fumarate. The Pt– $\eta^2$ -C=C planes are oriented in an angle of  $56.05(19)^\circ$  and

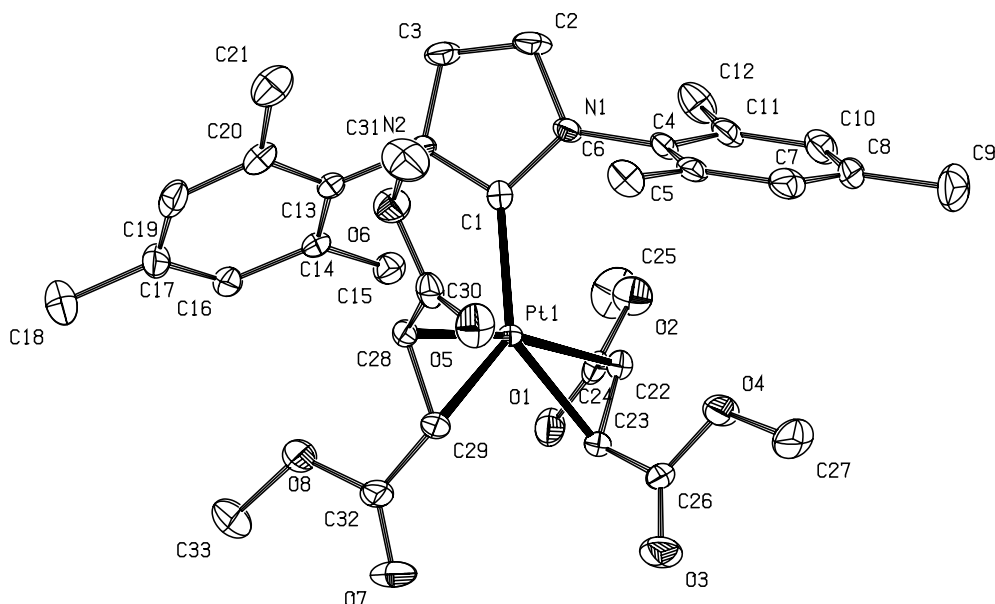


Fig. 5. Displacement ellipsoid plot of **1a** with ellipsoids drawn at the 50% probability level. Hydrogens are omitted for clarity.

Table 2

Selected bond lengths (Å) and angles (deg) for **1a** (e.s.d. in parentheses)

Pt(1)–C(1)	2.072(2)
Pt(1)–C(23)	2.098(3)
Pt(1)–C(29)	2.101(3)
C(28)–C(29)	1.422(4)
Pt(1)–C(22)	2.130(3)
Pt(1)–C(28)	2.120(3)
C(22)–C(23)	1.427(4)
C(1)–Pt(1)–C(22)	96.96(10)
C(1)–Pt(1)–C(28)	94.21(10)
C(1)–Pt(1)–C(23)	136.16(10)
C(1)–Pt(1)–C(29)	133.38(10)

56.7(2)° with respect to the NHC-plane. These Pt– $\eta^2$ -C=C planes are mutually oriented almost in one plane, making an angle of 10.8(2)°. The mesityl substituents on the nitrogens of the NHC-ligand are tilted and make an angle of 68.77(14)° and 66.28(14)°, respectively, relative to the plane of the imidazole ring.

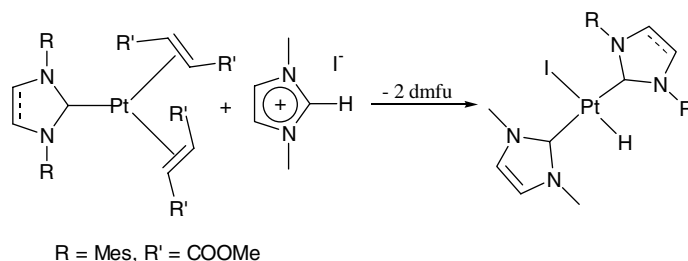
Recently, the X-ray crystal structures of zero-valent platinum(carbene) compounds with a diene ligand [Pt(1,3-dimethyl-imidazol-2-ylidene)( $\eta^4$ -divinyltetramethylsiloxane)] [10] has been reported. The Pt–C(carbene) bond of this compound is slightly shorter (2.051 Å)

and the Pt–C(alkene) bonds are slightly longer (2.103 and 2.178 Å) compared to **1a**.

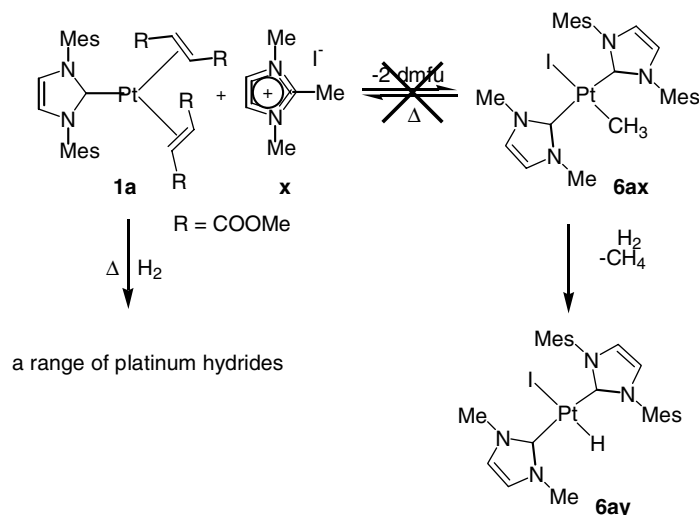
### 2.7. Reactivity of platinum(carbene)(alkene)<sub>2</sub> towards H<sub>2</sub>

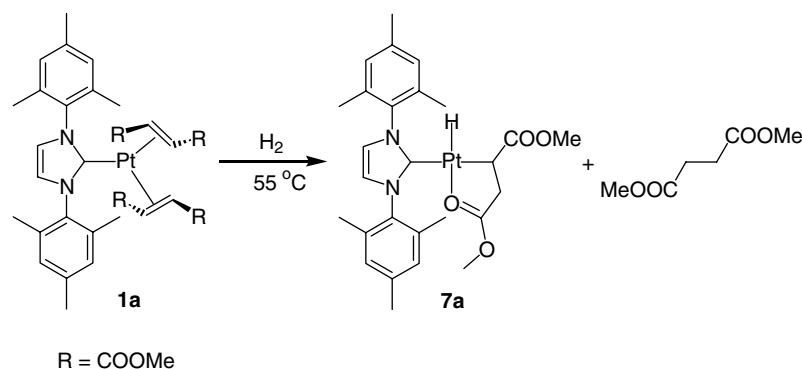
The new platinum(carbene)(alkene)<sub>2</sub>-complexes are reactive towards C–H bonds of imidazolium salts (Scheme 6) [21]. We were also interested to see whether these compounds are reactive towards C–C bonds, for instance of 2-methyl-imidazolium salts. MO-calculations have shown that C–C bond fission is in principle feasible, insertion of Pt into this C–C bond is an exothermic reaction [38].

Therefore, we investigated the reactivity of Pt(IMes)(dmfu)<sub>2</sub> towards (**x**) (Scheme 7). This should in principle result in a thermodynamically stable product (biscarbene)platinum(methyl)(iodide) (**6ax**). However, when carrying out this reaction under various conditions (in benzene or acetone at reflux temperatures), we did not observe any other compounds than the starting materials. We added dihydrogen gas to the reaction mixture to see if the putative compound **6ax** could be trapped by reaction with H<sub>2</sub>. This reaction was carried out in acetone-*d*<sub>6</sub> in an NMR tube and was followed



Scheme 6. Example of C–H activation of imidazolium salts [21].

Scheme 7. Reactivity of **1a** towards C–C bonds and dihydrogen.



Scheme 8. Formation of a platinum hydride by addition of H<sub>2</sub> to **1a** and multiple migration–insertions of coordinated dmfu.

by <sup>1</sup>H NMR spectroscopy. Indeed platinum hydrides were observed in the expected chemical shift-range similarly to known analogues [21] at about –14.5 ppm, indicating a hydride *trans* to an iodide, as in *trans*-hydrido 3,5-dimethyl-imidazol-2-ylidene iodo 3,5-dimesityl-imidazol-2-ylidene platinum(II) (**6ay**) after reductive elimination of methane.

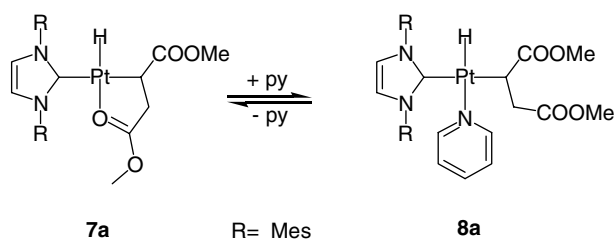
As a reason for the observation of several platinum hydrides, we considered direct reaction of dihydrogen with **1a** to give a product that is reactive towards **x**. So, H<sub>2</sub> was bubbled through a solution of **1a** in benzene-*d*<sub>6</sub> in an NMR-tube at 55 °C for 30 min. At this temperature a reaction occurred and, surprisingly, no platinum metal was observed.[39]. After the reaction, a <sup>1</sup>H NMR spectrum was taken and dimethyl succinate and platinum complex **7a** were observed as the main products. This reaction takes place surprisingly cleanly, and yields mononuclear (hydrido)platinum(carbene) **7a** (Scheme 8). Apparently, successive oxidative addition of dihydrogen, migration–insertion involving the coordinated dmfu and reductive elimination of the second hydride with the incipient alkylplatinum species (rather than β-elimination) take place. After formation of dimethyl succinate, another sequence of addition and migration–insertion takes place, but this fails to eliminate and terminates as compound **7a**.

Compound **7a** has only been characterized in solution by <sup>1</sup>H NMR, <sup>195</sup>Pt NMR and IR spectroscopy. The hydride is found at –27.07 ppm with a large <sup>1</sup>J<sub>PtH</sub> coupling of 1900 Hz, which is in agreement with a very weak *trans*-ligand such as the carbonyl in this case. The <sup>195</sup>Pt-resonance of **7a** is found at –3940 ppm, indicative of the +2 oxidation state for the platinum center of **7a** [35], which implies an oxidative shift of +1300 ppm upon conversion of **1a** into **7a**. <sup>13</sup>C NMR spectroscopy failed due to the limited stability of **7a** in organic solvents like benzene or acetone. The IR of the product revealed, apart from carbonyl signals from coordinated and free dimethyl fumarate and succinate, a band at 1646 cm<sup>–1</sup>, which is ascribed to a carbonyl: Pt...O=C. Attempts to isolate complex **7a** failed; it probably reacts with C–H bonds of hydrocarbons, because the addition

of 1,2,3-trimethyl-imidazolium iodide (**x**) showed more than one platinum hydride signal in the <sup>1</sup>H NMR spectrum. This reactivity can be rationalized if one takes the coordination site that is occupied by the weakly coordinating carbonyl into account, which can be substituted for example by a C–H bond. Then, C–H bond activation of one of the methyl groups is feasible, which would be the first one taking place for a non-cationic Pt(II) compound [40].

In order to decrease the reactivity of **7a** towards hydrocarbons, we added 1 equivalent of pyridine in acetone-*d*<sub>6</sub> to stabilize the Pt<sup>II</sup> center (Scheme 9). Most of **7a** (δ<sub>Pt</sub> = –3920 ppm in acetone-*d*<sub>6</sub>) was converted in **8a** (δ<sub>Pt</sub> = –4081 ppm). With an excess of pyridine, **8a** is the only platinum complex observed by NMR. Evaporation of the solvent and the excess of pyridine gave a mixture of **7a** and **8a** instead of the expected pure **8a**, indicating that pyridine does not coordinate very strongly to platinum. The hemilabile coordination of the carbonyl is apparently quite strong. This is reminiscent of known cases for Pt [41] and Pd [42]-metallacycles, however these are cationic complexes.

In order to assure that the hydride in **7a** originates from the dihydrogen that was added to **1a**, we added D<sub>2</sub> to **1a**. Indeed, in this case the deuteride Pt-<sup>2</sup>H was observed at –26.6 ppm in the <sup>2</sup>H NMR spectrum. Furthermore, deuterated dimethyl succinate was formed. Hence, reaction of **1a** with dihydrogen constitutes a rather gentle method to arrive at a neutral hydrido platinum(II) carbene complex with a hemilabile coordinating carbonyl group, from which a free coordination site for bond activation reactions can be readily created.



Scheme 9. Addition of pyridine to **7a**.



### 3. Conclusion

Several zero-valent platinum-mono-carbene-bis-alkene complexes [Pt<sup>0</sup>(NHC)(dimethyl fumarate)] have been isolated and characterized. Importantly, impurities can be easily removed with apolar solvents, facilitating the purification of these compounds. The complexes are air-, moisture- and thermally stable for months in solution and in the solid state. Two routes for the synthesis of these complexes have been implemented, the route involving in situ preparation of the carbene is the most facile one for obtaining the [platinum(NHC)bis(alkene)] complexes in reasonable to good yield. The new platinum complexes could be valuable compounds for some Pt<sup>0</sup>-catalyzed reactions [11,20] and may provide information about intermediates of known Pt<sup>0</sup>(NHC)-catalyzed reactions.

The [Pt<sup>0</sup>(NHC)(dimethyl fumarate)] complex **1a** reacts under mild conditions with dihydrogen in a sequence of oxidative addition, migration–insertion involving the coordinated dmfu and reductive elimination, to form dimethyl succinate and, after a second sequence, the corresponding neutral hydrido platinum(II) carbene complex in which the carbonyl group of the ester moiety of the inserted second dmfu probably constitutes a cyclic (R)–C=O...Pt unit. Pyridine is able to break the carbonyl coordination, however, the coordination of pyridine is also quite weak. The presumed hemilability of the carbonyl group may facilitate the reaction of the neutral hydrido platinum(II) carbene complex towards certain C–H bonds, to give C–H bond activation.

### 4. Experimental

#### 4.1. General

All reactions involving air-sensitive compounds were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use, according to standard methods [43]. Pt(cod)<sub>2</sub> [22], Pt(nbe)<sub>3</sub> [22], 1,3-dimesityl-imidazolium chloride [30], 1,3-dimesityl-dihydroimidazolium chloride [30] were prepared according to literature procedures. NMR measurements were performed on a Varian Mercury300 spectrometer (<sup>1</sup>H: 300.13 MHz, <sup>13</sup>C 75.47 MHz), a Varian Inova500 spectrometer (<sup>1</sup>H: 499.88 MHz, <sup>13</sup>C: 125.70 MHz) and Bruker DRX300 spectrometer (<sup>1</sup>H: 300.13 MHz, <sup>13</sup>C: 75.47 MHz, <sup>195</sup>Pt: 64.13 MHz). <sup>195</sup>Pt NMR spectra were measured via a normal HMQC sequence at 298 K. <sup>13</sup>C NMR spectra were measured with <sup>1</sup>H decoupling. Positive chemical shifts (δ) are denoted for high-frequency shifts relative to the external TMS reference (<sup>1</sup>H, <sup>13</sup>C) or a Na<sub>2</sub>PtCl<sub>6</sub> reference (<sup>195</sup>Pt). HRMS measurements were performed

on a JEOL JMS SX/SX102A four sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. For Fast Atom Bombardment (FAB) mass spectrometry, the samples were loaded in a matrix solution (3-nitrobenzyl alcohol) onto a stainless steel probe and bombarded with xenon atoms with an energy of 3 KeV. During the high resolution FAB-MS a resolving power of 10,000 (10% valley definition) was used.

#### 4.2. Synthesis

##### 4.2.1. Method A: Synthesis of **1a** via the preparation of the free carbene

4.2.1.1. *1,3-Dimesityl-imidazol-2-ylidene*. The free carbene was synthesized by a slightly changed procedure described by Arduengo et al. [22]; 0.80 g (2.3 mmol) 1,3-bis(2,4,6-trimethylphenyl)-imidazolium chloride was dissolved in 50 ml THF at room temperature and one equivalent of KOtBu (1 M in THF, 2.35 ml) was added to the mixture. The solution was stirred for 4 h during which time a white solid precipitated from the solution. The mixture was then filtered over Celite filter aid and the filter was washed with 10 ml hexane. From the resulting clear yellowish filtrate the solvent was removed in vacuo. The residue was extracted with four portions of hot hexane (around 60 °C). The extracts were collected concentrated until precipitation of the carbene occurred. A small volume of dry hexane was added in order to dissolve the precipitated solids and the flask was left to stand overnight at –80 °C for crystallization. The supernatant was removed with a cannulae and the solid was dried in vacuo to give 0.52 g (74%) of the free carbene as an off white slightly sticky material.

4.2.1.2. *(1,3-Dimesityl-imidazol-2-ylidene)-bis-(η<sup>2</sup>-dimethyl fumarate) platinum(0) (1a)*. An amount of 149.8 mg (0.4911 mmol) 1,3-dimesityl-imidazol-2-ylidene is carefully transferred in a Schlenk tube under dinitrogen atmosphere to avoid any moisture. To this Schlenk tube 201.9 mg (0.4912 mmol) Pt(cod)<sub>2</sub> and 141.5 mg (0.9826 mmol) dmfu were added. The solids were dissolved in 20 ml THF and the resulting solution was stirred for 1 h at room temperature. Then 20 ml hexane is added and the amount of solvent is reduced to 10 ml in vacuo. Another 20 ml hexane is added and the volume of solvent is reduced to 5 ml during which an off white solid came out of the solution. The solvent is removed using a cannulae and the solids were washed twice with 5 ml of ether/hexanes 1:1 v/v to give 198.8 mg (51%) of an off white solid. <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>, δ (ppm)): 7.61 (2H, s, <sup>4</sup>J<sub>HPt</sub> = 10.5 Hz), 7.08 (2H, s), 6.96 (2H, s), 3.92 (2H, d, <sup>3</sup>J<sub>HH</sub> = 9.0 Hz, <sup>2</sup>J<sub>HPt</sub> = 46.0 Hz), 3.40 (6H, s), 3.30 (6H, s), 3.13 (2H, d, <sup>3</sup>J<sub>HH</sub> = 9.0 Hz, <sup>2</sup>J<sub>HPt</sub> = 63.0 Hz), 2.39 (6H, s), 2.35 (6H, s), 1.80 (6H, s). <sup>13</sup>C NMR (125.7 MHz, acetone-d<sub>6</sub>, δ (ppm)): 172.27, 170.69

( $^2J\{^{195}\text{Pt}, ^{13}\text{C}\} = 38.0$  Hz), 169.14 ( $^2J_{\text{CPT}} = 36.0$  Hz), 138.38, 136.21 ( $^3J_{\text{CPT}} = 9.0$  Hz), 135.40, 135.34, 129.42, 129.13, 124.90 ( $^3J_{\text{CPT}} = 42.2$  Hz), 50.22 ( $^1J_{\text{CPT}} = 146.6$  Hz), 50.16, 50.13, 48.98 ( $^1J_{\text{CPT}} = 191.1$  Hz), 20.41, 18.75, 17.51.  $^{195}\text{Pt}$  (64.3 MHz, acetone- $d_6$ ,  $\delta$  (ppm)): -5184. HRMS(FAB) ( $m/z$ ): Obs: 788.2512, Calc: 788.2514.

#### 4.2.2. Method B: synthesis of **1a** via one-pot synthesis by in situ generation of the free carbene

4.2.2.1. (1,3-Dimesityl-imidazol-2-ylidene)-bis-( $\eta^2$ -dimethyl fumarate) platinum(0) (**1a**). A Schlenk tube was charged with 132.8 mg (0.450 mmol) 1,3-bis(2,4,6-trimethylphenyl)-imidazolium chloride, 166.0 mg (0.404 mmol) Pt(cod) $_2$ , 128.3 mg (0.891 mmol) dimethyl fumarate (dmfu) and 63.5 mg (1.59 mmol) of 60% NaH in mineral oil. Then 20 ml THF was added to the solids. The mixture was stirred overnight at room temperature. The mixture was then filtered over Celite filter aid. The remaining solids were washed with another 10 ml THF and also filtered over the filter. 20 ml hexane was added to the combined filtrates, and the solvent was reduced to 5 ml under reduced pressure. Then 20 ml hexane was added to the residue and the mixture was centrifuged for 10 min at 3500 RPM. The solvent was decanted and the resulting off-white solid was washed with hexanes/ether 3:1 (2  $\times$  20 ml) removing the solvents again via centrifugation. The solids were dried further under vacuum yielding 152.6 mg (48%) of a pale yellow powder. Eventually this powder can be recrystallized from acetone. A second crop of product can be obtained from the combined washings. The products of methods A and B have identical  $^1\text{H}$  NMR spectra. Single crystals suitable for X-ray structure analysis could be obtained by slowly cooling down a saturated acetone solution from 55  $^\circ\text{C}$  to room temperature.

4.2.2.2. (1,3-Dimesityl-dihydroimidazol-2-ylidene)-bis-( $\eta^2$ -dimethyl fumarate) platina(0) (**2a**). A Schlenk tube was charged with 1.07 g (3.14 mmol) SIMesHCl, 1.09 g (2.65 mmol) Pt(cod) $_2$ , 0.79 g (5.49 mmol) dimethyl fumarate (dmfu) and 0.40 g (9.91 mmol) of 60% NaH in mineral oil. Then 30 ml THF was added to the solids. The mixture is stirred overnight at room temperature. The mixture was filtered over Celite. The solids were washed with another 10 ml THF and also filtered. Hexane (20 ml) was added to the combined filtrates, and the solvent was reduced to 5 ml under reduced pressure. Then 20 ml hexanes were added to the residue and the mixture was centrifuged for 10 min at 3500 RPM. The solvent was decanted and the resulting off-white solid was washed with hexanes/ether 3:1 (2  $\times$  20 ml) removing the solvents again via centrifugation. The solids were dried further under vacuum yielding 0.87 g (55%) of an off-white powder. Eventually this powder can be recrystallized from acetone.  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ ,  $\delta$  (ppm)):

7.03 (2H, s), 6.87 (2H, s), 4.20 (2H, m), 4.05 (2H, m), 3.89 (2H, d,  $^3J_{\text{HH}} = 9.0$  Hz,  $^2J_{\text{HPt}} = 43.2$  Hz), 3.49 (6H, s), 3.21 (6H, s), 3.17 (2H, d,  $^3J_{\text{HH}} = 9.0$  Hz,  $^2J_{\text{HPt}} = 52.8$  Hz), 2.65 (6H, s), 2.29 (6H, s), 1.91 (6H, s).  $^{13}\text{C}$  NMR (125.7 MHz, acetone- $d_6$ ,  $\delta$  (ppm)): 171.51 ( $^2J_{\text{CPT}} = 40.0$  Hz), 169.68 ( $^2J_{\text{CPT}} = 36.0$  Hz), 138.14, 137.33, 136.90, 136.86, 130.26, 129.98, 52.93 ( $^1J_{\text{CPT}} = 136.5$  Hz), 51.02, 50.89, 49.89 ( $^1J_{\text{CPT}} = 136.5$  Hz), 21.13, 19.13, 18.17.  $^{195}\text{Pt}$  NMR (64.3 Hz, acetone- $d_6$ ,  $\delta$  (ppm)): -5200. EA: Found: 50.26 (C), 5.31 (H), 3.48 (N) Calc: 50.19, 5.36, 3.55.

4.2.2.3. 1,3-Diphenyl-2-trichloromethyl-imidazolidine (**3**) [24]. Instead of chloral as used by Wanzlick et al., chloral hydrate was used. 2.31 g (10.9 mmol) 1,2-dianilinoethane was dissolved in 5 ml glacial acid. 1.86 g (11.2 mmol) chloral hydrate was added and the resulting mixture was stirred overnight at room temperature. A red solid was filtered off and the solid was washed with methanol (2  $\times$  5 ml) yielding 0.98 g (27%) of a white solid, which was identified by  $^1\text{H}$  NMR spectroscopy as pure **3**.  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ ,  $\delta$  (ppm)): 7.16–7.28 (8H, m), 6.80 (2H, tt,  $^3J_{\text{HH}} = 6.9$  Hz,  $^4J_{\text{HH}} = 1.5$  Hz), 6.86 (1H, s), 4.21 (2H, q,  $^3J_{\text{HH}} = 4.2$  Hz), 4.87 (2H, q,  $^3J_{\text{HH}} = 4.2$  Hz).

4.2.2.4. Bis-(1,3-diphenyl-2-imidazolidine) (**4**) [24]. An amount of 495.3 mg (1.45 mmol) 1,3-diphenyl-2-trichloromethyl-imidazolidine (**3**) was dissolved in a mixture of 4 ml xylenes and 1 ml collidine. This solution is heated on a oil bath to 185  $^\circ\text{C}$  for 1 h. After cooling down to room temperature, the solvents were removed by decantation and the yellow solid was washed with diethyl ether (2  $\times$  4 ml). A pale yellow solid was obtained in a yield of 225.4 mg (70%). As reason of the reactivity of this compound towards air and moisture combined with the bad solubility in common organic solvents, the dimer of 1,3-diphenyl-2-imidazolidine was used without identifications.

4.2.2.5. 1,3-Diphenyl-2-imidazolidinium tetrafluoroborate (**5**). An amount of 0.18 g (0.40 mmol) bis-(1,3-diphenyl-2-imidazolidine) (**4**) was suspended in 40 ml THF. To this solution 0.10 ml 54% HBF $_4$  (0.73 mmol) in diethyl ether was added. An orange glow could be seen and immediately a yellow solid precipitated from the solution. After 30 min stirring at room temperature, the solid was filtered off and was washed with diethyl ether (2  $\times$  10 ml). This yielded 0.20 g (80%) of a pale yellow solid.  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ ,  $\delta$  (ppm)): 9.86 (1H, s), 7.72 (4H, m), 7.60 (4H, m), 7.46 (2H, m), 4.92 (4H, s).  $^{13}\text{C}$  NMR (75.47 MHz, dms $o$ - $d_6$ ,  $\delta$  (ppm)): 152.65 (NCH), 136.97 (C), 130.59 ( $m$ -CH), 127.93 ( $p$ -CH), 119.31 ( $o$ -CH), 49.15 (CH $_2$ ).  $^{19}\text{F}$  NMR (282.4 MHz, acetone- $d_6$ ,  $\delta$  (ppm)): -151.7.

4.2.2.6. (1,3-Diphenyl-dihydroimidazol-2-ylidene)-bis( $\eta^2$ -dimethyl fumarate) platinum(0) (**2b**). To 59.2 mg (0.191) 1,3-diphenyl-2-imidazolidinium tetrafluoroborate (**5**), 73.6 mg (0.179 mmol) Pt(cod)<sub>2</sub>, 55.7 mg (0.387 mmol) dimethyl fumarate and 32 mg (0.80 mmol) 60% NaH in mineral oil in a Schlenk tube, 20 ml THF was added. This mixture was stirred overnight at room temperature. The mixture was filtered over Celite and the solids were washed with THF (2 × 5 ml). To the combined filtrates 15 ml of hexanes was added, and the volatiles were removed in vacuo. The solids were scraped from the wall and were washed with ether (2 × 5 ml) giving 110.7 mg (87%) of an off white solid. The impure compound was recrystallized from acetone yielding pure **2b** (yield: 65.0 mg, 49%). <sup>1</sup>H NMR (300 MHz, acetone-*d*<sub>6</sub>,  $\delta$  (ppm)): 7.47 (4H, dd, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz), 7.2–7.3 (6H, m), 4.70 (2H, m), 4.34 (2H, m), 3.54 (12H, s), 3.49 (2H, d, <sup>3</sup>J<sub>HH</sub> = 9.9 Hz, <sup>3</sup>J<sub>HPt</sub> = 57.0 Hz), 3.10 (2H, d, <sup>3</sup>J<sub>HH</sub> = 9.9 Hz, <sup>3</sup>J<sub>HPt</sub> = 60.6 Hz). <sup>13</sup>C NMR (125.7 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$  (ppm)): 196.89 (<sup>1</sup>J<sub>Cpt</sub> = 1332 Hz), 172.20 (<sup>2</sup>J<sub>Cpt</sub> = 41 Hz), 171.84 (<sup>2</sup>J<sub>Cpt</sub> = 44 Hz), 171.39, 129.04 (<sup>4</sup>J<sub>Cpt</sub> = 39.7 Hz), 126.47, 122.35, 52.10 (<sup>1</sup>J<sub>Cpt</sub> = 164.4 Hz), 51.75 (<sup>3</sup>J<sub>Cpt</sub> = 42.0 Hz), 51.41, 51.11, 46.06 (<sup>1</sup>J<sub>Cpt</sub> = 172.0 Hz). <sup>195</sup>Pt NMR (64.3 Hz, acetone-*d*<sub>6</sub>,  $\delta$  (ppm)): –5129.

4.2.2.7. *cis*-[3-Methoxy-1-(methoxycarbonyl)-3-oxopropyl][hydrido][1,3-dimesityl-imidazol-2-ylidene] platina(II) (**7a**). H<sub>2</sub> was bubbled through a solution of **1a** in benzene-*d*<sub>6</sub> in an NMR-tube at 55 °C for 30 min. After the reaction a <sup>1</sup>H NMR spectrum was taken, indicating that **1a** had completely been converted to dimethyl succinate and platinum complex **7a**. <sup>1</sup>H NMR (300 MHz, benzene-*d*<sub>6</sub>,  $\delta$  (ppm)): 6.64 (4H, s, ArH), 6.08 (2H, ImH), 3.47 (3H, br, CHCH<sub>2</sub>), 3.41 (3H, COOCH<sub>3</sub>), 2.95 (3H, s, COOCH<sub>3</sub>), 2.14 (6H, s, CCH<sub>3</sub>), 2.08 (6H, s, CCH<sub>3</sub>), 1.99 (6H, s, CCH<sub>3</sub>), –27.07 (1H, s, <sup>1</sup>J<sub>HPt</sub> = 1900 Hz). <sup>195</sup>Pt NMR (64.3 MHz, benzene-*d*<sub>6</sub>,  $\delta$  (ppm)): –3940. IR (benzene):  $\nu$ (C=O ... Pt) 1646 cm<sup>–1</sup>.

4.2.2.8. X-ray crystal structure determination of **1a**. X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (Mo K $\alpha$ ,  $\lambda$  = 0.71073 Å). The structures were solved with automated Patterson methods with the program DIRDIF99 [44] and refined with the program SHELXL97 [45] against *F*<sup>2</sup> of all reflections. The drawings, structure calculations, and checking for higher symmetry was performed with the program PLATON [46].

The crystal was found to be non-merohedrally twinned with a twofold rotation about the reciprocal *a*\* axis as twin operation. The cell parameters and the twin law were determined with the program DIRAX [47]. The intensities were obtained for both twin domains and the overlapping sections using EVAL14

Table 3

Crystal data and details of the structure determination of **1a**

Empirical formula	C <sub>33</sub> H <sub>40</sub> N <sub>2</sub> O <sub>8</sub> Pt
Formula weight	787.76
Crystal color and shape	Yellow block
Crystal size (mm <sup>3</sup> )	0.24 × 0.18 × 0.12
Crystal system	Mmonoclinic
Space group	P2 <sub>1</sub> /c (no. 14)
<i>a</i> (Å)	18.362(3)
<i>b</i> (Å)	10.5379(14)
<i>c</i> (Å)	16.5493(17)
$\beta$ (°)	92.063(15)
<i>V</i> (Å <sup>3</sup> )	3200.2(8)
<i>T</i> (K)	150
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.635
( $\mu$ (Mo K $\alpha$ ) (mm <sup>–1</sup> ))	4.438
Absorption correction range	0.63–0.77
Reflections collected/unique	46,720/11,514
Parameters	424
<i>R</i> <sub>1</sub> (obs./all refl.)	0.0255/0.0371
<i>wR</i> <sub>2</sub> (obs./all refl.)	0.0467/0.0498
GoF	1.031
$\rho$ <sub>min/max</sub> (e/Å <sup>3</sup> )	–0.81/0.73

[48]. An analytical absorption correction was applied with the program PLATON [46]. Reflections, equivalent with respect to the twin situation, were merged. The refinement used the HKLF5 option [49] of SHELXL97 [45] resulting in a twin ratio of 0.40:0.60. Details of the structure determinations are given in Table 3.

CCDC 273661 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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