Nucleophilic and electrophilic platinum compounds for C-H bond activation
Duin, M.A.

Citation for published version (APA):
Duin, M. A. (2004). Nucleophilic and electrophilic platinum compounds for C-H bond activation
Chapter 3§

Synthesis of Zerovalent Electron-rich Platinum Centers: 
Platinum(carbene)(alkene)$_2$ Complexes

3.1 Introduction

N-Heterocyclic carbenes (NHC’s) are being applied more and more frequently as ligands in homogeneous catalysis.\cite{2} For almost all d$^{10}$-metals, complexes with NHC ligands have been reported, which are able to catalyze reactions, such as Heck and Suzuki coupling (Pd, Ni),\cite{3-7} aryl amination (Pd, Ni),\cite{8,9} hydrosilylation (Pt),\cite{10,11} Grignard cross-coupling (Ni)\cite{12} and Stille coupling (Pd).\cite{13} These new NHC-catalysts have several advantages and potential for catalysis.\cite{4} Not only high turnover numbers, high rates, catalyst stability, due to high thermal and hydrolytic durability resulting from exceptionally stable M-C bonds (long shelf-life, stability to oxidation), but also the easy accessibility and no need for an excess of the ligand are promising features.

![Figure 3.1 Pd(0)- and Ni(0)-NHC complexes reported by Beller$^{[14]}$ and Cavell$^{[15]}$](image)

Despite the increasing interest in this class of NHC d$^{10}$-metal complexes there are only few examples of isolated and well-characterized nickel(0)-carbene or palladium(0)-carbene complexes known.\cite{14-18} One of these complexes (see Figure 3.1) is a highly efficient catalyst for telomerization of 1,3-dienes with alcohols (TON = 267000).\cite{14}

Concerning platinum(0) complexes with NHC’s only recently some in situ formed complexes have been reported which are active in hydrosilation,$^{[10,11]}$ and an early report by Arduengo et al. describing the synthesis of a platinum(0) biscarbene compound already in 1994.$^{[19]}$ Although, this complex is formally a 14-electron species, it is thermally rather stable. Probably, this is 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. When we started our studies, this complex by Arduengo was the only known NHC based Pt$^0$ complex, but this complex lacks reactivity, therefore one carbene ligand has to be replaced by one or two labile ligands in such a way that activity towards oxidative addition or catalysis is possible.

For creation of an electron-rich platinum center, we decided to study a new class of platinum(0) complexes containing one carbene ligand and two labile alkenes. The carbene ligand is used, because it is known that this type of ligands is capable of increasing the electron density of the metal. In this way achievement of C-X or C-H oxidative addition is more likely to occur.[20]

In the previous chapter, we described the efficient synthesis of zerovalent (diimine)Pt(alkene) complexes. The synthesis of these complexes starting from Pt(nbe)$_3$ (nbe = norbordiene) and Pt(cod)$_2$ (cod = 1,5-cyclooctadiene) appeared to be the pre-eminent method for making these zerovalent platinum complexes. Here, we will describe the synthesis of novel Pt$^0$(carbene)bis(alkene) compounds, prepared by a similar approach. Also the reactivity of these novel compounds towards dihydrogen will be reported.

### 3.2 Results and Discussion

#### 3.2.1 Synthesis of zerovalent platinum(carbene)(alkene)$_2$ complexes

*Synthesis of Pt(IMes)(dmfu)$_2$ and Pt(SIMes)(dmfu)$_2*

These new zerovalent platinum(carbene) complexes were prepared via two methods. The first method (A, see Scheme 3.1) consists of two steps: First, the free carbene, 1,3-dimesityl-imidazol-2-ylidene (IMes) or 1,3-dimesityl-dihydroimidazol-2-ylidene (SIMes) was prepared.[21] Second, one equivalent of Pt(cod)$_2$ (cod = 1,5-dicyclo-octadiene) and two equivalents of alkene (dimethylfumarate, 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 3.1) consists of the reaction of Pt(cod)$_2$, two equivalents of dmfu, one equivalent of a imidazolium salt (IMesHCl) or imidazolinium salt (SIMesHCl) and sodium hydride. The latter is used as base for deprotonation, leading to the in situ preparation of the free carbene. This reaction is somewhat more time consuming, but obviates the additional step of isolation of the free carbene and overall this method results in easier workup.

Pt(nbe)$_3$ can be used as starting material instead of Pt(cod)$_2$. However, according to $^1$H NMR spectroscopy, overnight stirring yields a mixture of Pt(carbene)(dmfu)(nbe) and Pt(carbene)(dmfu)$_2$. So, the substitution of the last nbe from Pt(carbene)(dmfu)(nbe) to Pt(carbene)(dmfu)$_2$ is not complete at room temperature. Therefore, addition of additional equivalents of dmfu is needed and stirring at elevated temperature (40-50 °C) is required. In situ preparation of Pt(cod)$_2$ by addition of cod to Pt(nbe)$_3$[22] before adding the other reagents, can overcome this problem. However, use of isolated Pt(cod)$_2$ is to be preferred, and leads to overall exhaustive displacement of cod by two dmfu ligands.

The Pt(carbene)(η$_2$-alkene)$_2$ complexes Pt(IMes)(dmfu)$_2$, (1a, IMes = 1,3-dimesityl-imidazol-2-ylidene) and Pt(SIMes)(dmfu)$_2$, (2a, SIMes = 1,3-dimesityl-dihydroimidazol-2-ylidene) can be handled in air without significant decomposition and are also stable for extended periods of time in solution, even in refluxing acetone. Their stability is surprising, taking into account that the complexes are known to easily undergo alkene dissociation.$^{[1,11]}$
Decreasing the size of the carbene ligands and synthesis of Pt(SIPh)(dmfu)$_2$

We would also like to decrease the steric bulk on the N-atom of the carbenes, to see the influence on the reactions which we are investigating (C-H activation reactions, Chapter 4). Therefore, we used several imidazolium salts like 1,3-dimethyl-imidazolium iodide (IMeHI), 1,3-diisopropyl-imidazolium chloride (IiPrHCl) and 1,3-(di(t-butyl)-imidazolium chloride (IxBuHCl) as starting salt. We used method B (in situ method) for making the (IR)Pt(dmfu)$_2$-complexes (see Scheme 3.2). All reactions resulted in off-white solids, but no clear carbene-containing products were found for R = iPr, tBu. In the case of R = Me, a carbene-containing product was formed according to $^1$H NMR spectroscopy. However, washing and crystallization did not yield pure products.

\[ \text{Pt(cod)$_2$} + 2\text{R'CH} = \text{N} - \text{R} + \text{I} + \text{NaH} \rightarrow [\text{IR} \cdot \text{Pt} \cdot \text{dmfu}]_2 \]

\[ R = \text{Me, iPr, tBu} \quad R' = \text{COOME} \]

Scheme 3.2 Attempted synthesis of (N-alkyl-NHC)Pt(dmfu)$_2$ complexes

Apparently, contrary to the N-mesityl analogues, N-alkyl NHC’s did not result in Pt(carbene) complexes using method B. We then decided to synthesize phenyl-substituted imidazolium and imidazolinium salts, which were synthesized from the corresponding a-diimines (Ar-N=CH-)$_2$. Under normal conditions,$^{[23]}$ the condensation of glyoxal with two equivalents of aniline in methanol, did not result in phenyl-DAB. The $^1$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)$_2$ (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 by Lemal et al.$^{[26-28]}$ They were actually able to observe a mixture of the dimer and monomer by $^1$H NMR spectroscopy, by using sterically larger aromatic substituents on the N-atoms. We decided to use this approach for synthesizing the saturated phenyl-NHC, and its corresponding platinum complex Pt(SIPh)(dmfu)$_2$ (2b, SIPh = 1,3-diphenyl-dihydroimidazol-2-ylidene). Various metal carbene complexes have already been prepared.
via this method. The synthesis of the "Wanzlick-dimer" 4 is straightforward and has been executed by a slightly modified literature method.

When the dimer 4 is treated with Pt(cod)_2 and two equivalents of dmfu, no platinum(carbene) complex was obtained, even gentle heating did not result in the formation of 2b (see Scheme 3.3). Using Pt(nbe)_3 instead of Pt(cod)/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 Pt(cod)(dmfu)/Pt(nbe)_2(dmfu) (see Chapter 2) is not reactive enough towards the free carbene 4'.

From the observed failure to form 2b according to Scheme 3.3, 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 3.3 lies extremely far to the left. The alternative, that the carbene 4' does form but cannot substitute an alkene from the Pt°(alkene)_n precursor can be excluded. It is known and has amply been demonstrated that NHC's can substitute all kinds of ligands and certainly one alkene.

As the direct synthesis of 2b was not possible starting from the dimer 4, we treated 4 with HBF_4 in ether under dry conditions. Adding this strong acid in THF resulted in the fast precipitation of imidazolinium salt 5. In a slow reaction, the addition of NaH, Pt(cod)_2 and 2 equivalents of dmfu to the imidazolinium salt 5 indeed gave 2b, c.f. Scheme 3.4.†

†Of course, direct synthesis of the imidazolinium salt 5 could be done starting from 1,2-dianilino-ethane and trimethoxy ortho-formate.
This successful formation of 2b according to Scheme 3.4 may have two reasons. The first possibility is, that NaH slowly deprotonates 5 to give the free carbene 4', which then immediately reacts with Pt(alkene)$_n$. However, we doubt that this explanation is correct. Already Wanzlick$^{[31]}$ noted 40 years ago, and Denk et al.$^{[32]}$ recently confirmed this, 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 3.5, the Pt(alkene)$_n$ precursor reacts with the imidazolinium salt 5 by C-H activation at the 2-position, giving the probably unstable hydridoPt$^\text{II}$(carbene) complex 6, which is then deprotonated by NaH to form 2b and dihydrogen.

\begin{center}
\textbf{Scheme 3.5 Proposed C-H activation intermediate 6}
\end{center}

$^1$H NMR spectroscopy

In agreement with the C$_2$-symmetry of complexes 1a, 2a and 2b, the $^1$H NMR spectra of the zerovalent platinum compounds show two different signals for the alkene-protons (see Table 3.1). Two of the protons of the alkenes are pointing toward the aromatic part of the carbene-ligand, and are found at lower frequency due to the anisotropic shielding of the aryl. 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.$^{[33]}$
Synthesis of Zerovalent Electron-rich Platinum Centers: Platinum(carbene)alkene)\(_2\) Complexes

**Figure 3.3** Prepared (carbene)Pt\(^0\)(dmfu)\(_2\) complexes

The saturated carbene is a stronger σ-donor than the unsaturated carbene,\(^{[34]}\) which leads to more π-backbonding to the dmfu in 2a as compared to 1a, and hence lower bond order and smaller \(^2J_{\text{PH}}\) 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 π-overlap with the NHC frame, thereby increasing the alkene C-C double bond character leading to higher values for \(^2J_{\text{PH}}\) in case of 2b.

**Table 3.1** \(^1\)H NMR spectroscopic data of the alkene-protons.

<table>
<thead>
<tr>
<th>compound</th>
<th>(\delta(H_A)) (ppm) (^2J_{\text{HP}}) (Hz)]</th>
<th>(\delta(H_B)) (ppm) (^2J_{\text{HP}}) (Hz)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(IMes)(dmfu)(_2) (1a)</td>
<td>3.92 [46.0]</td>
<td>3.13 [63.0]</td>
</tr>
<tr>
<td>Pt(SIMes)(dmfu)(_2) (2a)</td>
<td>3.89 [43.2]</td>
<td>3.17 [52.8]</td>
</tr>
<tr>
<td>Pt(SIPh)(dmfu)(_2) (2b)</td>
<td>3.49 [57.0]</td>
<td>3.10 [60.6]</td>
</tr>
</tbody>
</table>

\(^{195}\)Pt NMR spectroscopy

More information on the chemical properties of the metal center was sought by means of \(^{195}\)Pt NMR. The \(^{195}\)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 \(^{195}\)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. Although the angles between the ligands can have a large influence on the chemical shift in \(^{195}\)Pt NMR, the shift to higher frequency for 2b, as compared to 1a and 2a can be explained by the stronger donation of the mesityl-based NHC as compared to that of the phenyl-based NHC.

Recently another Pt(0) monocarbene complex with alkenes has been published (see Figure 3.2) with a chemical shift of -5343 ppm.\(^{[10]}\) Comparison of our complexes with this complex and with Pt\(^0\)(IMes)\(_2\) (see Figure 3.2) described by Arduengo et al.,\(^{[19]}\) indicates that the electron density on the platinum centers is quite similar. Other tris-coordinated platinum(0) complexes, like the
complexes described in chapter 2, Pt(alkene), have $^{195}$Pt chemical shifts around $-4000$ ppm. Compared to these, the present platinum(carbene)(bisalkene) 1a, 2a, 2b have their $^{195}$Pt resonances at much lower frequencies, which is due to the fact that carbenes are C-ligands, which cause larger ligand fields, hence lower chemical shifts.$^{[35,36]}$

**Variable temperature NMR spectroscopy of 2a and 2b**

When investigating the chemical and physical properties of 2b, line-broadening was observed in a $^1$H NMR spectrum of 2b in benzene-$d_6$ for the alkene hydrogen atoms slightly above room temperature (303 K). In order to probe the fluxional process, we measured the $^1$H NMR spectra of 2b and 2a in toluene-$d_8$ in the temperature range from 298 K to 378 K.

![Figure 3.4 VT $^1$H NMR spectra of 2b (*alkene protons region)](image)

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 $^2J[^1$H,$^{195}$Pt]-couplings superimposed (see Figure 3.4). 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 \(2a\) 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 due to better \(\sigma\)-donation of the SIMes-carbene, resulting in more \(\pi\)-backbonding to the dmfu's and as a result, stronger coordination of the dmfu's. 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 and less \(\sigma\)-donation of the carbene-ligand. This causes weaker coordination of dmfu, so dissociation is easier.

**X-ray structure determination of \(1a\)**

The molecular structure of one of the synthesized zerovalent carbene platinum bisalkene, \(1a\), was unambiguously proven by a single crystal X-ray structure analysis, which is depicted in Figure 3.5. Selected bond lengths and angles are presented in Table 3.2.

![Displacement ellipsoid plot of \(1a\) with ellipsoid drawn at the 50% probability level. Hydrogens are omitted for clarity.](image)

**Figure 3.5** Displacement ellipsoid plot of \(1a\) with ellipsoid drawn at the 50% probability level.

Hydrogens are omitted for clarity.

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°. The compound is approximately \(C_{2v}\) symmetric.
The C=C bonds of the coordinated dmfu’s (1.422 Å and 1.427 Å) are elongated compared to free dmfu (1.318 Å)\(^{[37]}\) caused by the donation of electron density from platinum into the \(\pi^*\)-orbitals of the dimethylfumarate. The Pt-\(\eta^2\)-C=C planes are oriented in an angle of 56.0° and -56.7 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°. The mesityl substituents on the nitrogens of the NHC-ligand are tilted in an angle of 68.8° and -66.3° relative to the imidazole plane.

Table 3.2 Selected bond lengths (Å) and angles (deg) for \(\text{Ia}\) (e.s.d. in parentheses).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(1) – C(1)</td>
<td>2.072(2)</td>
</tr>
<tr>
<td>Pt(1) – C(23)</td>
<td>2.098(3)</td>
</tr>
<tr>
<td>Pt(1) – C(29)</td>
<td>2.101(3)</td>
</tr>
<tr>
<td>C(28) – C(29)</td>
<td>1.422(4)</td>
</tr>
<tr>
<td>C(1) – Pt(1) – C(22)</td>
<td>96.96(9)</td>
</tr>
<tr>
<td>C(1) – Pt(1) – C(28)</td>
<td>94.21(9)</td>
</tr>
<tr>
<td>C(1) – Pt(1) – C(23)</td>
<td>136.15(11)</td>
</tr>
<tr>
<td>C(1) – Pt(1) – C(29)</td>
<td>133.39(11)</td>
</tr>
</tbody>
</table>

Recently, the X-ray crystal structure of a zerovalent platinum (carbene) compound with a diene ligand \([\text{Pt(1,3-dimethyl-imidazol-2-ylidene)}(\eta^4\text{-divinyltetramethylsiloxyane})]\) has been reported.\(^{[10]}\) The reported Pt-C(carbene) bond is slightly shorter (2.051 Å) and the Pt-C(alkene) bonds are slightly longer (2.103 Å and 2.178 Å) compared to \(\text{Ia}\).

3.2.2 Reactivity of platinum(carbene)(alkene)\(_2\) towards \(\text{H}_2\)

The new platinum(carbene)(alkene)\(_2\)-complexes are reactive towards C-H bonds of imidazolium salts\(^{[11]}\) (see Chapter 5). We were also interested to see whether these compounds are reactive towards C-C bonds, for instance imidazolium salts methylated at the 2-position. 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)\(_2\) towards 1,2,3-trimethyl imidazolium iodide (x) (see Scheme 3.6). This should in principle result in a thermodynamically stable product (biscarbene)platinum(methyl)(iodide) (7ax). 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, *in situ* formed 7ax could be trapped by reaction with H₂. This reaction was carried out in acetone-*d₆* in an NMR tube and was followed by ¹H NMR spectroscopy. Indeed platinum hydrides were observed in the expected chemical shift-range similarly to known analogues¹¹ (around -14.5 ppm, indicating a hydride *trans* to an iodide, as in *trans*-hydrido 3,5-dimethyl-imidazol-2-yliden iodo 3,5-dimesityl-imidazol-2-yliden platinum(II) (7ay) after reductive elimination of methane).

As 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, H₂ was bubbled through a solution of 1a in benzene-*d₆* in an NMR-tube at 55 °C for 30 minutes. At this temperature a reaction occurred and surprisingly no platinum metal was observed.² After the reaction, a ¹H NMR spectrum was taken and dimethyl succinate and platinum complex 7a were observed as main products. This reaction takes place surprisingly cleanly, and yields mononuclear (hydrido)platinum(carbene) 7a (see Scheme 3.7).

² Compare e.g. with bidentate ligands (see Chapter 2): Pt(NN)(dmfu) (NN=R-DAB) reacts at 75 °C to yield only platinum metal.²³⁹
7a has been characterized in solution by $^1$H NMR, $^{195}$Pt NMR and IR spectroscopy. The hydride is found at $-27.07$ ppm with a large $^1J_{PH}$ coupling of $1900$ Hz, which is in agreement with a very weak trans-ligand such as the carbonyl in this case. The $^{195}$Pt-resonance is found of $6a$ at $-3940$ ppm, indicating $+2$ oxidation state for the platinum center of $7a$, which implies an oxidative shift of $+1300$ ppm upon conversion of $1a$ into $7a$.

$^{13}$C NMR spectroscopy failed due to the low solubility in organic solvents of $7a$ like benzene or acetone. Also, the long term of stability for compounds such as $7a$ is questionable. Attempts to isolate the complex $7a$ failed. Complex $7a$ 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 $^1$H NMR spectrum. This reactivity can be rationalized from the coordination site that is occupied by the weakly coordinating carbonyl that can be displaced for example by a C-H bond. Then C-H bond activation of one of the methyl-groups can possibly take place. As far as we know, this is one of the first examples of C-H activation with non-cationic Pt(II) complexes.

In order to decrease the reactivity of $7a$ towards hydrocarbons, we added 1 equivalent of pyridine to $7a$ in acetone-$d_6$ to stabilize the Pt$^{ll}$ center. Not all of $7a$ ($\delta_{Pt} = -3920$ ppm in acetone-$d_6$) was converted in $8a$ ($\delta_{Pt} = -4081$ ppm). With an excess of pyridine, $8a$ is the only platinum complex observed. 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 the platinum center. The hemi-labile 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.
To assure that the hydride in 7a originates from the dihydrogen that was added to 1a, we added \( ^2\text{H}_2 \) to 1a. Indeed, in this case Pt-\( ^2\text{H} \) was observed at -26.6 ppm in the \( ^2\text{H} \) NMR spectrum and also deuterated dimethylsuccinate was formed.

So, reaction of 1a with dihydrogen constitutes a very gentle method to arrive at a neutral hydrido platinum(II) carbene complex with a hemilabile coordinating carbonyl, from which a free coordination site for bond activation reactions is easily created.

### 3.3 Conclusions

The first examples of zerovalent platinum mono-carbene bis(alkene) complexes have been isolated and characterized as white solids. Importantly, the impurities can be easily removed with apolar solvents, which facilitate the purification of these compounds very much. These 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 found and we showed that the route *via in situ* preparation of the carbene is the most facile one for obtaining the (carbene) platinum bis(alkene) complexes in good yield.

From variable temperature experiments using \(^1\text{H} \) spectroscopy it can be concluded that the coordination of the alkenes is more labile when a less electron-density-donating carbene ligand is present in the complex. These Pt(0) complexes are valuable compounds for some Pt(0) catalyzed reactions\(^{[11]} \) and may be of interest for comparison with (carbene)Pd(0)-catalyzed reactions, to give more information about intermediates in these reactions.

The (carbene)Pt(0) complexes react under very mild conditions with dihydrogen to form neutral hydrido platinum(II) carbene complexes with a hemilabile coordinating carbonyl. Pyridine is able to break this platinum carbonyl coordination; however the coordination of pyridine is also quite weak. The hemilability of the carbonyl facilitates the reaction of these neutral hydrido platinum(II) carbene complexes towards certain C-H bonds, to give C-H bond activation.
3.4 Experimental Section

3.4.1 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.\textsuperscript{[43]} \textsuperscript{22} \textsuperscript{13}\textsuperscript{1} \textsuperscript{1}Pt(cod)\textsubscript{2}, \textsuperscript{[22]} \textsuperscript{1}Pt(nbe)\textsubscript{3}, \textsuperscript{[30]} \textsuperscript{1},\textsuperscript{3}-dimesityl-imidazolium chloride, \textsuperscript{[30]} \textsuperscript{1},\textsuperscript{3}-dimesityl-dihydroimidazolium chloride were prepared according to literature procedures. NMR measurements were performed on a Varian Mercury300 spectrometer (\textsuperscript{1}H: 300.13 MHz, \textsuperscript{13}C 75.47 MHz), a Varian Inova500 spectrometer (\textsuperscript{1}H: 499.88 MHz, \textsuperscript{13}C: 125.70 MHz) and Bruker DRX300 spectrometer (\textsuperscript{1}H: 300.13 MHz, \textsuperscript{13}C: 75.47 MHz, \textsuperscript{195}Pt: 64.13 MHz). \textsuperscript{195}Pt NMR spectra were measured via a normal HMQC sequence at 298K. \textsuperscript{13}C NMR spectra were measured with \textsuperscript{1}H decoupling. Positive chemical shifts (\textdelta) are denoted for high-frequency shifts relative to the external TMS reference (\textsuperscript{1}H, \textsuperscript{13}C) or a Na\textsubscript{2}PtCl\textsubscript{6} reference (\textsuperscript{195}Pt). HRMS measurements were performed on a JEOL JMS SX/SX102A four sector mass spectrometer, coupled to a JEOL MS-8P9021D/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. The elemental analysis of 2a was carried out by Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

3.4.2 Synthesis

Method A: Synthesis of 1a via the preparation of the free carbene

1,3-Dimesityl-imidazol-2-ylidene (free carbene)

The free carbene is synthesized by a slightly changed procedure described by Arduengo \textit{et al.} 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 1 equivalent of KOTBu (1M in THF, 2.35 ml) was added to the mixture. The solution was stirred for 4 hours 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 \textit{in vacuo}. The residue was extracted with 4 portions of hot hexane (around 60 °C). The extracts were collected and 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 \textminus80°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.

\(1,3\)-Dimesityl-imidazol-2-ylidine)-bis-(1\(^1\)-dimethylfumaraat) platinum(0) (Ia)

An amount of 149.8 mg (0.4911 mmol) 1,3-dimesityl-imidazol-2-ylidine 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)_2 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 one hour 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. \(^1\)H NMR (500 MHz, acetone-d\(_6\), \(\delta\) (ppm)): 7.61 (2H, s, \(J_{\text{HH}} = 10.5\) Hz), 7.08 (2H, s), 6.96 (2H, s), 3.92 (2H, d, \(J_{\text{HH}} = 9.0\) Hz, \(J_{\text{HPt}} = 46.0\) Hz), 3.40 (6H, s), 3.30 (6H, s), 3.13 (2H, d, \(J_{\text{HH}} = 9.0\) Hz, \(J_{\text{HPt}} = 63.0\) Hz), 2.39 (6H, s), 2.35 (6H, s), 1.80 (6H, s). \(^{13}\)C NMR (125.7 MHz, acetone-d\(_6\), \(\delta\) (ppm)): 172.27, 170.69 (\(J_{^{195}\text{Pt}, ^{13}\text{C}} = 38.0\) Hz), 169.14 (\(J_{\text{CP}} = 36.0\) Hz), 138.38, 136.21 (\(J_{\text{CP}} = 9.0\) Hz), 135.40, 135.34, 129.42, 129.13, 124.90 (\(J_{\text{CP}} = 42.2\) Hz), 50.22 (\(J_{\text{CP}} = 146.6\) Hz), 50.16, 50.13, 48.98 (\(J_{\text{CP}} = 191.1\) Hz), 20.41, 18.75, 17.51. \(^{195}\)Pt (64.3 MHz, acetone-d\(_6\), \(\delta\) (ppm)): -5184. HRMS (FAB) (m/z): Obs: 788.2512, Calc: 788.2514.

Method B: Synthesis of Ia via one-pot synthesis by in situ generation of the free carbene

\(1,3\)-Dimesityl-imidazol-2-ylidine)-bis-(1\(^1\)-dimethylfumaraat) platinum(0) (Ia)

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) dimethylfumarate (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 x 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 $^1$H NMR spectra. Single crystals suitable for X-ray structure analysis could be obtained by slowly cooling down a saturated acetone solution from 55 °C to room temperature.

(1,3-Dimesityl-dihydroimidazol-2-ylidene)-bis-(η$^2$-dimethylfumarate) platina(O) (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) dimethylfumarate (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 x 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. $^1$H NMR (500 MHz, acetone-$d_6$, δ(ppm)): 7.03 (2H, s), 6.87 (2H, s), 4.20 (2H, m), 4.05 (2H, m), 3.89 (2H, d, $^3$J$_{HH} = 9.0$ Hz, $^2$J$_{HP} = 43.2$ Hz), 3.49 (6H, s), 3.21 (6H, s), 3.17 (2H, d, $^3$J$_{HH} = 9.0$ Hz, $^2$J$_{HP} = 52.8$ Hz), 2.65 (6H, s), 2.29 (6H, s), 1.91 (6H, s). $^{13}$C NMR (125.7 MHz, acetone-$d_6$, δ(ppm)): 171.51 ($^2$J$_{CP} = 40.0$ Hz), 169.68 ($^2$J$_{CP} = 36.0$ Hz), 138.14, 137.33, 136.90, 136.86, 130.26, 129.98, 52.93 ($^1$J$_{CP} = 136.5$ Hz), 51.02, 50.89, 49.89 ($^1$J$_{CP} = 136.5$. Hz), 21.13, 19.13, 18.17. $^{195}$Pt NMR (64.3 Hz, acetone-$d_6$, δ(ppm)): -5200. EA: Found: 50.26 (C), 5.31 (H), 3.48 (N) Calc.: 50.19, 5.36, 3.55.

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 (2x 5 ml) yielding 0.98 g (27%) of a white solid, which was identified by $^1$H NMR spectroscopy as pure 3. $^1$H NMR (300 MHz, acetone-$d_6$, δ(ppm)): 7.16-7.28 (8H, m), 6.80 (2H, tt, $^3$J$_{HH} = 6.9$ Hz, $^4$J$_{HH} = 1.5$ Hz), 6.86 (1H, s), 4.21 (2H, q, $^3$J$_{HH} = 4.2$ Hz), 4.87 (2H, q, $^3$J$_{HH} = 4.2$ Hz).
Bis-(1,3-diphenyl-2-imidazolidine) (4)

An amount of 495.3 mg (1.45 mmol) 1,3-diphenyl-2-trichloromethyl-imidazolidine (3) was dissolved in a mixture of 4 ml xylene and 1 ml collidine. This solution is heated on a oil bath to 185 °C for one hour. After cooling down to room temperature, the solvents were removed by decantation and the yellow solid was washed with diethyl ether (2x 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.

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 minutes stirring at room temperature, the solid was filtered off and was washed with diethyl ether (2x 10 ml). This yielded 0.20 g (80%) of a pale yellow solid. $^1$H NMR (300 MHz, acetone-$d_6$, δ/ppm): 9.86 (1H, s), 7.72 (4H, m), 7.60 (4H, m), 7.46 (2H, m), 4.92 (4H, s). $^{13}$C NMR (75.47 MHz, dmsod-$d_6$, δ/ppm): 152.65 (NCH), 136.97 (C), 130.59 (m-CH), 127.93 (p-CH), 119.31 (o-CH), 49.15 (CH$_2$). $^{19}$F NMR (282.4 MHz, acetone-$r_6$, δ/ppm): -151.7.

(1,3-Diphenyl-dihydroimidazol-2-ylidene)-bis-(η²-dimethylfumarate) platinum(0) (2b)

To 59.2 mg (0.191) 1,3-diphenyl-2-imidazolidinium tetrafluoroborate (5), 73.6 mg (0.179 mmol) Pt(cod)$_2$, 55.7 mg (0.387 mmol) dimethylfumarate 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 (2x 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 (2x 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%). $^1$H NMR (300 MHz, acetone-$d_6$, δ/ppm): 7.47 (4H, dd, $^3$J$_{HH}$ = 8.4 Hz, $^4$J$_{HH}$ = 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, $^3$J$_{HH}$ = 9.9 Hz, $^3$J$_{HP}$ = 57.0 Hz), 3.10 (2H, d, $^3$J$_{HH}$ = 9.9 Hz, $^3$J$_{HP}$ = 60.6 Hz). $^{13}$C NMR (125.7 MHz, CD$_2$Cl$_2$, δ/ppm): 196.89 $^1$J$_{CP}$ = 1332 Hz, 172.20 ($^2$J$_{CP}$ = 41 Hz), 171.84 ($^2$J$_{CP}$ = 44 Hz), 171.39, 129.04 ($^4$J$_{CP}$ = 39.7 Hz),
126.47, 122.35, 52.10 (\(1J_{CP} = 164.4\) Hz), 51.75 (\(3J_{CP} = 42.0\) Hz), 51.41, 51.11, 46.06 (\(1J_{CP} = 172.0\) Hz). \(^{195}\)Pt NMR (64.3 Hz, acetone-\(d_6\), \(\delta\)(ppm)): -5129.

### 3.4.3 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 \(F^2\) 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-merohedrically twinned with a twofold rotation around hkl = (100) 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.\(^{48}\) 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 3.2.

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C(<em>{33})H(</em>{40})N(_2)O(_8)Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula Weight</td>
<td>787.76</td>
</tr>
<tr>
<td>Crystal color and shape</td>
<td>yellow block</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.24 x 0.18 x 0.12 mm(^3)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group P2(_1)/c (no. 14)</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>18.362(3) Å</td>
</tr>
<tr>
<td>b</td>
<td>10.5379(14) Å</td>
</tr>
<tr>
<td>c</td>
<td>16.5493(17) Å</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>90 °</td>
</tr>
<tr>
<td>(\beta)</td>
<td>92.063(15) °</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>90 °</td>
</tr>
<tr>
<td>(V)</td>
<td>3200.2(8) Å(^3)</td>
</tr>
<tr>
<td>(T)</td>
<td>150 K</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
</tbody>
</table>
Synthesis of Zerovalent Electron-rich Platinum Centers: Platinum(carbene)alkene)₂ Complexes

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, D&lt;sub&gt;calc&lt;/sub&gt;</td>
<td>1.635 g/cm³</td>
</tr>
<tr>
<td>μ(Mo&lt;sub&gt;Kα&lt;/sub&gt;)</td>
<td>4.438 mm⁻¹</td>
</tr>
<tr>
<td>Transmission range</td>
<td>0.63-0.77</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>46720 / 9843</td>
</tr>
<tr>
<td>Parameters</td>
<td>424</td>
</tr>
<tr>
<td>R₁ (obs. / all refl.)</td>
<td>0.0255 / 0.0371</td>
</tr>
<tr>
<td>wR₂ (obs. / all refl.)</td>
<td>0.0467 / 0.0498</td>
</tr>
<tr>
<td>GoF</td>
<td>1.045</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;min/max&lt;/sub&gt;</td>
<td>-0.81 / 0.73 e/Å³</td>
</tr>
</tbody>
</table>

3.4.4 Reactions with dihydrogen

cis-[3-Methoxy-1-(methoxycarbonyl)-3-oxopropyl][hydrido][1,3-dimesityl-imidazol-2-ylidene] platina(II) (7a)

H₂ was bubbled through a solution of 1a in benzene-d₆ in an NMR-tube at 55 °C for 30 minutes. After the reaction a ¹H NMR spectrum was taken, indicating that 1a had completely been converted to dimethyl succinate and platinum complex 7a. ¹H NMR 7a (300 MHz, benzene-d₆, δ(ppm)): 6.64 (4H, s, ArH), 6.08 (2H, ImH), 3.47 (3H, br, CHCH₂), 3.41 (3H, COOCH₃), 2.95 (3H, s, COOCH₃), 2.14 (6H, s, CCH₃), 2.08 (6H, s, CCH₃), 1.99 (6H, s, CCH₃), -27.07 (1H, s, J<sub>HPt</sub> = 1900 Hz). ¹⁹⁵Pt (64.3 MHz, benzene-d₆, δ(ppm)): -3940.

3.5 References


63
Chapter 3

Synthesis of Zerovalent Electron-rich Platinum Centers: Platinum(carbene)alkene\textsubscript{2} Complexes


65