Isophthalaldimine compounds of palladium, platinum and rhodium.
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Chapter 4

Isophthalaldimine platinum(II) acetylide compounds†

4.1 Introduction

Stable *cis*-diorganoplatinum(II) compounds with didentate\textsuperscript{2,3} and tridentate\textsuperscript{3,4} ligands are known. As was stated in the previous chapter, *trans*-diorganoplatinum(II) compounds are accessible when they contain a covalently bound meridional coordinating [D-C-D] ligand,

![Diagram](image)

Figure 4-1.

(A, Figure 4-1, D = PR\textsubscript{2}\textsuperscript{5} and D = NR\textsubscript{2}\textsuperscript{6,9}). Specifically, it has been shown that isophthalaldimine platinum(II) compounds with a methyl group *trans* to the ipso carbon atom were accessible. According to Scheme 4-1, oxidative addition of 1, followed by transmetallation of 2 with dimethylzinc yielded 3, but only for R = 2,6-dimethylphenyl and R = 2,6-diisopropylphenyl. In this chapter, the attempts to extend the scope of the transmetallation reaction to other imine substituents in the synthesis of isophthalaldimine platinum(II) *acetylide* compounds (4, Scheme 4-2) will be described. The question is whether

†. This chapter has partly been published.\textsuperscript{1}
the strong mutual trans influence of the carbon fragments is outweighed by the chelate effect of the imine moieties, as was found for 3h and 3m, which may result in the formation of compounds of type 4. However, a difference in bonding of a Csp³ carbon to platinum in the case of methyl (3) and of a Csp carbon in the case of acetylide (4) may reflect in the products obtained from a transmetallation reaction of compounds 2 and a lithium acetylide.

Trans aryl platinum(II) acetylide compounds are accessible via a transmetallation, as has been shown for the related bis(dimethylaminomethyl)phenyl [N-C-N] ligand, of which its trans platinum(II) acetylide derivatives have been synthesized and studied before.⁶⁻⁸.

\[ \text{Scheme 4-2. Envisaged synthesis of isophthalaldimine platinum(II) acetylide compounds 4} \]

If the isophthalaldimine ligand retains its meridional coordination mode, compounds of type 4 may be formed. However, if only one of the imine moieties remains coordinated, the ligand can in principle also act as a cis-coordinating κC,κN-didentate ligand, making cis-diorganometallic compound available.

If transmetallation with lithium acetylides occurs selectively and stable compounds of type 4 are obtained, such compounds may be suitable building blocks for the preparation of organometallic oligomers which may have interesting physical properties such as non linear optic or conducting properties. If compounds of type 2 could be reacted with compounds of type 2 which have a LiC≡C- substituent on the 4-position of the platinum bound aryl ring, long conjugated chains may be in reach.⁶,⁷,¹⁰ In these chains, the imine substituents may act as solubilizing groups, thus overcoming the often encountered problem of insolubility of such oligomers.

### 4.2 Synthesis of isophthalaldimine platinum(II) acetylide compounds

The synthesis of isophthalaldimine platinum(II) acetylide compounds was carried out by reaction of the isophthalaldimine platinum(II) bromide compounds 2a-m with a lithium acetylide. Because of the indicative signals in the \(^1\text{H} \text{NMR} \) spectrum, LiC≡CSiMe₃ was used. Compounds 2h and 2m were also reacted with LiC≡C-p-tolyl, in these cases the compounds formed are identified with a quote (').

The transmetallation reactions of the platinum(II) bromides 2 with the lithium acetylides was performed analogously to the procedure described in Chapter 2 for the palladium(II) bromide.
Precursors, by adding a THF solution of LiC≡CSiMe₃ to a solution of 2 in THF at -60°C. ¹H, ¹⁹⁵Pt NMR and IR spectroscopic analysis indicated that different products 4, 5, and 6 were formed, depending on the substituent on the imine moiety, see Scheme 4-3 and Table 4-1. In the reactions between LiC≡CSiMe₃ and 2a (R = methyl), 2b (R = isopropyl) and 2j (R = 3,5-di-(trifluoromethyl)-phenyl) a complex mixture of unidentified products was formed.

### Table 4-1. Products formed in the reaction of 2 and LiC≡CR' and their ¹⁹⁵Pt NMR and IR data.

<table>
<thead>
<tr>
<th>Suffix</th>
<th>Imine substituent (R)</th>
<th>²⁵Pt (ppm)</th>
<th>Compound(s) formed</th>
<th>²⁵Pt (ppm)</th>
<th>v_CCN (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>tert-butyl</td>
<td>-3626</td>
<td>4c</td>
<td>-3609</td>
<td>2030</td>
</tr>
<tr>
<td>d</td>
<td>cyclohexyl</td>
<td>-3648</td>
<td>4d</td>
<td>-3580</td>
<td>2026</td>
</tr>
<tr>
<td>e</td>
<td>phenyl</td>
<td>-3606</td>
<td>5e</td>
<td>-3642</td>
<td>1951</td>
</tr>
<tr>
<td>f</td>
<td>4-methylphenyl</td>
<td>-3611</td>
<td>5f</td>
<td>-3643</td>
<td>1949</td>
</tr>
<tr>
<td>g</td>
<td>4-methoxyphenyl</td>
<td>-3608</td>
<td>5g</td>
<td>-3640</td>
<td>1949</td>
</tr>
<tr>
<td>h</td>
<td>2,6-dimethylphenyl</td>
<td>-3562</td>
<td>4h/6h</td>
<td>-3440/-3920</td>
<td>2024/2005</td>
</tr>
<tr>
<td>h'</td>
<td></td>
<td></td>
<td>4h'/6h'</td>
<td>-3421/-3944</td>
<td>2098</td>
</tr>
<tr>
<td>i</td>
<td>3,5-dimethylphenyl</td>
<td>-3599</td>
<td>5i</td>
<td>-3634</td>
<td>1948</td>
</tr>
<tr>
<td>k</td>
<td>2,4,6-trimethylphenyl</td>
<td>-3557</td>
<td>4k/6k</td>
<td>-3444/-3916</td>
<td>2037</td>
</tr>
<tr>
<td>l</td>
<td>2,6-diethylphenyl</td>
<td>-3527</td>
<td>4l/6l</td>
<td>-3406/-3915</td>
<td>2025/2006</td>
</tr>
<tr>
<td>m</td>
<td>2,6-diisopropylphenyl</td>
<td>-3517</td>
<td>4m</td>
<td>-3406</td>
<td>2032</td>
</tr>
<tr>
<td>m'</td>
<td></td>
<td></td>
<td>4m'</td>
<td>-3384</td>
<td>2095</td>
</tr>
</tbody>
</table>

a. In CDCl₃.
b. In C₆D₆.
c. One signal was obtained.
d. Compound 4k.
4.2.1 Trans isophthalaldimine platinum acetylide compounds

In the transmetallation of the platinum(II) bromide precursors 2c, 2d, 2h, 2k, 2l and 2m with LiC=CSiMe3 a trans isophthalaldimine platinum acetylide compound was formed. However, only 4c, 4d, 4k and 4m could be isolated, see Scheme 4-4. Compounds 4h and 4l were obtained in an inseparable mixture with 6h and 6l, respectively. For 2h and 2m an analogous reaction, performed with LiC=CC-p-tolyl, lead to the formation of 4h' and 4m', only the latter could be obtained pure.

The formation of a trans isophthalaldimine platinum acetylide compound was initially derived from 1H NMR spectroscopic analysis of the reaction mixture. The 1H NMR spectrum revealed complete conversion of 2 and the formation of a new compound having two equivalent imine moieties (similar to 3h and 3m in Chapter 3) and the typical additional resonance of the SiMe3 protons. Furthermore, 195Pt NMR, IR spectroscopic (see Table 4-1) and elemental analysis (of 4m) were in agreement with this conclusion.

**NMR spectroscopy**

In the 1H NMR spectrum of the compounds 4, the 3J(1H,195Pt) of the imine proton slightly decreases due to the larger cis influence of the acetylide compared to the bromide. For example, this coupling is 133 Hz in 4m, compared to 144 Hz in 2m. In the 13C NMR spectrum, the chemical shift of the ipso phenyl carbon moves ≈ 20 ppm to higher frequencies (similar as found for 3h and 3m in Chapter 3) and the 1J(13C,195Pt) (when observable) significantly decreases as a result of the strong trans influence of the acetylide (for example, from 178.6 ppm, 927 Hz in 2m, to 198.9 ppm, 616 Hz in 4m). Compounds 2m and 4m were also characterized by means of 15N NMR spectroscopy, there was a minor change observed in the chemical shift and the 1J(195Pt,15N) (from -148 ppm, 477 Hz in 2m, to -153 ppm, 464 Hz in 4m, for 1m the δ15N is -34 ppm). In the 195Pt NMR spectrum, the chemical shift changes about 80-100 ppm to higher frequencies, compared to 2. This change in the chemical shift is small and can not be easily explained, since both ligand field strength and the geometry around the platinum change.
Figure 4-2. Displacement ellipsoid plot of 4m with ellipsoids drawn at the 50% probability level. Hydrogens are omitted for clarity.

**X-ray crystal structure determination of 4m**

For one trans arylplatinum(II) acetylide compound, 4m (R = 2,6-diisopropylphenyl) the structure was unambiguously proven by an single crystal X-ray structure analysis. The molecular structure of 4m is depicted in Figure 4-2, selected bond lengths and angles are presented in Table 4-2.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Length (Å)</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(1)-N(1)</td>
<td>2.050(2)</td>
<td>C(33)-C(34)</td>
</tr>
<tr>
<td>Pt(1)-N(2)</td>
<td>2.043(2)</td>
<td>C(34)-Si(1)</td>
</tr>
<tr>
<td>Pt(1)-C(1)</td>
<td>1.945(2)</td>
<td>N(1)-C(7)</td>
</tr>
<tr>
<td>Pt(1)-C(33)</td>
<td>2.065(3)</td>
<td>N(2)-C(8)</td>
</tr>
<tr>
<td>N(1)-Pt(1)-N(2)</td>
<td>157.21(9)</td>
<td>C(1)-Pt(1)-C(33)</td>
</tr>
<tr>
<td>C(1)-Pt(1)-N(1)</td>
<td>78.55(9)</td>
<td>Pt(1)-C(33)-C(34)</td>
</tr>
<tr>
<td>C(1)-Pt(1)-N(2)</td>
<td>78.76(9)</td>
<td>C(33)-C(34)-Si(1)</td>
</tr>
</tbody>
</table>

In the crystal structure of 4m the platinum has a distorted square-planar environment with a sum of cis angles of 359.9° and geometric features which are virtually identical to those found in 3m in Chapter 3. The N-Pt-C angles of the five membered chelate rings amount to
78.55(9)° and 78.76(9)°, and are equal, within standard deviations, to the values found in 2h and 3m in Chapter 3. The trans N-Pt-N angle of 157.21(9)° is similar to 3m and slightly smaller compared to 2h (160.0(6)°). The Pt-Caryl and Pt-N bond lengths have expected values, 1.945(2) Å and 2.043(2)-2.050(2) Å, respectively. The acetylide group is coordinated end-on with a Pt-Cacetylide bond length of 2.065(2) Å, which is relatively long, this is probably caused by the small N-Pt-N angle and the trans influence of the aryl group. In the structure of 4m the five- and six-membered rings in the coordination plane of the platinum are each almost planar. For the Pt(1), N(1), C(1), C(6), C(7) plane, the largest deviation is 0.009(2) Å, for the Pt(1), N(1), C(1), C(2), C(8) plane this is 0.016(2) Å, for the aryl ring, the largest deviation is 0.006(3) Å. These three planes are almost coplanar, the angles between the first and the second is 2.87(10)°, between the first and the third 2.77(12)° and between the second and the third 1.08(12)°.

4.2.2 Dimeric cis isophthalaldimine platinum(II) acetylide compounds

For compounds 2e, 2f, 2g and 2i (R = phenyl, 4-methylphenyl, 4-methoxyphenyl and 3,5-dimethylphenyl, respectively) a cis isophthalaldimine platinum(II) acetylide compound of type 5 was obtained from the reaction of 2 and LiC≡CSiMe₃, no compound of type 4 was obtained at all in these cases.

The formation of compounds 5 was inferred from ¹H, ¹⁹⁵Pt NMR and IR spectroscopic analysis of the reaction mixture. For example, when the reaction mixture obtained from the reaction of 2g and LiC≡CSiMe₃ in THF was analyzed by means of ¹H spectroscopic analysis, the ¹H NMR spectrum (C₆D₆) showed two inequivalent imine moieties (HC=N at 10.1 ppm and 7.4 ppm). Based on the ¹H NMR spectra of compounds 2, 3 and 4 and the absence of ¹⁹⁵Pt satellites it was concluded that the 10.1 ppm resonance originated from an imine moiety that was not coordinating to the platinum. The inequivalence of the imine moieties in 5g is reflected in their ¹⁵N NMR chemical shift, which is -57 ppm for the non-coordinating nitrogen, and -133 ppm for the nitrogen of the coordinating imine. For the coordinating imine moiety at 7.4 ppm, the small ³J(¹H,¹⁹⁵Pt) of 73 Hz as compared to the starting material (139 Hz) pointed at a group trans to this imine with a much larger trans influence than an imine group. It was inferred that an acetylide group was in the position trans to this imine group. This implied that another ligand was completing the square planar coordination sphere around the platinum. In the infrared spectrum of a solid sample the C≡C bond resonated at a lower wave number (νC≡C = 1949 cm⁻¹) compared to 4c, 4d and 4m (νC≡C = 2026 - 2032 cm⁻¹), which pointed at a side-on coordination of the acetylide. When FD-MS revealed the dimeric nature of this species, it was concluded that the acetylide moiety was in a position cis to the aryl ipso carbon and that the compound had dimerized across the platinum-acetylide moiety to furnish 5g, see Scheme 4-5. The dimeric nature of 5g in solution was supported by ¹H NOE experiments and IR spectroscopy of a benzene solution of this compound. After
single crystals of 5g had been obtained, its molecular structure was unambiguously proven by an X-ray structure analysis (vide infra).

The spectra of the other cis isophthalaldimine platinum(II) acetylide compounds (5e, 5f and 5i) show many similarities to those of 5g. For all compounds 5 the $^{195}\text{Pt}$ chemical shift lies in the range -3634 ppm to -3643 ppm, in the infrared spectrum the $\nu_{\text{C=C}}$ lies in the range 1948 cm$^{-1}$ to 1951 cm$^{-1}$.

\begin{equation}
\text{Scheme 4-5.} \text{ Transmetallation of 2 and a lithium acetylide to form 5.}
\end{equation}

In the $^{13}\text{C}$ NMR spectra of the dimeric cis-diorganoplatinum compounds of type 5, the $J(^{13}\text{C}, ^{195}\text{Pt})$ couplings were not observed at all. Probably the satellite signals are broad, as was found in the $^1\text{H}$ NMR spectrum for the imine proton, and were probably hidden in the baseline of the spectrum. It is noteworthy that, whereas in the $^1\text{H}$ NMR spectrum of the dimeric cis-diorganoplatinum compounds the satellites were broad compared to the other types of isophthalaldimine platinum(II) compounds, in the $^{195}\text{Pt}$ NMR spectrum the signal for the $^{195}\text{Pt}$ nucleus was much narrower, the peak width at half height was $\approx$ 100 Hz for compounds of type 5, compared to up to $\approx$ 1300 Hz for compounds of type 2, 3 and 4.

\textit{X-ray crystal structure determination of 5g}

The molecular structure of 5g is depicted in Figure 4-3, a view of the crystal packing is presented in Figure 4-4 and selected bond lengths and angles are presented in Table 4-3.

Compound 5g is a dimer with two acetylide units acting as bridging ligands. They are each coordinated \textit{end-on} to one and \textit{side-on} to the other platinum, respectively. The Pt(1)···Pt(2) distance is 3.15573(19) Å, indicating that there is no bonding interaction.\textsuperscript{11} As expected, the Pt-C\textsubscript{acetylide} \textit{end-on} distances of 1.945(3) and 1.935(4) Å are much smaller than the Pt-C\textsubscript{acetylide} \textit{side-on} distances of 2.330(3)-2.397(3) Å. The different coordination mode of the acetylide unit in compounds 4m and 5g is not reflected in the C≡C distances, which are the same within standard deviations. The Pt-C\textsubscript{aryl} distance is slightly smaller in 4m (1.945(2) Å) than in 5g (2.018(3) Å and 2.010(3) Å), which probably is a consequence of the tridentate coordination in 4m as compared to the didentate coordination in 5g.\textsuperscript{7}
Figure 4-3. Displacement ellipsoid plot of 5g with ellipsoids drawn at the 50% probability level. Hydrogens are omitted for clarity.

Figure 4-4. A view of the crystal packing of 5g.
The core of compound 5g can be considered as a 6-membered Pt-C-C-Pt-C-C ring. This ring is not planar, but severely puckered with a dihedral angle of 75.07(12)° between the two Pt-C-C-Pt units. The Pt₂(C≡C)₂ core is much more puckered than in a related Pt₂(C≡C)₂ structure published by Forniès,¹² in which the analogous dihedral angle is 45°. This geometry is probably strongly dependent on the steric demands of the ligand system. In the structure of 5g these steric demands are also reflected in the planarity and coplanarity of the five- and six-membered rings in the coordination planes of the platinum atoms; compared to the structures of 2h, 3m and 4m more distortion is observed for 5g. Pt(1); for the Pt(1), N(1), C(1), C(6), C(7) plane, the largest deviation is 0.024(4) Å, for the C(1), C(2), C(3), C(4), C(5), C(6) plane, the largest deviation is 0.009(4) Å and the angle between these planes is 4.59(17)°. Pt(2); for the Pt(2), N(3), C(28), C(33), C(34) plane, the largest deviation is 0.053(2) Å, for the C(28), C(29), C(30), C(31), C(32), C(33) plane, the largest deviation is 0.032(3) Å and the angle between these planes is 6.32(16)°.

**Table 4-3. Selected bond lengths (Å) and angles (deg) for 5g**

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(1)-N(1)</td>
<td>2.087(3)</td>
</tr>
<tr>
<td>Pt(2)-N(3)</td>
<td>2.090(3)</td>
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<td>Pt(1)-C(1)</td>
<td>2.018(3)</td>
</tr>
<tr>
<td>Pt(2)-C(28)</td>
<td>2.010(3)</td>
</tr>
<tr>
<td>Pt(1)-C(23)</td>
<td>1.945(3)</td>
</tr>
<tr>
<td>Pt(2)-C(50)</td>
<td>1.935(4)</td>
</tr>
<tr>
<td>Pt(1)-C(50)</td>
<td>2.376(3)</td>
</tr>
<tr>
<td>Pt(1)-C(51)</td>
<td>2.330(3)</td>
</tr>
<tr>
<td>C(1)-Pt(1)-N(1)</td>
<td>81.01(12)</td>
</tr>
<tr>
<td>C(28)-Pt(2)-N(3)</td>
<td>80.54(13)</td>
</tr>
<tr>
<td>N(1)-Pt(1)-C(23)</td>
<td>170.93(14)</td>
</tr>
<tr>
<td>N(3)-Pt(2)-C(50)</td>
<td>169.65(13)</td>
</tr>
<tr>
<td>C(1)-Pt(1)-C(23)</td>
<td>102.20(13)</td>
</tr>
<tr>
<td>C(28)-Pt(2)-C(50)</td>
<td>99.69(14)</td>
</tr>
</tbody>
</table>

Although organometallic compounds that are dimers via π-coordination of a M-C≡C moiety are known (M = Ti,¹³ Zr,¹⁴ Rh, Ir,¹⁵ Re,¹⁶ and Pt¹²,¹⁷), such compounds remain relatively rare. Moreover, most of these were synthesized from dimeric precursors ([LₓM-Cl]₂, Ir, Rh, Ti, Zr) or by exchange of the acetylide between the two metal centers (Pt, Zr). Clearly in the case of 5g the Pt₂(C≡C)₂ core results from a dimerization of two independently formed Pt-C≡C-R units, as is the case for the rhenium dimer.¹⁶
4.2.3 Monomeric cis isophthalaldimine platinum(II) acetylide compounds

For reactions of 2h, 2k and 2l and LiC≡CSiMe₃, and of 2h and LiC≡C-p-tolyl, the ¹H NMR spectroscopic analysis of the reaction mixture pointed at the presence of a compound with similar structural features as the dimeric cis-diorganoplatinum compounds of type 5. This compound was obtained in a mixture together with a trans-diorganoplatinum compound of type 4, see below in §4.2.4.

As in the dimeric cis-diorganoplatinum compounds, the ¹H NMR spectrum clearly showed that one imine was not coordinating and the low ³J(¹H,¹⁹⁵Pt) of the coordinating imine moiety pointed at an acetylide trans to this imine. So, a cis-diorganoplatinum compound had been formed in these cases as well. However, In the infrared spectrum the value of the νC≡C did definitely not point at side-on coordination of the acetylides. The difference in the surrounding of the platinum compared to the dimeric cis-diorganoplatinum compounds (5) was reflected in the chemical shift found in the ¹⁹⁵Pt NMR spectrum. Whereas the dimeric cis-diorganoplatinum compounds were found in the spectrum at -3634 to -3643 ppm, these cis-diorganoplatinum compounds were found at -3915 to -3944 ppm. It was concluded that these compounds were monomeric cis-diorganoplatinum compounds of type 6, see

Scheme 4-6. A ligand other than an acetylide moiety is coordinating to the position trans to the ipso aryl carbon to retain the square planar configuration of the platinum(II).

Unfortunately, it remains unclear what the nature of the ligand L (see Scheme 4-6) is. Since THF is abundantly present as the reaction medium and THF is known to form complexes with platinum(II),¹⁸ it is expected that THF is coordinating to the platinum center. Unfortunately, no suitable crystals for a single crystal X-ray structure analysis could be obtained, which was due to the instability of these compounds and due to the fact that the compounds of type 6 were obtained in a mixture together with a compound of type 4.

An indication for the coordination of THF was thought to have been found in the ¹H NMR spectrum of a sample of the crude reaction mixture in C₆D₆. A small change in the chemical shifts of residual THF was observed, from 1.363 (free THF) to 1.356 ppm and 3.518 (free THF) to 3.532 ppm. However, this small shift appeared to be caused by the solvation of lithium bromide (formed in the reaction) by the THF in the benzene environment.
Attempts to obtain $^{17}$O NMR data for compound $6h'$ (R = 2,6-dimethylphenyl, R' = p-tolyl) in C$_6$D$_6$ were unsuccessful. Probably, the already broad $^{17}$O chemical shift of the THF oxygen was broadened by the exchange between coordinated and uncoordinated THF.

The involvement of THF in the formation of compound $6h$, $6h'$, $6k$ and $6l$ was concluded from the reaction of $2k$ (R = 2,4,6-trimethylphenyl) and LiC≡CSiMe$_3$. When this reaction was carried out in THF, it lead to a mixture of $4k$ and $6k$. However, when the reaction was carried out in toluene, only $4k$ was detected by $^1$H and $^{195}$Pt NMR spectroscopic analysis.

The investigations of the reactions in toluene are hampered by the low solubility of the compounds 2 in toluene, especially at low temperatures. It was also found that the reactivity of LiC≡CSiMe$_3$ in toluene was lower than in THF, often starting compounds (2) remained present in the product mixture.

**4.2.4 Discrimination between different organoplatinum acetylide compounds**

A very useful tool for the discrimination between the compounds of type 4, 5 and 6 is $^1$H, $^{195}$Pt HMQC spectroscopy. The number of different products and the structural types of these products in the reaction mixture could easily be determined using a fast procedure (=20 min.) by analyzing a sample in C$_6$D$_6$ by this technique. An example of the resulting spectrum is

![Figure 4-5. $^1$H, $^{195}$Pt HMQC of 4h' and 6h'.](image-url)
given in Figure 4-5. The example shown concerns a sample obtained from the reaction of 2h (R = 2,6-dimethylphenyl) and LiC≡C-p-tolyl (R' = p-tolyl). For this case, the \(^1\)H NMR spectrum is difficult to interpret, especially the aromatic region shows many peaks. From the two dimensional \(^1\)H,\(^{195}\)Pt HMQC spectrum it becomes immediately clear that two platinum compounds are present. The structure of these compounds can be determined when comparing the spectrum to \(^{195}\)Pt NMR data of previously characterized isophthalaldimine compounds. Based on the \(^{195}\)Pt chemical shift, the number of coordinated imine protons, and their \(^3\)(H,\(^{195}\)Pt), it can be concluded that the monomeric cis-diorganoplatinum 6h' (H\(^1\)-H\(^3\), \(\delta^{195}\)Pt = -3944 ppm, \(\delta^{195}\Pt = 70 \) Hz) and the trans-diorganoplatinum compound 4h' (H\(^4\), \(\delta^{195}\Pt = -3421 \) ppm, \(\delta^{195}\Pt = 133 \) Hz) are present.

### 4.2.5 The formation of 4-6

Summarizing the results from the previous paragraphs and recalling Scheme 4-3, it is seen that compound of type 4, 5 or 6 are formed from the reaction between compounds 2 and a lithium acetylide an isophthalaldimine platinum acetylide (see Scheme 4-7). Furthermore, it appears that the imine substituent has a decisive influence on which type of diorganoplatinum compound is formed: A compound of type 4 is formed at low temperature selectively only for the sterically bulky alkyl (R = tert-butyl and cyclohexyl) and aryl (R = 2,6-diisopropylphenyl) substituents. In contrast, compounds of type 5 are formed for the least sterically demanding aryl substituents used (R = phenyl, 4-methylphenyl, 4-methoxyphenyl and 3,5-dimethylphenyl). For substituents with a sterical bulk in between (R = 2,6-dimethylphenyl, 2,4,6-trimethylphenyl and 2,6-diethylphenyl) a mixture of compounds 4 and 6 is formed.

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**Scheme 4-7.** Transmetallation of 2 to form 4, 5 or 6.
To gain insight in the processes leading to these different types of compounds, including the decisive influence of the imine substituent, a number of reactions of compounds 2 and a lithium acetylide (e.g. LiC≡CSiMe₃ and LiC≡C-p-tolyl) were monitored in time by ¹H and ¹⁵⁵Pt NMR spectroscopy. Particularly, the reactions of 2h and 2k with LiC≡C-p-tolyl and of 2k with LiC≡CSiMe₃, which lead to a mixture of 4h' and 6h', a mixture of 4k' and 6k' and a mixture of 4k and 6k, respectively. And the reactions of 2f and 2g and LiC≡CSiMe₃ which lead to compounds 5f and 5g, respectively, were investigated. The reaction was performed either in THF, or in toluene (if the solubility of the starting compound 2 was sufficient) and at different temperatures.

From these studies (vide infra) a number of conclusions were drawn (see also Scheme 4-8):

1. Compounds of type 6 are only formed in THF and only in a mixture with the corresponding compounds of type 4.
2. Once 4 and 6 have been formed, their ratio remains constant and there is no interconversion between 4 and 6.
3. The ratio between 4 and 6 is dependent on the reaction temperature; At low temperature, a larger amount of 4 is formed.
4. Compounds of type 5 are formed from the corresponding 4, which is formed first in the transmetallation, both in THF, toluene and benzene-d₆. The conversion of 4f to 5f was monitored in time (vide infra) and was virtually quantitative. For large imine substituents, this conversion does not occur and 4 is stable.
5. Compounds of type 6 are a 'dead-end', although their structure is related to compounds of type 5, they seem not to be involved in the formation of compounds of type 5.

Scheme 4-8.

Ad 1 and 2

Compound 2h (R = 2,6-dimethylphenyl) was reacted with LiC≡C-p-tolyl at low temperature and immediately a sample of the reaction mixture was withdrawn which was analyzed at
room temperature by means of $^1$H and $^{195}$Pt NMR spectroscopy. After warming up to room temperature, the reaction mixture was analyzed again. A third analysis was performed after the reaction mixture had been stirred for 1 day at room temperature. It was found that for all reaction mixtures, the ratio of $4h'$ to $6h'$ remained nearly constant (some decomposition was observed); no conversion of $4h'$ into $6h'$ was observed. Similarly 2k ($R = 2,4,6$-trimethylphenyl) was reacted with LiC≡C-p-tolyl and LiC≡CSiMe$_3$, which both gave similar results.

From the reaction of 2k and LiC≡CSiMe$_3$, which resulted in a mixture of 4k and 6k in a 4 to 1 ratio, compound 4k could be isolated from the mixture ($\delta^{195}$Pt = -3444). It was investigated whether 4k could be converted into 6k after its formation in THF. To that end 4k was dissolved in THF-d8 and the solution was monitored by $^1$H and $^{195}$Pt NMR spectroscopy. No signals of 6k were observed, however, even after prolonged standing, heating or upon the addition of compounds which were present in the reaction mixture, LiBr or HC≡CSiMe$_3$ (originating from the preparation of LiC≡CSiMe$_3$). So, after the transmetalation is finished, 4k is not converted into 6k.

Ad 3

The transmetalation of 2h ($R = 2,6$-dimethylphenyl) and LiC≡C-p-tol was performed at -90°C, -50°C and room temperature. At -90°C 4h' was the predominant compound, less of 6h' was observed than at -50°C. Unfortunately, due to overlap of signals the ratio of the two compounds could not be quantified, but by superposition of the spectra, the difference was qualitatively very clear. At room temperature, virtually no 4h' was observed and 6h' was the predominant species.

For the transmetalation of 2m ($R = 2,6$-diisopropylphenyl) and LiC≡CSiMe$_3$ an analogous result was found. This reaction leads to the selective formation of 4m at -60°C, but when the reaction was performed at room temperature, a small amount of 6m (< 5%, $\delta^{195}$Pt = -3917 ppm) was detected by $^1$H and $^{195}$Pt NMR spectroscopy.

Ad 4 and 5

In the reactions in which the dimeric cis-diorganoplatinum compounds 5f and 5g are obtained, these compounds are formed from 4f and 4g respectively. The conversion of 4f and 4g to, respectively, 5f and 5g was monitored by $^1$H and $^{195}$Pt NMR spectroscopy. A solution of LiC≡CSiMe$_3$ in THF was added to a solution of 2g and an internal standard (cyclodecane) at -60°C. Directly after the addition an aliquot of the reaction mixture was analyzed by $^1$H and $^{195}$Pt NMR spectroscopy at room temperature in C$_6$D$_6$. From the obtained $^1$H and $^{195}$Pt NMR spectra it was concluded that 2g was consumed and that three isophthalalaldimine platinum acetylide compounds had been formed, their identification is based on a comparison of the spectroscopic data to the compounds described in the previous paragraphs. Next to a small amount of the expected product 5g ($\delta^{195}$Pt = -3639 ppm, $^3$J($^1$H,$^{195}$Pt) = 73 Hz), in this
sample also \(4g\) (\(\delta^{195}\text{Pt} = -3504\) ppm, \(3J(1^1\text{H},195\text{Pt}) = 128\) Hz) and \(6g\) (\(\delta^{195}\text{Pt} = -3901\) ppm, \(3J(1^1\text{H},195\text{Pt}) = 79\) Hz) were present.

Also in the spectra from the reaction of \(2f\) and \(\text{LiC}==\text{CSiMe}_3\) signals of \(4f\) (\(\delta^{195}\text{Pt} \approx -3541\) ppm, \(v_{\text{C=C}} = 2032\) cm\(^{-1}\)), and \(6f\) (\(\delta^{195}\text{Pt} = -3906\) ppm), next to \(5f\) (\(\delta^{195}\text{Pt} = -3643\) ppm, \(v_{\text{C=C}} = 1948\) cm\(^{-1}\)) were observed.

When the reaction progress was monitored at room temperature, it was found that for the reactions of both \(2f\) and \(2g\) the amount of \(5f\) and \(5g\) increased at the expense of \(4f\) and \(4g\), respectively. The amount of \(6f\) and \(6g\) remained almost constant, up to the complete conversion of \(4f\) and \(4g\) to \(5f\) and \(5g\), respectively. This shows that \(6f\) and \(6g\) are not involved in the formation of \(5f\) and \(5g\), respectively, see Scheme 4-9.

\[ \text{Scheme 4-9.} \]

Based on this new knowledge, it is suggested that in the preparation of \(5e, f, g\) and \(5i\) (described in §4.2.2) next to \(5\), also a certain amount of \(6\) must have been formed, which decomposed during the work-up and as a result only \(5\) was obtained, albeit in a yield suffering from the formation of the 'side-product' \(6\).

The conversion of \(4f\) to \(5f\) was also observed in toluene. When after the reaction of \(2f\) and \(\text{LiC}==\text{CSiMe}_3\) in toluene, the reaction mixture was analyzed by \(^1\text{H}\) and \(^{195}\text{Pt}\) NMR spectroscopy, mainly the \textit{trans}-diorganoplatinum compound \(4f\) was observed, however, also some \(5f\) (and \(2f\)) was observed. A slow conversion of \(4f\) to \(5f\) was observed; when \(4f\) was kept at room temperature in the reaction mixture in toluene and the reaction mixture analyzed by \(^1\text{H}\) NMR spectroscopy in \(\text{C}_6\text{D}_6\), \(5f\) was formed at the expense of \(4f\) (compared to an internal standard). Also in the samples of the reaction mixture in \(\text{C}_6\text{D}_6\) \(4f\) was converted to \(5f\). The remaining starting material \(2f\) which was present apparently did not take part in the reaction, which allowed spectroscopic monitoring of this conversion in time at different temperatures.

**Kinetics of the conversion of \(4f\) to \(5f\) in benzene.**

The reaction was monitored at 15, 25 and 35 °C by \(^1\text{H}\) NMR spectroscopy and the pseudo reaction rates were determined. The conversion of \(4f\) to \(5f\) at 35 °C is plotted in Figure 4-6a, the integral in the \(^1\text{H}\) NMR is given in arbitrary units. The nearly constant sum of the
integrals of 4f and 5f illustrates the clean conversion of 4f to 5f. Analysis of the kinetic data showed that the conversion of 4f to 5f is a first-order reaction as plotting ln(4f) against time resulted in linear curves with regression constants of 0.994, 0.996 (analyzed until 96% conversion) and 0.986 (analyzed until 75% conversion) for the reactions at 15, 25 and 35 °C, respectively. From the relative reaction rates at these temperatures the activation energy of the reaction (E_A) could be determined from an Eyring plot (see Figure 4-6b) and was found to be 100 ± 19 kJ/mol.

![Figure 4-6.](image)

4.2.6 Discussion

4.2.6.1 Postulated mechanism for the conversion of 4 to 5

Two mechanisms for the conversion of 4 into 5, which fit the first order kinetics in 4 (see §), can readily be envisaged (Scheme 4-10). A reversible dissociation of an imine moiety results in 1, this is followed by either:

1. Interaction of two molecules of 1 in an associative pathway via side-on coordination of the platinum-acetylidy moiety (II, Scheme 4-10). At this stage the isomerization of the acetylide occurs from a position trans to the aryl carbon, to a position cis. This isomerization can occur via a twisting mechanism or via a metathesis in which the acetylides are exchanged between the platinum centers: First dimerization followed by isomerization.

2. Isomerization of the acetylide from a position trans to the aryl carbon, to a position cis, which gives a monomeric cis-diorganoplatinum compound (which is a structural analogous of compounds of type 6 without a coordinating ligand, III, Scheme 4-10). Subsequently two of these molecules dimerize: First isomerization followed by dimerization

If the pre-equilibrium between 4 and I lies on the left-hand-side, the formation of either I or III is the rate determining step, in concert with the observed first order in 4.
Scheme 4-10. Two possible mechanisms for the conversion of 4 to 5.

The second mechanism, involving the trans to cis isomerization in the absence of an additional ligand (in toluene), seems not plausible. Isomerizations in square planar complexes generally occur via associative mechanisms; by a consecutive ligand exchange (with a cationic intermediate)\(^1\) or by a pseudorotation (involving a five-coordinate intermediate)\(^2\). Dissociative processes are less common.\(^2\) Both the consecutive ligand exchange and the dissociative mechanisms proceed in organoplatinum halide complexes via halide dissociation. Such a pathway is not possible in this case, since aryl or acetylidy dissociation to yield a cationic intermediate is highly unfavorable. The fact that compounds of type 6 seem not to be involved in the formation of compounds 5 from 4 in THF (vide supra) does not support III as intermediate. Also, it has been shown (vide supra) that (in THF) 4 is not converted to 6. Moreover, the second mechanism is in contradiction with the isolation of trans-diorganoplatinum compound of type 4 for bulky alkyl and aryl imine substituents. If III is formed for small aryl substituents, its formation for large substituents should be much faster due to the steric hindrance these large substituents have with the acetylidy substituent.

The first mechanism fits better with experiment, it explains that compounds of type 4 are obtained for imine large substituents and not compounds of type 5. Due to the steric hindrance caused by the large imine substituents the formation of neither a compound of type II (Scheme 4-10), nor a compound of type 5 is possible. In the dimeric cis-diorganoplatinum compounds 5, the imine and the acetylidy substituent are in close proximity, as can be seen in the molecular structure of 5g in Figure 4-3. In this structure, the Pt-C-C-Pt-C-C ring is folded and the acetylidy group with its substituent is positioned next to the 4-methoxyphenyl...
substituent of the coordinating imine. For an ortho-substituted phenyl group on the imine, for example the 2,6-dimethylphenyl substituent, the ortho methyl groups and the acetylide (substituent) of the other monomer suffer from too much repulsion and the dimer can not be formed (Figure 4-7).

![Figure 4-7.](image)

4.2.6.2 Formation of 6

According to the reactions described by Yamamoto for dimethylpalladium diphosphine complexes (see also Chapter 2), the compounds of type 6 may be formed from the corresponding compounds of type 4, see Scheme 4-11.

![Scheme 4-11.](image)

Although no direct evidence for this mechanism has been obtained, it explains the results obtained so far. Support for this mechanism was obtained from the reaction of 2a (R = methyl) and LiC≡CSiMe3. As described at the beginning of this chapter, a complex mixture was obtained for this specific case and the compounds formed were not fully characterized.
However, when the reaction was performed with 2a and an excess (2.5 equivalents) of LiC≡CSiMe₃ at room temperature, a compound could be identified which had two inequivalent imine moieties, both coordinating to one platinum nucleus ($\delta^1H = 7.24$ ppm, $^3J(\text{H},^{195}\text{Pt}) = 66$ Hz, $5.97$ ppm, $^3J(\text{H},^{195}\text{Pt}) = 124$ Hz, $^{195}\text{Pt} = -3454$ ppm) and apparently two acetylide moieties ($\delta^1H = 0.74$ ppm, $0.44$ ppm, IR: 2023, 2004 cm$^{-1}$), which points to a compound of type B, see Scheme 4-11. Unfortunately, due to its instability, this compound could neither be isolated nor fully characterized by means of $^{13}$C NMR spectroscopy and elemental analysis and therefore provides no solid evidence for the proposed mechanism. The fact that this compound was identified for the reaction of 2a and LiC≡CSiMe₃ and no 6a was obtained, may be explained by the small imine substituents in this case, giving little steric hindrance and the strong coordination of the alkyl substituted imine moiety compared to the aryl substituted ones.

In the reaction of 2b (R = isopropyl) and LiC≡CSiMe₃ a similar compound was formed as was inferred from $^1$H,${}^{195}$Pt spectroscopy; however due to the complexity of the product mixture, only the imine protons could be assigned in the $^1$H NMR spectrum ($\delta^1H = 7.83$ ppm, $^3J(\text{H},^{195}\text{Pt}) = 65$ Hz, $5.92$ ppm, $^3J(\text{H},^{195}\text{Pt}) = 136$ Hz, $^{195}\text{Pt} = -3539$ ppm).

**Influence of imine substituent**

The mechanism outlined above explains the influence of the imine substituents on the structure of the isophthalalaldimine platinum(II) acetylide compounds formed in the transmetallation, the temperature dependence of the 4 to 6 ratio and also the absence of compounds of type 6 in the product mixture obtained in toluene. The fact that from the reaction of 2m (R = 2,6-diisopropylphenyl) and LiC≡CSiMe₃ at low temperature only 4m was obtained and no 6m can be explained by the shielding of the platinum center from the additional LiC≡CSiMe₃ by the isopropyl groups of the bulky substituents, due to which this side reaction is very slow (at low temperature).

**Temperature dependence of the 4 to 6 ratio**

At room temperature the side reaction (see Scheme 4-11) becomes faster than the reaction of 2 and LiC≡CSiMe₃, as a result, at room temperature more 6 is formed at the expense of 4.

**Absence of 6 in toluene**

Unlike THF, toluene can not attack intermediate C. If the diacetylide anions B and C are formed, it is more likely that these compounds are in a reversible equilibrium with 4, than that they transform to 6.

A mechanism similar to reactions described by Stille and coworkers for palladium(II)$^{25}$ in which a five coordinate intermediate in the metathesis step can lead to either to cis- or a trans-diorganopalladium compounds, seems not a suitable explanation for the formation of 4 and 6.
4.3 Reactivity of diorganoplatinum compounds towards additional ligands

4.3.1 Reactions of dimeric cis-diorganoplatinum compounds

To investigate the coordination strength of the dimeric core of 5f and 5g, it was subjected to additional coordinating ligands, such as (substituted) pyridine, carbon monoxide and triphenylphosphine. These ligands were able to cleave the dimeric compound, see Scheme 4-12.

![Scheme 4-12.]

4.3.1.1 Nitrogen ligands

When an excess of (substituted) pyridine was added to a C₆D₆ solutions of dimeric cis-diorganoplatinum compounds 5f (R = 4-methylphenyl) and 5g (R = 4-methoxyphenyl), the dimeric structure was easily broken up to yield two monomeric cis-diorganoplatinum pyridine complexes (7f and 7g), see Scheme 4-12. The acetylide were no longer side-on coordinated, as was apparent from the infrared spectrum of 7g, the C≡C vibration was found at 2042 cm⁻¹ which is much higher than in 5g (νC≡C = 1949 cm⁻¹). In the ¹⁹⁵Pt NMR spectrum, the ¹⁹⁵Pt resonance shifts from around -3640 ppm (5f, -3643 ppm, 5g -3640 ppm) to around -3670 ppm (7f, -3672 ppm, 7g -3670 ppm). This change in the chemical shift is very small and can not be easily explained, since both ligand field strength and the geometry around the platinum change.

Also when 2,4,6-collidine was reacted with 5g, a cleavage of the dimer was observed and the monomeric cis-diorganoplatinum compound 7g' was obtained (δ¹⁹⁵Pt = -3659 ppm). Compared to the pyridine reaction (completion within = 15 min), this reaction is very slow (at room temperature), even with a large excess of 2,4,6-collidine (= 1 day).

Compounds 7f,g and 7g' are structurally related to their isophthalaldiminne platinum(II) methyl analogue (5m in Chapter 3).
4.3.1.2 Carbon monoxide

When carbon monoxide was bubbled through a solution of 5g in C₆D₆ in an NMR tube, ¹H NMR spectroscopic analysis showed partial conversion of 5g to a new compound. After the contents of the NMR tube had been heated to reflux in the tube for 5 min, the formation of the carbon monoxide complex 8g (Scheme 4-12) was complete. The coordination of CO and not of the acetylide moiety stems with the CO and C≡C vibrations observed in the infrared spectrum (ν₇CO = 2097 cm⁻¹, νC≡C = 2058 cm⁻¹). Compound 8g is structurally related to its isophthalaldimine platinum(II) methyl analogue (7m in Chapter 3).

4.3.1.3 Phosphine ligands

When PPh₃ is added to compound 5g, also a cleavage of the dimeric structure takes place, however, the strongly coordinating PPh₃ can break, next to the side-on coordination of the acetylide (as in Scheme 4-12), also the chelating coordination of the imine moiety, which subsequently leads to the formation of three compounds, 9g, 10g and 11g, see Scheme 4-13. From the amounts of compounds 9g, 10g and 11g present directly after the addition of PPh₃ to 5g and the amounts present after 30 min, the processes on the right hand side in Scheme 4-13 were inferred.

![Scheme 4-13. Schematic representation of the reactions occurring upon the addition of PPh₃ or dppe to 5g.](image)

The ¹H, ³¹P and ¹⁹⁵Pt NMR spectroscopic data of 9g, 10g and 11g are consistent with their assigned structures.

**Reaction progress**

The addition of PPh₃ to 5g leads partly to the cleavage of the dimeric structure to furnish 9g. The remaining PPh₃ reacts with the formed 9g and replaces its chelating imine to yield
compound 10g which was found to have a limited lifetime; this cis-diorganoplatinum compound isomerizes to the trans-diorganoplatinum compound 11g. This isomerization is may be induced by a trace of free PPh₃ via an associative mechanism, involving a pseudorotation. However, it was found that when 10g had disappeared, also more of 5g was converted. It was inferred from the ratios of 5g, 9g, 10g and 11g found directly after the addition of PPh₃ and after 30 minutes and the absence of free PPh₃ (directly after the addition of PPh₃) that the PPh₃ required for the formation of 9g from 5g apparently is released from 10g; e.g. the formation of 10g from 9g and PPh₃ is reversible (see Scheme 4-13). As expected, the ratio between the increase of 9g and the increase of 11g is dependant on the ratio of 5g and 9g present in the reaction mixture.

**Diphenyldiphosphinoethane**

A structural analogue of the cis-diorganoplatinum diphosphine compound 10g was obtained by the reaction of 5g and a cis coordinating diphosphine, dppe (diphenyldiphosphinoethane). Addition of (small excess of) dppe to a C₆D₆ solution of 5g resulted in the clean formation 12g, see Scheme 4-13. The ³¹P NMR spectrum of 12g shows two doublets at 43.16 ppm (¹J(³¹P,¹⁹⁵Pt) = 2391 Hz) and at 40.11 ppm (¹J(³¹P,¹⁹⁵Pt) = 1753 Hz) with a ²Jpp of 4.5 Hz.

### 4.3.2 Reactions of trans-diorganoplatinum compound 4m and additional ligands

To investigate the coordination strength of the imine moieties in 4m, it was subjected to additional ligands, e.g. pyridine and carbon monoxide. Displacement of a chelating nitrogen in a square planar platinum [N-C-N] compound by an additional monodentate ligand has not often been studied.

**4m and pyridine**

When the trans arylplatinum(II) acetylide compound 4m was subjected to a reaction in toluene-d₈ with a large excess of pyridine, it was concluded based on the ¹H NMR spectrum of the reaction mixture and of the free ligand, 1m, that one imine moiety was displaced by a pyridine molecule and that 13m had been formed, see Scheme 4-14.

![Scheme 4-14](image-url)

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The signals of the protons of both the dissociated and the coordinated imine moieties were obscured by other signals in the aromatic region of the spectrum. However, the chemical shift of the proton riding the coordinating imine could be derived from the $^1$H,$^{195}$Pt HMQC spectrum, the chemical shift was 7.75 ppm. It is noteworthy that the $^3J(^1$H,$^{195}$Pt) of this imine proton decreases from 133 Hz to 106 Hz, due to the stronger trans influence of pyridine, compared to an imine moiety.

A large excess of pyridine was required to complete the slow reaction of 4m to 13m, which was found to be reversible, because, when after a complete reaction of 4m and pyridine all the volatiles were extensively removed by heating the solid product in vacuo for a few hours, it was found that 4m had been formed again.

When the formed trans arylplatinum(II) acetylide pyridine complex 13m was kept in the reaction medium (toluene-d$_8$ and an excess of pyridine), it was slowly converted to the cis arylplatinum(II) acetylide pyridine complex 7m, as was inferred from $^1$H and $^{195}$Pt NMR spectroscopy. This slow conversion at room temperature could be completed by heating the reaction mixture to 100°C for 1h, see Scheme 4-14. For 7m, in the $^1$H NMR spectrum the proton of the dissociated imine was found at 10.98 ppm, the proton of the coordinating imine was found at 8.1 ppm with a $^3J(^1$H,$^{195}$Pt) of 67 Hz, which is consistent with an acetylide in a position trans to this coordinating imine. The chemical shift of the Pt-nucleus was -3657 ppm. These NMR data of 7m are comparable to the data obtained for the analogous pyridine complexes 7f and 7g, described in § 4.3.1.1.

**4m and 2,4,6-collidine**

When the trans arylplatinum(II) acetylide compound 4m was subjected to the sterically more demanding 2,4,6-collidine instead of pyridine, no reaction was observed.

**4m and carbon monoxide**

Analogously to the pyridine reaction 4m was reacted with carbon monoxide. When CO was bubbled through a C$_6$D$_6$ solution of 4m in an NMR-tube for five minutes, the trans arylplatinum(II) acetylide carbon monoxide complex 14m (Scheme 4-14) was formed, as was inferred from $^1$H, $^{195}$Pt NMR and infrared spectroscopy. The $^1$H NMR spectrum of 14m was, as expected, similar to 13m, in the $^{195}$Pt NMR spectrum, the resonance was found at -4087 ppm. Coordination of CO was inferred from the CO vibration in the infrared spectrum of 14m at 2093 cm$^{-1}$. The C=O vibration was found at 2062 cm$^{-1}$, which is remarkably higher than for 4m ($\nu_{C=O}$ = 2032 cm$^{-1}$). As for the reaction of 4m and pyridine, the displacement of a coordinating imine by carbon monoxide was found to be reversible. Compound 14m is stable in vacuum, however, when subsequently it is dissolved in toluene and heated for reflux for 5 min, loss of carbon monoxide and re-coordination of the imine occurs, as was inferred from the $^1$H NMR spectrum of the product.
Similar to 13m, 14m isomerizes slowly to the cis arylplatinum(II) acetylide carbon monoxide complex 8m (Scheme 4-14), which is similar to 8g (see §4.3.1.2) as are its NMR and IR spectroscopic data. For 8m the chemical shift of the proton riding the coordinating imine is 7.60 ppm with a $^3J(^1H, ^{195}Pt)$ of 73 Hz, its $\delta^{195}Pt$ is -3928 ppm. In 8m the CO and C≡C vibrations are similar to 14m (8m: $v_{CO} = 2101 \text{ cm}^{-1}$, $v_{C≡C} = 2058 \text{ cm}^{-1}$). Remarkably, the isomerization of 14m to 8m at room temperature is not influenced by light irradiation, in contrast to the photochemical trans to cis isomerization of the arylplatinum(II) methyl carbon monoxide complex described in Chapter 3.

4.3.2.1 Discussion
From the observed conversions of 13m and 14m to, respectively, 7m and 8m, it can be concluded that the latter are thermodynamically more stable. The relative instability of 13m and 14m can be explained by the trans disposition of the aryl and the acetylide groups, both having a strong trans influence.

When 4m was subjected to a large excess of pyridine in toluene or benzene, or when 4m was dissolved in pure deuterated pyridine, one imine arm is displaced by pyridine to form 13m. In contrast to this, when the isophthalaldimine platinum(II) bromide compound 2m was subjected to pyridine, no reaction with pyridine was observed. This means that the susceptibility of one imine moiety in 4m for displacement by pyridine is induced by the weakening of the Pt-N bonds caused by the stronger cis influence of the acetylide in 4m compared to the bromide in 2m (which is also reflected in the $^3J(^1H, ^{195}Pt)$ of the imine proton). In 13m, the remaining coordinating imine moiety of the dientate coordinating isophthalaldimine ligand is not susceptible for displacement by a pyridine molecule. Apparently, most of the tension in the molecule, caused by the adjacent five- and six-membered rings, is released by the dissociation of one imine group. Also in 7f, 7g or 7m the coordinated imine moiety, which is in a position trans to an acetylide, is not susceptible for displacement by pyridine. However, in the analogous PPh$_3$ complex 9g, an additional PPh$_3$ can displace the corresponding imine moiety to furnish 10g.

4.4 Conclusions
Synthesis of isophthalaldimine platinum(II) acetylide compounds provides a new series of diorganoplatinum compounds having a Csp$^2$ and a Csp carbon directly bound to the platinum. These can be in a trans and in a cis configuration. The structure of the diorganoplatinum(II) compounds formed appears to be very much influenced by the substituent on the imine moiety. For sterically demanding imine substituents the unfavorable mutual trans-disposition of two carbon moieties is outweighed by the chelate effect of the imine moieties and trans-diorganoplatinum compounds (4) have been isolated, comparable to the trans-isophthalaldimine platinum(II) compounds described in Chapter 3. However, in
contrast to the results described in Chapter 3, also stable diorganoplatinum(II) compounds are formed with relatively small aryl substituents, these are dimeric cis-isophthalaldimine platinum(II) acetylide compounds (5). For aryl substituents with an intermediate size, monomeric cis-diorganoplatinum compounds (6) are formed, which were obtained in a mixture with a compound of type 4.

The results obtained from the reactions of compounds 4m, 5f and 5g and additional ligands support the postulates in §4.2. The formation of compounds of type 7 and 8 support the postulated structure for compounds of type 6. The latter could, unfortunately, not be isolated as a pure compound. Secondly, the reactions of 4m and pyridine and carbon monoxide support the mechanism postulated for the conversion of 4 to 5 in paragraph §4.2.6.1 (Scheme 4-10). In this mechanism an initial reversible dissociation of an imine moiety was proposed, which indeed was found in the reactions of 4m and pyridine and carbon monoxide. Furthermore, if in Scheme 4-14 one envisages the pyridine (or the carbon monoxide) as a side-on coordinating acetylide moiety of another molecule, the conversion 4m to 13m (or 14m) to 7m (or 8m) becomes the conversion of 4 to 5.

As described in the introduction, the platinum acetylide compounds of type 4 may be suitable building blocks for the preparation of organometallic oligomers which may have interesting physical properties such as non linear optic or conducting properties.6,7,10 However, the transmetallation of compound 2 and the lithium acetylides used was not selective towards compounds of type 4 (in THF also compounds of type 6 were formed) and the compounds of type 5 were not stable enough to link the oligomers via side-on coordination found in these compounds. Therefore, the preparation of such oligomers was not further pursued.

4.5 Experimental section
General comments. 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.26 NMR measurements were performed on a Bruker AMX300/Varian Mercury300 spectrometer (1H: 300.13 MHz, 13C: 75.47 MHz, 31P: 121.63 MHz) and a Varian Inova500 spectrometer (1H: 499.88 MHz, 13C: 125.70 MHz, 17O: 67.8 MHz) and Bruker DRX300 spectrometer (31P: 121.49 MHz, 195Pt: 64.3 MHz, 15N: 30.42 MHz). 195Pt NMR spectra were measured via a normal HMQC sequence at 298K. 15N NMR spectra were measured by a standard gs-HMQC sequence at 298K. 13C and 31P NMR spectra were measured with 1H decoupling. NOE measurements were performed on argon purged solutions. Positive chemical shifts (δ) are denoted for high-frequency shifts relative to a TMS reference (1H, 13C), a 85% H3PO4 reference (31P), a Na2PtCl6 reference (195Pt) and a CH3NO2 reference (15N). Infrared spectra were measured on a Biorad FTS-7 and a Biorad FTS-60A spectrometer from a CD6 solution in a NaCl cell. 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 measurements a resolving power of 10,000 (10% valley definition) was used. Field desorption mass spectrometry was carried out on the same apparatus, the samples were dissolved in dichloromethane and then loaded onto an emitter with the dipping technique. An emitter current of 0-30mA was used to desorb the samples. The ion source temperature was generally = 100°C.

Materials: Compounds 2a-m are described in chapter 3. Lithium trimethylsilylacetylide and lithium p-tolylacetylide were prepared by a reaction of the corresponding acetylenes with n-BuLi in THF or toluene. All other chemicals were obtained from commercial sources and were used as received, unless stated otherwise.

General procedure for the reactions of 2a-m and a lithium acetylide: A solution of 2 in THF (or in some cases toluene) was cooled to -60°C and 1.1-1.2 equivalents of a solution of the lithium acetylide in the reaction solvent was added dropwise. The reaction mixture was slowly warmed up to room temperature after which an aliquot was withdrawn from the reaction mixture, which was evaporated to dryness and analyzed in C6D6 by, in most cases, 1H NMR, 195Pt NMR and infrared spectroscopy.

Trans-σ-trimethylsilylethynyl-κC,κN,κN'-bis-(N-tert-butyl)-isophtalaldimine-2-ylplatina(II) (4c)

To a solution of 2c (109 mg, 0.21 mmol) in THF (20 mL) at -90°C a solution of lithium trimethylsilylacetylide 0.082 M in THF (3.1 ml, 0.25 mmol, 1.2 eq) was added. After slowly warming to room temperature, the solvent was evaporated under reduced pressure and the residue was extracted three times with 10 mL of pentane. After evaporation of the solvent under reduced pressure and drying the residue in vacuo 94.6 mg of a brown solid was obtained, which was identified by 1H, 13C and 195Pt NMR spectroscopy as nearly pure (= 95%) 4c. Due to the high solubility of 4c in polar (MeOH) and apolar (pentane) solvents, it could not further be purified by washing or recrystallization. Based on a purity of 95%, the yield was 80%. 1H NMR (500 MHz, CD2Cl2) δ = 8.47 (s, 3JHPt = 138 Hz, 2H; HC=N), 7.51 (d, 3JHH = 7.5 Hz, 2H), 7.14 (t, 3JHH = 7.5 Hz, 1H), 1.74 (s, 18H), 0.18 (s, 9H, Si(CH3)3). 13C NMR (126 MHz, CD2Cl2) δ = 188.4 (1JCPt = 639 Hz, C-Pt), 172.1 (2JCPt = 84 Hz, C=N-C), 157.3 (1JCPt = 968 Hz, Pt-CCSi), 143.1 (2JCPt = 95 Hz, C), 124.4 (CH), 121.5 (2JCPt = 203 Hz, Pt-CCSi), 120.8 (CH), 63.5 (2JCPt = 23 Hz, C=N-C), 27.9 (C(CH3)3), -0.89 (Si(CH3)3). 195Pt NMR (CDCl3): δ = -3609. IR: νC=C = 2030 cm⁻¹. HRMS(FAB): m/z calcd [(M+H)+ C21H33N2SiPt]: 536.2062. Found 536.2069.

Trans-σ-trimethylsilylethynyl-κC,κN,κN'-bis-(N-cyclohexyl)-isophtalaldimine-2-ylplatina(II) (4d)

Compound 4d was prepared, analogous to 4c, from 2d (105.1 mg, 0.184 mmol) and lithium trimethylsilylacetylide (2.7 mL of a 0.082 M solution in THF, 0.22 mmol, 1.2 eq.). After evaporation of the volatiles under reduced pressure, the residue was extracted seven times with 20 mL of pentane. After evaporation of the solvent under reduced pressure and drying the residue in vacuo 102.8 mg of an orange solid was obtained, which was identified by 1H, 13C and 195Pt NMR spectroscopy as nearly pure (= 95%) 4d. As for 4c, due to the high solubility of 4d in polar (MeOH) and apolar (pentane) solvents, it could not further be purified by washing or recrystallization. Based on a purity of 95%,
the yield was 90%. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta = 8.50$ (s, $^3$J$_{HPt} = 133$ Hz, 2H; $HC=\text{N}$), 7.51 (d, $^3$J$_{HH} = 7.5$ Hz, 2H), 7.11 (t, $^3$J$_{HH} = 7.5$ Hz, 1H), 3.94 (m, 2H), 2.14 - 2.01 (m, 8H), 1.92 - 1.90 (m, 4H), 1.73 - 1.71 (m, 2H), 1.51 - 1.38 (m, 6H), 0.22 (s, 9H, Si(CH$_3$)$_3$). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta = 188.7$ ($^1$J$_{CPt} = 638$ Hz, C-Pt), 173.2 ($^2$J$_{CPt} = 87$ Hz, C-N-C), 155.4 ($^4$J$_{CPt} = 968$ Hz, Pt-CCSi), 142.3 ($^3$J$_{CPt} = 95$ Hz, C), 123.7 (CH), 120.8 (CH), 117.7 ($^2$J$_{CPt} = 202$ Hz, Pt-CCSi), 69.4 ($^2$J$_{CPt} = 25$ Hz, C=N-C), 31.3 (CH$_2$), 23.5 (CH$_2$), 0.6 (Si(CH$_3$)$_3$). $^{195}$Pt NMR (CDCl$_3$): $\delta = -3580$. IR: $\nu_{C\equiv C}$ = 2026 cm$^{-1}$. HRMS(FAB): $m/z$ calc'd ([M+H]$^+$ C$_{25}$H$_{37}$N$_2$SiPt) 588.2375. Found 588.2360.

**Trans-σ-trimethylsilylethynyl-κC,κN,κN'-bis-(N-2,4,6-trimethylphenyl)-isophtalaldimine-2-yl-platina(ii) (4k)**

To a solution of 2k (53 mg, 0.083 mmol) in 30 mL of THF at -60°C a solution of lithium trimethylsilylacetylide 0.068 M in THF (1.5 ml, 0.10 mmol, 1.2 eq) was added. After slowly warming up to room temperature, the solvent was evaporated under reduced pressure. The residue was washed twice with pentane and subsequently extracted with diethyl ether. The ether extract was evaporated to dryness under reduced pressure and the residue was washed with a small amount of pentane and dried in vacuo to yield 17 mg (0.026 mmol, 31%) of an orange crystalline solid which was identified by $^1$H, $^{13}$C and $^{195}$Pt NMR spectroscopy as pure 4k. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta = 7.31$ (s, $^3$J$_{HPt} = 133$ Hz, 2H; $HC=\text{N}$), 7.11, 6.83 (t, $^3$J$_{HH} = 7.7$ Hz, 1H), 6.74 (s, 4H), 2.18 (s, 12H, Ar-CH$_3$), 2.15 (s, 6H, Ar-CH$_3$), 0.02 (s, 9H, Si(CH$_3$)$_3$). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta = 197.3$ ($^1$J$_{CPt} = 632$ Hz, C-Pt), 181.6 ($^2$J$_{CPt} = 74$ Hz, C-N-C), 155.3 ($^4$J$_{CPt} = 1018$ Hz, Pt-CCSi), 147.6 (C=N-C), 144.3 ($^2$J$_{CPt} = 95$ Hz, C), 136.5 (C), 131.0 (C), 128.5 (CH), 127.3 (CH), 123.1 (CH), 114.7 ($^2$J$_{CPt} = 207$ Hz, Pt-CCSi), 20.8 (CH$_3$), 18.4 (CH$_3$), -1.0 (Si(CH$_3$)$_3$). $^{195}$Pt NMR (C$_6$D$_6$): $\delta = -3444$. IR: $\nu_{C\equiv C}$ = 2024 cm$^{-1}$. HRMS(FAB): $m/z$ calc'd ([M+H]$^+$ C$_{31}$H$_{37}$N$_2$SiPt) 660.2376. Found 660.2368.

**Trans-σ-trimethylsilylethynyl-κC,κN,κN'-bis-(N-2,6-diisopropylphenyl)-isophtalaldimine-2-yl-platina(ii) (4m)**

Compound 4m was prepared, analogous to 4c, from 2m (100 mg, 0.138 mmol) and lithium trimethylsilylacetylide (2.2 ml, of a 0.068 M solution in THF, 0.152 mmol, 1.1 eq). After evaporation of the volatiles under reduced pressure, the residue was extracted three times with 10 mL of pentane. After evaporation of the solvent under reduced pressure and drying the residue in vacuo the obtained solid was crystallized from MeOH. After cooling to -20°C for 4 days, the orange crystals were isolated by removing the mother liquor. Washing with a small amount of cold MeOH and drying in vacuo yielded 81.8 mg (0.11 mmol, 80%) of orange crystals which were identified by $^1$H, $^{13}$C and $^{195}$Pt NMR spectroscopy as pure 4m. $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 8.45$ (s, $^3$J$_{HPt} = 133$ Hz, 2H; $HC=\text{N}$), 7.77 (d, $^3$J$_{HH} = 7.8$ Hz, 2H), 7.35 (t, $^3$J$_{HH} = 7.8$ Hz, 1H), 7.17 (m, 6H), 3.16 (septet, $^3$J$_{HH} = 7$ Hz, 4H; CH$_3$CH$_2$CH$_3$), 1.26 (d, $^3$J$_{HH} = 7$ Hz, 12H; CH$_3$CH$_2$CH$_3$), 1.16 (d, $^3$J$_{HH} = 7$ Hz, 12H; CH$_3$CH$_2$CH$_3$), -0.42 (s, 9H, Si(CH$_3$)$_3$). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta = 198.9$ ($^1$J$_{CPt} = 616$ Hz, C-Pt), 179.8 ($^2$J$_{CPt} = 73$ Hz, C=N-C), 154.8 ($^4$J$_{CPt} = 1048$ Hz, Pt-CCSi), 147.3 (C=N-C), 144.5 ($^2$J$_{CPt} = 95$ Hz, C), 141.5 (C), 127.4 (CH), 127.2 (CH), 123.0 (CH), 123.0 (CH), 115.5 ($^2$J$_{CPt} = 211$ Hz, Pt-CCSi), 27.9 (CH$_3$CH$_2$CH$_3$), 24.4 (CH$_3$CH$_2$CH$_3$), 23.0 (CH$_3$CH$_2$CH$_3$), 1.24 (Si(CH$_3$)$_3$). $^{195}$Pt NMR (C$_6$D$_6$): $\delta = -3406$. $^{15}$N NMR (30.42 MHz, CDCl$_3$): $\delta = -153$ ($^1$J$_{PN} = 464$ Hz). IR: $\nu_{C\equiv C}$ = 2032 cm$^{-1}$. HRMS(FAB): $m/z$ calc'd ([M+H]$^+$ C$_{37}$H$_{49}$N$_2$SiPt) 744.3315. Found 744.3311. Anal. Calc'd for
C_{37}H_{48}N_{2}PtSi: C, 59.73; H, 6.50; N, 3.77. Found: C, 59.80; H, 6.55; N, 3.82. Single crystals suitable for X-ray structure determination were obtained by slow cooling of a methanolic solution.

**Trans-σ-(4-methylphenyl)-ethynyl-κC,κN,κN'-bis-(N-2,6-diisopropylphenyl)-isophtalaldimine-2-yl-platina(II) (4m')**

Compound 4m' was prepared, analogous to 4m, from 2m (38.5 mg, 0.053 mmol) and lithium p-tolylacetylide (0.45 ml, of a 0.146 M solution in THF, 0.066 mmol, 1.2 eq). The yield was 18.2 mg (0.024 mmol, 45%) of orange crystals which were identified by $^1$H, $^{13}$C and $^{195}$Pt NMR spectroscopy as pure 4m'. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ = 8.53 (s, $^3$J$_{HH}$ = 134 Hz, 2H; HC=N), 7.87 (d, $^3$J$_{HH}$ = 7.5 Hz, 2H), 7.33 (t, $^3$J$_{HH}$ = 7.5 Hz, 1H), 7.29 (2$^\text{nd}$ order multiplet, 2H), 7.24 (2$^\text{nd}$ order multiplet, 4H), 6.81 (d, $^3$J$_{HH}$ = 8 Hz, 2H), 6.42 (d, $^3$J$_{HH}$ = 8 Hz, 2H), 3.26 (septet, $^3$J$_{HH}$ = 7 Hz, 2H; CH$_3$CH(CH$_3$)$_3$), 2.24 (s, 3H), 1.30 (d, $^3$J$_{HH}$ = 7 Hz, 12H; CH$_3$CHCH$_3$). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ = 197.5 (C-Pt), 180.4 (2$^\text{nd}$ order multiplet, 2H). Due to the low solubility and stability of 5e in common solvents, no satisfactory $^{13}$C NMR spectrum could be obtained. $^{195}$Pt NMR (CDCl$_3$): $\delta$ = -3644. IR: $\nu_{C\equiv C}$ = 2095 cm$^{-1}$. HRMS (FAB): m/z calc (M+H$^+$) C$_{41}$H$_{37}$N$_2$PtSi 762.3391. Found 762.3380.

**cis-μ$_2$-trimethylsilylthethyl-κC,κN-bis-(N-phenyl)-isophtalaldimine-2-yl-platina(II) dimer (5e)**

To a solution of 2e (47 mg, 0.077 mmol) in THF (25 mL) at -60°C, a solution of lithium trimethylsilylacetylide 0.068 M in THF (1.35 mL, 0.09 mmol, 1.2 eq) was added. After stirring at -60°C for 30 min, the mixture was allowed to warm to room temperature overnight. The solvent was evaporated under reduced pressure and the residue was extracted three times with 20 mL of diethyl ether. After evaporation of the solvent under reduced pressure the residue was dissolved in THF and the product was crystallized by slow diffusion of pentane. The mother liquor was decanted and the residue was washed with a small amount of diethyl ether, twice with pentane (5 mL) and dried in vacuo to yield 26.3 mg (0.023 mmol, 11%) of a dark brown solid which was identified by $^1$H and $^{195}$Pt NMR spectroscopy as 5e. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ = 9.98 (s, 2H; HC=N), 8.93 (d, $^3$J$_{HH}$ = 7.8 Hz, 2H), 7.32 (s, $^3$J$_{HH}$ = 78 Hz, 2H; HC=N), 7.31 - 7.28 (m), 7.17 - 7.02 (m, obscured by solvent), 6.98 - 6.82 (m), -0.27 (s, 18H, Si(CH$_3$)$_3$). Due to the low solubility and stability of 5e in common solvents, no satisfactory $^{13}$C NMR spectrum could be obtained. $^{195}$Pt NMR (CDCl$_3$): $\delta$ = -3508. IR: $\nu_{C\equiv C}$ = 1951 cm$^{-1}$. MS(FD): m/z calc ([M+H]$^+$) C$_{50}$H$_{49}$N$_4$Pt$_2$Si$_2$ 1151.3. Found 1151.6.

**cis-μ$_2$-trimethylsilylthethyl-κC,κN-bis-(N-4-methylphenyl)-isophtalaldimine-2-yl-platina(II) dimer (5f)**

Compound 5f was prepared, analogous to 5e, from 2f (52 mg, 0.089 mmol) and lithium trimethylsilylacetylide (1.5 mL of a 0.068 M solution in THF, 0.1 mmol, 1.2 eq). The yield was 24 mg (0.020 mmol, 45%) of a dark brown solid which was identified by $^1$H, $^{13}$C and $^{195}$Pt NMR spectroscopy as pure 5f. $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ = 10.03 (s, 2H; HC=N), 8.96 (d, $^3$J$_{HH}$ = 7.8 Hz, 2H), 7.41 (s, $^3$J$_{HH}$ = 77 Hz, 2H; HC=N), 7.27 (d, $^3$J$_{HH}$ = 8 Hz, 4H), 7.07 (t, $^3$J$_{HH}$ = 7.6 Hz, 2H), 6.96 (2H), 6.99 (br, s, 8H), 6.95 (d, $^3$J$_{HH}$ = 8 Hz, 4H), 2.10 (s, 6H; CH$_3$), 2.05 (s, 6H; CH$_3$), -0.24 (s, 18H, Si(CH$_3$)$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) $\delta$ = 177.3 (C=N-Pt), 166.0 (C=N), 153.9 (C-Pt), 150.5
(C-N=C), 148.9 (C-C=N-Pt), 146.6 (C-N-Pt), 141.3 (C-N=N-C), 137.0 (C=CH3), 134.8 (C=CH2), 132.9 (CH), 131.2 (CH), 129.8 (CH), 129.3 (CH), 124.8 (CH), 124.6 (CH), 122.2 (CH), 112.7 (C=C), 112.4 (C=C), 20.8 (CH3), 20.7 (CH3), 0.4 (Si(CH3)2).\(^{199}\)Pt NMR (C6D6): \(\delta = -3643\). \(^{15}\)N NMR (30.42 MHz, C6D6): \(\delta = -55\) (not coordinated). IR: \(\nu_{\text{C=C}} = 1949\) cm\(^{-1}\). MS(FAB): \(m/z\) calcld ([M+H]+ C54H57N4Pt2Si2) 1207.3412. Found 1207.3402.

**Cis-\(\sigma,\mu^2\)-trimethylsilylthynyl-\(\kappa\)C,\(\kappa\)N-bis-(N-4-methoxyphenyl)-isophtalaldimine-2-y!-platina(II) dimer (5g)**

Compound 5g was prepared, analogous to 5e, from 2g (101.6 mg, 0.164 mmol) and lithium trimethylsilylacetylene (2.7 mL of a 0.068 M solution in THF, 0.18 mmol, 1.1 eq). After evaporation of the solvent under reduced pressure, the residue was extracted with a 15 mL of pentane. After evaporation of the solvents under reduced pressure the residue was washed with pentane (10 mL) and crystallized by a slow diffusion of pentane into a concentrated dichloromethane solution. Washing of the product with 10 mL of pentane and drying *in vacuo* yielded 58 mg (0.46 mmol, 55%) of a dark brown solid which was identified by \(^1\)H, \(^{13}\)C and \(^{199}\)Pt NMR spectroscopy as pure 5g. 220°C decomp. \(^1\)H NMR (500 MHz, C6D6) \(\delta = 10.07\) (s, 2H; HCN=), 8.96 (d, \(J_{\text{HH}} = 8\) Hz, 2H), 7.42 (J, \(J_{\text{HPt}} = 73\) Hz, 2H; HC≡N), 7.42 (d, \(J_{\text{HH}} = 9\) Hz, 4H), 7.11 (dd, \(J_{\text{HH}} = 8\) Hz, \(J_{\text{HH}} = 7\) Hz, 2H), 7.08 (d, \(J_{\text{HH}} = 9\) Hz, 4H), 6.99 (d, \(J_{\text{HH}} = 7\) Hz, 2H), 6.82 (d, \(J_{\text{HH}} = 9\) Hz, 4H), 6.77 (d, \(J_{\text{HH}} = 9\) Hz, 4H), 3.37 (s, 6H; OCH3), 3.26 (s, 6H; OCH3), -0.13 (s, 18H, Si(CH3)3). \(^{13}\)C NMR (126 MHz, C6D6) \(\delta = 176.9\) (C≡N-Pt), 164.8 (C≡N), 159.2 (COCH3), 158.4 (COCH3), 153.7 (C-Pt), 148.9 (C=C=N-Pt), 146.0 (C=N=C), 142.2 (C=N-Pt), 141.3 (C=C-N-C), 132.5 (CH), 130.8 (CH), 124.6 (CH), 125.9 (CH), 123.5 (CH), 114.6 (CH), 114.1 (CH), 111 (PtCCSi) (PtCCSi not observed), 55.1 (OCH3), 54.8 (OCH3), 0.6 (Si(CH3)3). \(^{199}\)Pt NMR (C6D6): \(\delta = -3640\). \(^{15}\)N NMR (30.42 MHz, C6D6): \(\delta = -133\) (coordinated), -57 (not coordinated). IR: \(\nu_{\text{C≡N}} = 1949\) cm\(^{-1}\). MS(FD): \(m/z\) calcld ([M]+ C54H56N4O2Pt2Si2) 1271. Found 1271. Anal. Calcd for C54H56N4O2Pt2Si2: C, 51.01; H, 4.44; N, 4.41. Found: C, 51.02; H, 4.51; N, 4.45. Single crystals suitable for X-ray structure determination were obtained by slow diffusion of pentane into a diluted dichloromethane solution.

**Cis-\(\sigma,\mu^2\)-trimethylsilylthynyl-\(\kappa\)C,\(\kappa\)N-bis-(N-3,5-dimethylphenyl)-isophtalaldimine-2-y!-platina(II) dimer (5i)**

Compound 5i was prepared, analogous to 5e, from 2i (47 mg, 0.077 mmol) and lithium trimethylsilylacetylene (1.35 mL of a 0.068 M solution in THF, 0.092 mmol, 1.2 eq). The yield was 23 mg (0.018 mmol, 23%) of a orange brown solid which was identified by \(^1\)H, \(^{13}\)C and \(^{199}\)Pt NMR spectroscopy as pure 5i. \(^1\)H NMR (500 MHz, toluene-d8) \(\delta = 9.99\) (s, 2H; HCN=), 8.95 (d, \(J_{\text{HH}} = 6.5\) Hz, 2H), 7.63 (s, \(J_{\text{HPt}} = 74\) Hz, 2H; HC≡N), 7.25 - 7.20 (m, 2H), 6.97 (s, 4H), 6.88 (s, 4H), 6.77 (s, 2H), 6.74 (s, 4H), 2.35 (s, 12H, CH2), 2.27 (s, 12H, CH2) 0.19 (s, 18H, Si(CH3)3). \(^{13}\)C NMR (126 MHz, toluene-d8) \(\delta = 177.8\) (C≡N-Pt), 166.1 (C≡N), 154.5 (C-Pt), 153.5 (C), 149.7 (C), 148.9 (C), 141.7 (C), 138.3 (C), 138.2 (C), 133.0 (CH), 131.0 (CH), 129.1 (CH), 127.1 (CH), 124.4 (CH), 122.9 (CH), 119.7 (CH), 112.1 (C=C), 111.9 (C=C), 21.2 (CH2), 21.2 (CH2), 0.2 (Si(CH3)3). \(^{199}\)Pt NMR (C6D6): \(\delta = -3634\). IR: \(\nu_{\text{C≡N}} = 1948\) cm\(^{-1}\). (HRMS(FAB): \(m/z\) calcld ([M+H]+ C37H49N2SiPt) 1263.4039. Found 1263.4053.
Reactions in which a mixture of 4 and 6 is formed

Compounds of type 4 and type 6 are formed in a mixture and are (except for 4k) not obtained pure, some indicative signals are assigned. $^1$H (300 MHz) and $^{195}$Pt NMR both are measured in C$_6$D$_6$.

Reaction of 2h and LiC≡SiMe$_3$; 4h, $^1$H NMR: $\delta$ = 7.21 (s, $^3$J$_{HP}$ = 133 Hz; HC≡N). $^{195}$Pt NMR: $\delta$ = -3440. 6h, 10.47 (s, HC≡N), 8.98 (H$_A$), 7.47 (s, $^3$J$_{HP}$ = 68 Hz; HC≡N). $^{195}$Pt NMR: $\delta$ = -3920.

Reaction of 2h and LiC≡C-p-toly; 4h', $^1$H NMR: $\delta$ = 7.29 (s, $^3$J$_{HP}$ = 133 Hz; HC≡N), 2.18 (2,6-(CH$_3$)-phenyl), 1.95 (4-(CH$_3$)-phenyl). $^{195}$Pt NMR: $\delta$ = -3421. 6h', $^1$H NMR: $\delta$ = 10.49 (s, HC≡N), 8.96 (H$_A$), 7.65 (s, $^3$J$_{HP}$ = 70 Hz; HC≡N), 2.36 (2,6-(CH$_3$)-phenyl), 2.06 (2,6-(CH$_3$)-phenyl), 1.99 (4-(CH$_3$)-phenyl). $^{195}$Pt NMR: $\delta$ = -3944.

Reaction of 2k and LiC≡CSiMe$_3$; 6k, 10.46 (s, HC≡N), 9.00 (H$_A$), 7.58 (s, $^3$J$_{HP}$ = 68 Hz; HC≡N). $^{195}$Pt NMR: $\delta$ = -3916.

Reaction of 2k and LiC≡C-p-toly; 4k', $^1$H NMR: $\delta$ = 7.40 (s, $^3$J$_{HP}$ = 133 Hz; HC≡N). 6k', 10.53 (s, HC≡N), 9.00 (d, $^3$J$_{HH}$ = 8 Hz; H$_A$), 7.76 (s, $^3$J$_{HP}$ = 70 Hz; HC≡N).

Reaction of 2l and LiC≡CSiMe$_3$; 4l, $^1$H NMR: $\delta$ = 4.42 (s, $^3$J$_{HP}$ = 133 Hz; HC≡N). $^{195}$Pt NMR: $\delta$ = -3406. 6h, 10.45 (s, HC≡N), 8.98 (H$_A$), 7.62 (s, $^3$J$_{HP}$ = 72 Hz; HC≡N). $^{195}$Pt NMR: $\delta$ = -3915.

**Cis-σ-trimethylsilyl ethynyl-kC,kN-bis-(N-4-methylphenyl)-isophtalaldimine-2-yl-pyridine-platina(II) (7f)**

To a solution of 5f in C$_6$D$_6$ an excess of pyridine-d$_5$ was added. The quantitative formation of a new compound was observed, which was identified by $^1$H and $^{195}$Pt NMR spectroscopy as the pyridine complex 7f. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ = 11.38 (s, 1H; HC≡N), 8.84 (d, $^3$J$_{HH}$ = 7.3 Hz, 1H), 7.74 (s, $^3$J$_{HH}$ = 66 Hz, 1H; HC≡N), 7.66 (d, $^3$J$_{HH}$ = 8 Hz, 2H), 7.05 - 6.96 (m, 2H), 6.45 (d, $^3$J$_{HH}$ = 8 Hz, 2H), 6.37 (d, $^3$J$_{HH}$ = 8 Hz, 2H), 2.14 (s, 3H; CH$_3$), 1.84 (s, 3H; CH$_3$), 0.03 (s, 9H, Si(CH$_3$)$_3$). $^{195}$Pt NMR (C$_6$D$_6$): $\delta$ = -3672.

**Cis-σ-trimethylsilyl ethynyl-kC,kN-bis-(N-4-methoxyphenyl)-isophtalaldimine-2-yl-pyridine-platina(II) (7g)**

To a solution of 5g in C$_6$D$_6$ an excess of pyridine was added. In the $^1$H and $^{195}$Pt NMR spectra the quantitative formation of a new compound was observed, which was identified as the pyridine complex 7g. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ = 10.89 (s, 1H; HC≡N), 8.82 (d, $^3$J$_{HH}$ = 7.2 Hz, 1H), 8.37 (d, $^3$J$_{HH}$ = 5 Hz, 2H, py), 7.77 (s, $^3$J$_{HH}$ = 67 Hz, 1H; HC≡N), 7.74 (d, $^3$J$_{HH}$ = 9 Hz, 2H), 7.03 - 6.98 (m, 2H), 6.91 (d, $^3$J$_{HH}$ = 9 Hz, 2H), 6.50 (br s, py), 6.44 (d, $^3$J$_{HH}$ = 8 Hz, 2H), 6.25 (d, $^3$J$_{HH}$ = 9 Hz, 2H), 3.32 (s, 3H; OCH$_3$), 3.14 (s, 3H; OCH$_3$), 0.03 (s, 9H, Si(CH$_3$)$_3$). $^{195}$Pt NMR (C$_6$D$_6$): $\delta$ = -3670. IR: $\nu_{CC≡C}$ = 2042 cm$^{-1}$. (HRMS(FAB): m/z calc'd [M+H]$^+$ C$_{32}$H$_{34}$O$_2$N$_3$SiPt) 715.2070. Found 715.2077.

**Cis-σ-trimethylsilyl ethynyl-kC,kN-bis-(N-4-methoxyphenyl)-isophtalaldimine-2-yl-2,4,6-collidine-platina(II) (7g')**

To a solution of 5g in C$_6$D$_6$ an excess of 2,4,6-collidine was added. No reaction was observed after 1h. After three days at room temperature in the $^1$H and $^{195}$Pt NMR spectra the quantitative formation of a new compound was observed, which was identified as the 2,4,6-collidine complex 7g'. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ = 10.93 (s, 1H; HC≡N), 8.93 (br, 1H), 7.79 (d, $^3$J$_{HH}$ = 9 Hz, 2H), 7.75 (s, $^3$J$_{HP}$ = ...
Cis-σ-trimethylsilylethynyl-κC,κN-bis-(N-4-methoxyphenyl)-isophtalaldimine-2-yl-carbonyl-platinum(II) (8g)

Carbon monoxide was bubbled through a solution of 5g in C₆D₆ and subsequently the contents of the NMR tube was heated to reflux for 5 min. In the ¹H and ¹⁹⁵Pt NMR spectra the quantitative formation of a new compound was observed, which was identified as the carbon monoxide complex 8g. ¹H NMR (300 MHz, C₆D₆) δ = 10.65 (s, 1H; HC=Н), 6.90 (d, 3J_HH = 8 Hz, 1H), 7.68 (d, 3J_HH = 9 Hz, 2H), 7.39 (s, 3J_HH = 71 Hz, 1H; HCH=N), 6.97 (t, 3J_HH = 7.5 Hz, 1H), 6.89 (d, 3J_HH = 9 Hz, 2H), 6.73 (d, 3J_HH = 8 Hz, 1H), 6.59 (d, 3J_HH = 9 Hz, 2H), 6.46 (d, 3J_HH = 9 Hz, 2H), 3.30 (s, 3H; OCH₃), 3.14 (s, 3H; OCH₃), 0.12 (s, 9H, Si(CH₃)₃). ¹⁹⁵Pt NMR (C₆D₆): δ = -3966.

Reaction of 5g and triphenylphosphine; Formation of 9g, 10g and 11g.

To a solution of 5g in C₆D₆ in an NMR tube was added a solution of 2 equivalents PPh₃ in C₆D₆, in portions of ~0.4 equivalent. Directly after the addition and after ~30 min the solution was analyzed by means of ¹H and ³¹P NMR spectroscopy. Compound 9g, 10g and 11g were only obtained in a mixture and are identified by indicative signals. 9g: ¹H NMR (300 MHz, C₆D₆) δ = 10.72 (s, 1H; CH=N), 7.72 (s, 3J_HH = 67 Hz; CH=N), 6.34 (d, 3J_HH = 9Hz, 2H), 5.96 (d, 3J_HH = 9 Hz, 2H), 3.31 (s, 3H; OCH₃), 3.08 (s, 3H; OCH₃) -0.30 (s, 9H; Si(CH₃)₃), ³¹P NMR (C₆D₆): δ = 22.3 (1J_Pp = 1886 Hz). ¹⁹⁵Pt NMR (C₆D₆): δ = -4142. 10g: ¹H NMR (300 MHz, C₆D₆) δ = 10.28 (s, 2H; CH=N), 8.10 (d, 3J_HH = 7.8 Hz), 7.55 (d, 3J_HH = 9 Hz), 3.43 (s, 6H; OCH₃), 3.08 (s, 3H; OCH₃) -0.22 (s, 9H; Si(CH₃)₃), ³¹P NMR (C₆D₆): δ = 23.2, 18.0. 11g: ¹H NMR (300 MHz, C₆D₆) δ = 9.60 (s, 2H; CH=N), 3.42 (s, 6H; OCH₃), -0.23 (s, 9H; Si(CH₃)₃), ³¹P NMR (C₆D₆): δ = 21.5 (1J_Pp = 2890 Hz). ¹⁹⁵Pt NMR (C₆D₆): δ = -4418.

Cis-σ-trimethylsilylethynyl-κC-bis-(N-4-methoxyphenyl)-isophtalaldimine-2-yl-κP,κP'-diphenylphosphinoethane-platinum(II) (12g)

To a solution of 5g in C₆D₆ an excess of diphenylphosphinoethane was added. The quantitative formation of a new compound was observed, which was identified by ¹H and ³¹P NMR spectroscopy as 12g. ¹H NMR (300 MHz, C₆D₆) δ = 9.74 (s, CH=Н, 2H), 8.10-8.04 (m, 2H), 7.4-6.6 (m), 3.36 (2, 6H, OCH₃), 1.8-1.5 (broad), 0.00 (s, 9H, Si(CH₃)₃), ³¹P NMR (C₆D₆): δ = 43.16 (d, 2J_pp = 4.5 Hz, 1J_Pp = 2391 Hz), 40.11 d, 2J_pp = 4.5 Hz, 1J_Pp = 1753 Hz).

Trans-σ-trimethylsilylethynyl-κC,C-κN-bis-(N-2,6-diisopropylphenyl)-isophtalaldimine-2-yl-pyridine-platinum(II) (13m)

To a solution of 4m in toluene-d₈ an excess of pyridine-d₅ was added. Slowly (~1 day), the formation of a new compound was observed, which was identified by ¹H and ¹⁹⁵Pt NMR spectroscopy as the trans-diorganoplatinum pyridine complex 13m. ¹H NMR (300 MHz, toluene-d₈/pyridine-d₅) δ = 8.62 (d, 3J_HH = 7 Hz, 1H), 7.81 (s, 3J_Hp = 106 Hz, 1H; HCH=N), 3.74 (septet, 3J_HH = 7 Hz, 2H), 2.72 (septet, 3J_HH = 7 Hz, 2H), 1.62 (d, 3J_HH = 7 Hz, 6H), 1.13 (d, 3J_HH = 5 %).
7 Hz, 6H), 0.97 (d, $^3J_{HH} = 7$ Hz, 12H), 0.00 (s, 9H, Si(CH$_3$)$_3$). Some of the signals were obscured by signals of the starting material and the solvent. $^{195}$Pt NMR (toluene-d$_8$/pyridine-d$_5$): $\delta = -3216$.

**Cis-\(\sigma\)-trimethylsilylthienyl-\(\kappa\)C,\(\kappa\)N-bis-(\(N\)-2,6-diisopropylphenyl)-isophtalaldimine-2-yl-pyridyl-platina(II) (7m)**

While there was still some starting material present, the NMR tube was heated to 100°C for 1 h, during which all 4m was converted to 13m, and 13m was quantitatively converted to the cis-diorganoplatinum pyridine complex 7m as was inferred from $^1$H and $^{195}$Pt NMR spectroscopy. $^1$H NMR (300 MHz, toluene-d$_8$/pyridine-d$_5$) $\delta = 10.98$ (s, 1H; $HC=NC$), 8.90 (d, $^3J_{HH} = 8$ Hz, 1H), 8.08 (s, $^3J_{HH} = 67$ Hz, 1H; $HC=NC$), 7.20 - 7.14 (m, 3H), 6.86 - 6.65 (m, 4H), 3.41 (septet, $^3J_{HH} = 7$Hz, 2H), 3.26 (septet, $^3J_{HH} = 7$ Hz, 2H), 1.30 (d, $^3J_{HH} = 7$ Hz, 12H), 0.86 (d, $^3J_{HH} = 7$ Hz, 6H), 0.80 (d, $^3J_{HH} = 7$ Hz, 6H), -0.11 (s, 9H, Si(CH$_3$)$_3$). $^{195}$Pt NMR (toluene-d$_8$/pyridine-d$_5$): $\delta = -3658$.

**Trans-\(\sigma\)-trimethylsilylthienyl-\(\kappa\)C,\(\kappa\)N-bis-(\(N\)-2,6-diisopropylphenyl)-isophtalaldimine-2-yl-carbonyl-platina(II) (14m)**

Carbon monoxide was bubbled through a solution of 4m in C$_6$D$_6$. Slowly ($\approx$ 1 day), the formation of a new compound was observed, which was identified by $^1$H and $^{195}$Pt NMR spectroscopy as the trans-diorganoplatinum carbon monoxide complex 14m. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta = 8.52$ (s, 1H), 8.49 (m, 1H), 7.53 (s, $^3J_{HPt} = 95$ Hz, 1H; $HC=NC$), 7.07-6.87 (m, obscured by solvent), 3.18 (septet, $^3J_{HH} = 7$ Hz, 2H), 3.08 (septet, $^3J_{HH} = 7$ Hz, 2H), 1.37 (d, $^3J_{HH} = 7$ Hz, 6H), 1.07 (d, $^3J_{HH} = 7$ Hz, 12H), 0.93 (d, $^3J_{HH} = 7$ Hz, 6H), 0.00 (s, 9H, Si(CH$_3$)$_3$). $^{195}$Pt NMR (C$_6$D$_6$): $\delta = -4087$. IR: $v_{CO} = 2093$ cm$^{-1}$, $v_{CC} = 2062$ cm$^{-1}$.

**Cis-\(\sigma\)-trimethylsilylthienyl-\(\kappa\)C,\(\kappa\)N-bis-(\(N\)-2,6-diisopropylphenyl)-isophtalaldimine-2-yl-carbonyl-platina(II) (8m)**

At room temperature compound 14m (in C$_6$D$_6$) very slowly isomerizes to the trans-diorganoplatinum carbon monoxide complex 8m as was inferred from $^1$H and $^{195}$Pt NMR spectroscopy. After 9 days at room temperature the isomerization was approximately 40% complete when the monitoring of the reaction was stopped, therefore 8m was not obtained pure. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta = 10.90$ (s, 1H; $HC=NC$), 9.01 (d, $^3J_{HH} = 8$ Hz, 1H), 7.60 (s, $^3J_{HPt} = 73$ Hz, 1H; $HC=NC$), 7.18-6.85 (m, obscured by solvent), 3.33 (septet, $^3J_{HH} = 7$ Hz, 2H), 3.15 (2H), 1.28 (d, $^3J_{HH} = 7$ Hz, 12H), 0.98 (d, $^3J_{HH} = 7$ Hz, 6H), 0.83 (d, $^3J_{HH} = 7$ Hz, 6H), -0.03 (s, 9H, Si(CH$_3$)$_3$). $^{195}$Pt NMR (C$_6$D$_6$): $\delta = -3928$. IR: $v_{CO} = 2101$ cm$^{-1}$, $v_{CC} = 2058$ cm$^{-1}$.

**Reaction of 2a and LiC=CSiMe$_3$**

To a solution of 2a (98 mg, 0.23 mmol) in 20 mL of THF was added LiC=CSiMe$_3$ (6.9 mL of a 0.082 M solution in THF, 0.56 mmol) dropwise at room temperature. Directly an aliquot was withdrawn from the reaction mixture, the solvent was evaporated under reduced pressure and the residue was extracted with C$_6$D$_6$, from $^1$H and $^{195}$Pt NMR spectroscopic analysis it was concluded that the reaction was not complete. After 2 h an aliquot was withdrawn, the THF was evaporated and the residue was extracted with toluene. The toluene was evaporated under reduced pressure, the residue was washed with pentane and dried *in vacuo* to yield a red solid which was analyzed by means of $^1$H
Platinum Acetylide Compounds

and $^{1}H,^{195}Pt$ HMQC NMR spectroscopy. $^{1}H$ NMR (300 MHz, C$_{6}$D$_{6}$) $\delta = 7.24$ (s, $^{3}J_{HH} = 66$ Hz; HC=N), 6.75 (d, $^{3}J_{HH} = 8$ Hz, 1H), 6.70 (d, $^{3}J_{HH} = 8$ Hz, 1H), 6.60 (t, $^{3}J_{HH} = 8$ Hz, 1H), 5.97 (s, $^{3}J_{HH} = 124$ Hz, 1H; HC=N), 3.71 (s, $^{3}J_{HH} = 18$ Hz, 3H; C=N-CH$_{3}$), 2.92 (s, $^{3}J_{HH} < 4$ Hz, 3H; C=N-CH$_{3}$), 0.74 (s, 9H), 0.44 (s, 9H). $^{195}Pt$ NMR (C$_{6}$D$_{6}$): $\delta = -3454$.

Table 4-4. Crystal data and details of the structure determination of 4m and 5g.

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$^{a}$ $w = 1 / [\sigma^{2}(F_{o}^{2}) + (0.0246P)^{2} + 0.3410P]$ where P = (F$_{o}^{2}$ + 2F$_{c}^{2}$)/3

$^{b}$ $w = 1 / [\sigma^{2}(F_{o}^{2}) + (0.0249P)^{2} + 1.1959P]$ where P = (F$_{o}^{2}$ + 2F$_{c}^{2}$)/3
Chapter 4

Crystal structure determinations

Data collection and cell refinement were carried out on a Nonius KappaCCD diffractometer with rotating anode, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at a temperature of 150(2) K. The structures were solved by Patterson methods (DIRDIF-9727) and refined with SHELXL-9728 against F² of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups in structure 5g. In structure 4m the hydrogens were refined freely with isotropic displacement parameters. Details of the structure determinations are given in Table 4-4.

Kinetics of the conversion of 4f to 5f

The reaction of compound 2f and LiC≡CSiMe₃ was carried out in toluene according to the general procedure. After warming up to room temperature, all the volatiles were evaporated under reduced pressure and the residue was dried in vacuo and was dissolved in a few mL of C₆D₆ and cyclododecane was added as an internal standard. An NMR tube was loaded with 0.5 mL of this stock-solution and was placed in a NMR spectrometer which was thermostated (e.g. 25°C). The reaction progress was followed by recording a series of ¹H NMR spectra in a period of time. In the NMR spectrum suitable signals of the trans-diorganoplatinum compound 4f (SiMe₃, 0.30 ppm) the dimeric cis-diorganoplatinum compound 5f (SiMe₃, -0.23 ppm) and the internal standard (cyclododecane, (CH₂)₁₀, 1.4 ppm) were integrated for quantification. The reaction was followed at 15, 25 and 35 °C. Plotting ln(4f) against time resulted in a linear curve, which was fitted with the least squares method. For T = 15 °C the reaction profile was analyzed until completion of the reaction, for T = 25 °C the reaction profile was analyzed until 96% completion of the reaction and for T = 35 °C the reaction profile was analyzed until 75% completion of the reaction.

4.6 References
