Isophthalaldimine compounds of palladium, platinum and rhodium.
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Citation for published version (APA):
Chapter 3

Isophthalaldimine platinum(II) methyl compounds†

3.1 Introduction

Both cis and trans (square planar) diorganoplatinum(II) compounds are relevant to mechanistic considerations concerning C-C bond formation\(^2-^4\) and to fundamental structural investigations. The strong trans influence exerted by hydrocarbyl ligands will bias the geometry of tetracoordinate diorganoplatinum(II) compounds PtR\(_2\)L\(_2\) towards cis-complexes, unless chelate effects are overriding. The former holds for a number of published diorganoplatinum compounds which contain monodentate,\(^5-^7\) didentate\(^8-^11\) or tridentate\(^10,12-14\) ligands. Much fewer examples of trans-diorganoplatinum(II) compounds are known. Some of these compounds are stabilized by two monodentate phosphine ligands,\(^7,15\) however, in that case isomerization to the (more stable) cis-diorganoplatinum(II) diphosphine compounds may occur.\(^16\) In most of the other known trans-diorganoplatinum(II) compounds the remaining two (neutral) ligands bound to the platinum are forced in a trans configuration by using a meridional coordinating and covalently bound [D-C-D] ligand (A, see Figure 3-1).

![Figure 3-1.](image)

Since the first paper concerning a platinum(II) [P-C-P] compound, having phosphines as donors, published by Moulton and Shaw in 1976,\(^17\) many papers concerning platinum(II) [D-C-D] compounds having different donor groups have appeared. Platinum [P-C-P] compounds having phosphines\(^18,19\) and phosphinidenes\(^20\) as donor groups, platinum [S-C-S] compounds with sulphides,\(^21\) and platinum [N-C-N] compounds having pyrazoles,\(^22,23\) oxazolines\(^24\) and amines\(^3,25\) as coordinating groups have been prepared.

† This chapter has partly been published.\(^1\)
The forced trans coordinating mode of the donor groups has resulted in trans-diorganoplatinum(II) compounds which contain [P-C-P]\(^{19,26-28}\) and [N-C-N]\(^{3,29-31}\) ligands. However, it appears that only two examples of trans-organoplatinum(II) methyl compounds have appeared. These platinum [P-C-P] methyl compounds (B, R = Ph, see Figure 3-2) were isolated and spectroscopically identified by the groups of Venanzi (B, B')\(^{26}\) and Hughes (B)\(^{27}\).

![Figure 3-2.](image)

In our attempts to prepare trans-organoplatinum(II) methyl compounds (3, see Scheme 3-1) we apply the isophthalaldiminie ligand (C, see Figure 3-2) as meridional coordinating [N-C-N] ligand. The question is, what the resulting effect of chelation of the imine moieties as opposed to the strong mutual trans influence of the hydrocarbyl moieties will be and whether or not trans-isophthalaldiminie platinum(II) methyl compounds (3, see Scheme 3-1) can be formed. Analogous to the synthesis of the platinum [P-C-P] methyl compounds (B, see Figure 3-2), the trans-isophthalaldiminie platinum(II) methyl compounds (3) may be accessible from the corresponding platinum(II) halide compounds (2, see Scheme 3-1) via a transmetallation reaction.

Furthermore, the studies concerning the aryl-platinum-methyl compounds are very much related to the studies of primary processes involving C-C bonds, as studied by Milstein et al. in platinum diphosphine [P-C-P] compounds\(^{32}\) and by van Koten et al. in platinum\(^{3,33}\) diamine [N-C-N] compounds and deserve attention from this point of view.

![Scheme 3-1. General scheme](image)

### 3.2 Synthesis and characterization of isophthalaldiminie platinum(II) bromide compounds

The oxidative addition reactions of the C-Br bond of the isophthalaldiminie ligands 1 (prepared similar to described in Chapter 2) to a suitable Pt(0)-precursor (Pt(dba)\(_2\)\(^{+}\) or Pt(dipdba)\(_2\)\(^{+}\)) resulted in the formation of the platinum(II) bromide precursors 2, see
Scheme 3-1 and Table 3-1. The oxidative addition reaction was accompanied by decomposition of the Pt(0)-precursor, therefore, to accomplish full conversion of 1, an excess of the Pt(0)-precursor was required. After separation from free dba or dipdba by washing with, in most cases, low boiling petroleum ether and/or recrystallization, compounds 2a-m were isolated as orange to brown air stable solids, see Table 3-1 for their definition and yields. Some of these compounds (2g and 2m) have been described. Very recently, a paper concerning an analogous oxidative addition for the synthesis of bis(aminomethyl)phenyl [N-C-N] platinum(n) bromide compounds has been published. A procedure for the synthesis of [N-C-N] platinum(n) halide compounds which consists of the oxidative addition of C-Br bonds to [Pt(p-tolyl)2SEt2]2 and probably involves a Pt(IV) intermediate, recently described by Canty et al., has been attempted starting from 1f. However, no 2f was observed in the reaction mixture.

Compounds 2a-m have been identified by means of 1H, 13C and 195Pt NMR and mass spectroscopy, for 2h by single crystal X-ray crystallographic analysis and for 2m with an elemental analysis.

Very recently, a paper of Richards and coworkers has appeared, in which the synthesis and characterization of related isophthalaldimine platinum(II) compounds is described. In their

<table>
<thead>
<tr>
<th>Suffix</th>
<th>Imine substituent (R)</th>
<th>Yield of 1 (%)</th>
<th>Yield of 2 (%)</th>
<th>δ195Pt (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>methyl</td>
<td>80</td>
<td>76</td>
<td>-3618</td>
</tr>
<tr>
<td>b</td>
<td>isopropyl</td>
<td>95a</td>
<td>36</td>
<td>-3667</td>
</tr>
<tr>
<td>c</td>
<td>tert-butyl</td>
<td>88</td>
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<td>92</td>
<td>64</td>
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<td>e</td>
<td>phenyl</td>
<td>84</td>
<td>73</td>
<td>-3606</td>
</tr>
<tr>
<td>f</td>
<td>4-methylphenyl</td>
<td>88a</td>
<td>63</td>
<td>-3611</td>
</tr>
<tr>
<td>g</td>
<td>4-methoxyphenyl</td>
<td>94a</td>
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<td>-3608</td>
</tr>
<tr>
<td>h</td>
<td>2,6-dimethylphenyl</td>
<td>84</td>
<td>88</td>
<td>-3562</td>
</tr>
<tr>
<td>i</td>
<td>3,5-dimethylphenyl</td>
<td>80</td>
<td>41</td>
<td>-3599</td>
</tr>
<tr>
<td>j</td>
<td>3,5-di-(trifluoromethyl)-phenyl</td>
<td>60</td>
<td>34</td>
<td>-3557</td>
</tr>
<tr>
<td>k</td>
<td>2,4,6-trimethylphenyl</td>
<td>99a</td>
<td>79</td>
<td>-3527</td>
</tr>
<tr>
<td>l</td>
<td>2,6-diethylphenyl</td>
<td>92</td>
<td>71</td>
<td>-3517</td>
</tr>
<tr>
<td>m</td>
<td>2,6-diisopropylphenyl</td>
<td>76a</td>
<td>63</td>
<td>-3599</td>
</tr>
</tbody>
</table>

a. The synthesis of this compound is described Chapter 2.

†. dba = dibenzylideneacetone, dipdba = 4,4'-diisopropyldibenzylideneacetone.
study, platinum chloride compounds (R = t-Bu, Cy, Bu, Bn, Ph) have been prepared by
cycloplatination of the parent isophthalaldimine ligand by K₂PtCl₄ in glacial acetic acid.
Both the N-t-Bu and the N-Ph substituted compounds have been characterized by means of
an X-ray structure analysis by these authors.

NMR spectroscopy
The ¹H and ¹³C NMR data of 2a-m are consistent with their assigned structures,¹ which are
directly comparable to their palladium(II) analogues (Chapter 2) and are similar to data
published recently.³⁵ The equivalence and coordination of both imine moieties was inferred
from (1) the coordination induced shift which amounts to 0.3 to 0.65 ppm (¹H) for the imine
protons, (2) their ³J(¹H,¹⁹⁵Pt) couplings of 139 Hz - 153 Hz (¹⁹⁵Pt, I = ½, 33.8% natural
abundance). The coordination of Cᵢₚₛₒ of the aryl ring was inferred from its chemical shift at
170-180 ppm, from the ¹J(¹³C,¹⁹⁵Pt) coupling of 926 - 943 Hz³¹,³⁵ and the ⁴J(¹H,¹⁹⁵Pt)
coupling of 7 - 8 Hz which was observed in some cases. The ¹⁹⁵Pt chemical shift (see
Table 3-1) increases with an increase in the steric bulk, this can be explained in view of an
increasing deviation from an ideal square planar surrounding caused by the steric bulk,
resulting in a lower ligand field, which leads to an increase of the chemical shift.³⁶

X-ray crystal structure determination
A single crystal X-ray structure analysis was performed for compound 2h (R =
2,6-dimethylphenyl). The molecular structure of 2h is depicted in Figure 3-3, selected bond
lengths and angles are presented in Table 3-2.

**Figure 3-3.** Displacement ellipsoid plot of 2h, drawn at the 50% probability level. Hydrogen atoms and
disordered, cocrystallized solvent molecules have been omitted for clarity.

The structure of 2h is related to the structures of the palladium halide compounds described
in Chapter 2, the structures of the tert-butyl and phenyl substituted isophthalaldimine
platinum chloride compounds published by Richards and coworkers, the structure of a 2,6-bis(2-pyridinyl)phenyl platinum chloride compound by Echavarren, and the structure of a bis(oxazolinyl)phenyl platinum chloride compound reported by Motoyama.

Table 3-2. Selected bond lengths (Å) and angles (deg) for 2h

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(1) - N(1)</td>
<td>2.032(11)</td>
<td>Pt(1) - Br(1)</td>
<td>2.492(17)</td>
</tr>
<tr>
<td>Pt(1) - N(2)</td>
<td>2.043(12)</td>
<td>Pt(1) - C(1)</td>
<td>1.897(14)</td>
</tr>
<tr>
<td>N(1) - C(7)</td>
<td>1.335(18)</td>
<td>N(2) - C(8)</td>
<td>1.306(19)</td>
</tr>
<tr>
<td>N(1) - C(9)</td>
<td>1.432(19)</td>
<td>N(2) - C(17)</td>
<td>1.444(19)</td>
</tr>
<tr>
<td>N(1) - Pt(1) - N(2)</td>
<td>160.0(6)</td>
<td>Br(1) - Pt(1) - C(1)</td>
<td>176.4(4)</td>
</tr>
<tr>
<td>N(1) - Pt(1) - C(1)</td>
<td>79.4(6)</td>
<td>N(2) - Pt(1) - C(1)</td>
<td>80.6(6)</td>
</tr>
<tr>
<td>Br(1) - Pt(1) - N(1)</td>
<td>100.9(4)</td>
<td>Br(1) - Pt(1) - N(2)</td>
<td>99.1(4)</td>
</tr>
<tr>
<td>C(7) - N(1) - C(9)</td>
<td>120.3(12)</td>
<td>C(8) - N(2) - C(17)</td>
<td>120.0(13)</td>
</tr>
</tbody>
</table>

In the crystal structure of 2h the platinum has a distorted square-planar environment with a sum of cis angles of 360.0°. The N-Pt-C angles of the five membered chelate rings amount to 79.4(6)° and 80.6(6)°, which is significantly smaller than the ideal values of 90° and is caused by ring strain. The values are similar to the angles found in the above mentioned related crystal structures. The ring strain caused by the adjacent 5- and 6-membered rings results in a distorted trans N-Pt-N angle of 160.0(6)° in 2h, which is comparable to the structures published by Echavarren and Motoyama and is slightly larger than found for the palladium compounds described in Chapter 2 (157.01(6)° - 158.34(14)°) and the structures published by Richards, 157.2(2)° and 157.9(2)°. The Pt-Caryl bond is 1.897(14) Å, which is comparable to the value found for the above mentioned structures. The Pt-N bond lengths are 2.032(11) and 2.043(12) Å, which is the same within standard deviations as analogous bond lengths reported and slightly shorter than for the palladium compounds described in Chapter 2 (2.0970(16) Å - 2.1374(14) Å) and than for the ones described by Richards (2.061(5) Å - 2.097(5) Å).

If the structure of 2h is compared to a platinum bromide compound derived from the 2,6-bis(dimethylaminomethyl)phenyl [N-C-N] ligand system it is found that the Pt-C and the N-Pt-C angles of the five membered chelate rings are similar within standard deviations. However, the Pt-N bonds (2.07(1) Å and 2.09(1) Å) are slightly shorter in 2h (2.032(11) Å and 2.043(12) Å). Also the N-Pt-N angle is slightly smaller in 2h (160.0(6)° compared to 164.4(4)°). This is caused by the higher strain arising from the shorter imine C=N(R) double bond as compared to the amine C-NR2 single bond. In the structure of 2h the five- and six-membered rings in the plane of the platinum are each almost planar. For the Pt(1), N(1), C(1), C(2), C(7) plane, the largest deviation is 0.008(16) Å, for the Pt(1), N(2), C(1), C(6),
C(8) plane this is 0.018(7) Å, for the aryl ring, the largest deviation is 0.026(13) Å. These three planes are almost coplanar, the angles between the first and the second is 1.6(7)°, between the first and the third 1.7(7)° and between the second and the third 0.8(7)°.

The molecules of compound 2h crystallize in the trigonal space group R₃. There are channels present in the crystal which are filled by disordered solvent molecules. These channels run along the crystallographic threefold axis (Figure 3-4.). Some of the solvent molecules could be identified as THF (0.4 molecules THF per molecule of 2h), others were modelled as diffuse electron density.

3.3 Trans aryl platinum(II) methyl compounds

3.3.1 Synthesis via transmetallation

Synthesis of thermally stable methyl derivatives 3 was attempted, first by transmetallation of the isophthalaldimine platinum(II) bromide compounds with methyl lithium, see Scheme 3-2, an approach which is successful for [P-C-P] ligands. When compounds 2g (R = 4-methoxyphenyl) and 2m (R = 2,6-diisopropylphenyl) were reacted with methyl lithium at -60°C by slowly adding the methyl lithium to a solution of 2g or 2m in THF, the orange reaction mixture immediately turned green. The reaction mixture was slowly warmed to room temperature and it was analyzed by ¹H NMR spectroscopy. In the case of 2m no signal
indicative of a Pt-CH$_3$ moiety was observed and the signals due to the isopropyl groups in the $^1$H NMR spectrum pointed at the formation of many different isopropyl groups. It was concluded that the methyllithium had reacted with one or both an imine moieties, but no transmetallation had taken place. In contrast to the case for palladium (Chapter 2) no transmetallation was observed for 2g. In these reactions, either the transmetallation reaction was slower in the case of the platinum compared to palladium, giving rise to more side reactions, or the platinum compounds are more susceptible to reduction by the methyl lithium.

Scheme 3-2. Attempted transmetallation of compounds 2 with methyllithium

Since the use of methyl lithium did not lead to the isophthalaldimine platinum methyl compounds 3, the milder methyl transferring reagent dimethylzinc was applied. The transmetallation reaction of 2m with one equivalent of dimethylzinc was performed at room temperature in THF. When the solution of dimethylzinc was added, the color of the light orange reaction mixture slowly turned to red. When the reaction mixture was analyzed by $^1$H NMR spectroscopy, the spectrum pointed at the clean formation of an additional compound with similar structural features as 2m and an additional resonance at 0.7 ppm ($^3$J(H,$^{195}$Pt) = 53 Hz, C$_6$D$_6$) originating from the methyl group coordinated to the platinum. However, the conversion was only 14%. When the reaction (see Scheme 3-3) was performed with a an excess (30-40 equiv.) of dimethylzinc a change of the color from light orange to dark red was observed and from $^1$H NMR spectroscopy it appeared that the conversion was complete. After work-up, 3m was isolated as red prisms in 95% yield.

Scheme 3-3. Transmetallation of 2h,m and Me$_2$Zn to form 3h,m.

Similarly treating compound 2h (R = 2,6-dimethylphenyl) with an excess of dimethylzinc at room temperature afforded the isophthalaldimine platinum methyl compound 3h in 80% isolated yield.
In the $^1$H NMR spectrum of $3h$ and $3m$ (C$_6$D$_6$) the signal of Pt-methyl group appears at 0.7 ppm, with a $^3J(^1$H,$^{195}$Pt) of 53 Hz. It is noteworthy that, compared to both $2h$ and $2m$, the $^3J(^1$H,$^{195}$Pt) of the imine proton decreases from 144 Hz to 125 Hz due to the larger cis influence of the methyl group compared to the bromide. In the $^{13}$C NMR spectrum of $3h$, the ipso aryl carbon is found at 204.0 ppm ($^1J(^{13}$C,$^{195}$Pt) = 591 Hz) and the platinum methyl carbon at 8.7 ppm ($^1J(^{13}$C,$^{195}$Pt) = 604 Hz). For $3m$, the ipso aryl carbon is found at 204.6 ppm (the $^1J(^{13}$C,$^{195}$Pt) could not be determined) and the platinum methyl carbon at 10.2 ppm ($^1J(^{13}$C,$^{195}$Pt) = 623 Hz). In $3h$ the signal for the imine carbon is found at 180.6 ppm (180.3 ppm for $3m$), the $^2J(^{13}$C,$^{195}$Pt) decreases from 106 Hz in $2h$ (108 Hz in $2m$) to 52 Hz in $3h$ (56 Hz in $3m$). The $^{195}$Pt chemical shift changes from -3563 in $2h$ (-3517 ppm in $2m$) to -3096 ppm in $3h$ (-3074 ppm in $3m$), which is expected in view of the increased ligand field.$^{36}$

Only for sterically demanding aryl substituents on the imine moieties an isophthalaldimine platinum(II) methyl compound could be obtained. For compound $2a$ (R = methyl) an analogous reaction with dimethylzinc resulted in the complete conversion of $2a$ into mixtures of unidentified compounds. For compound $2g$ (R = 4-methoxyphenyl) an isophthalaldimine platinum methyl compound $3g$ could be observed in a sample of the reaction mixture ($\delta^{195}$Pt = -3145 ppm), however this compound could not be isolated since it readily decomposed. No reductively eliminated C-C coupled product was observed.

**Figure 3-5.** a) Displacement ellipsoid plot of $3m$, drawn at the 50% probability level. b) View onto the Pt - CH$_3$ moiety of $3m$, along the Pt - C$_{aryl}$ bond. All hydrogen atoms except the methyl group have been omitted for clarity.

**X-ray crystal structure determination**

The structure of $3m$ was analyzed by means of a single crystal X-ray structure determination. The molecular structure of $3m$ is depicted in Figure 3-5, selected bond lengths and angles are
presented in Table 3-3. It constitutes the first structure of a mono nuclear \textit{trans} aryl platinum methyl compound. Of the two known \textit{trans} aryl platinum methyl compounds, the X-ray structures have not been determined.\textsuperscript{26,27} So far, only one example of a \textit{trans} aryl-Pt-C\textit{sp}\textsuperscript{3} compound has appeared, in this diphenylphosphine substituted [D-C-D] platinum compound, published by Hughes and coworkers, the platinum has a σ-bonded \textit{n}-C\textsubscript{3}F\textsubscript{7} group \textit{trans} to the aryl carbon.\textsuperscript{27}

\begin{table}[h]
\centering
\begin{tabular}{llll}
\hline
 & Pt(1) - N(1) & 2.045(2) & Pt(1) - C(1) & 1.944(2) \\
Pt(1) - N(2) & 2.036(2) & Pt(1) - C(33) & 2.156(3) \\
N(1) - C(7) & 1.314(3) & N(2) - C(8) & 1.304(3) \\
N(1) - C(9) & 1.442(3) & N(2) - C(21) & 1.439(3) \\
N(1) - Pt(1) - N(2) & 157.63(8) & C(1) - Pt(1) - C(33) & 173.49(12) \\
N(1) - Pt(1) - C(1) & 78.93(9) & N(2) - Pt(1) - C(1) & 78.80(9) \\
N(1) - Pt(1) - C(33) & 102.22(10) & N(2) - Pt(1) - C(33) & 100.15(10) \\
C(7) - N(1) - C(9) & 118.9(2) & C(8) - N(2) - C(21) & 120.7(2) \\
\hline
\end{tabular}
\caption{Selected bond lengths (Å) and angles (deg) for 3m}
\end{table}

The molecular structure of 3m, reveals bond lengths and angles that are similar to those in the structure of 2h. The platinum has a distorted square-planar environment with a sum of cis angles of 360.1°. The lengths of the Pt-N bonds in 3m have, within standard deviations, the same values (2.036(2) - (2.045(2) Å) as in 2h (2.032(11) - (2.043(12) Å). In 3m the Pt-C\textit{aryl} bond is 1.944(2) Å which is longer compared to 2h (1.897(14) Å). This also leads to a distorted \textit{trans} N-Pt-N angle of 157.63(8)° that is slightly smaller compared to 2h (160.0(6)°). The Pt-C\textit{methyl} bond is relatively long (2.156(3) Å),\textsuperscript{9,10,12,38} however, similar values are reported for \textit{trans} phosphine platinum methyl complexes.\textsuperscript{39,40} The long Pt-C distances are due to the large mutual \textit{trans} influence of the aryl and methyl groups. This effect is also observed in the structure of the \textit{trans} aryl-platinum-C\textsubscript{3}F\textsubscript{7} [D-C-D] compound, published by Hughes,\textsuperscript{27} the Pt-CF\textsubscript{2}R bond is 2.186(8) Å. As in the structure of 2h, for 3m 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 0.027(2) Å, for the Pt(1), N(1), C(1), C(2), C(8) plane this is 0.034(2) Å, for the aryl ring, the largest deviation is 0.010(2) Å. These three planes are almost coplanar, the angles between the first and the second is 0.71(10)°, between the first and the third 2.95(11)° and between the second and the third 2.67(11)°.

As can be seen in Figure 3-5b, which is a view of the molecular structure along the Pt(1) - C(1) bond, in the crystal structure form of 3m both imine-aryl moieties bend to one side of the platinum plane, defined by Pt(1), N(1), N(2), C(33) and C(1), (to the right in the
figure), whereas the methyl group bends to the other side (to the left), the C(1) - Pt(1) - C(33) angle is 173.49(12)°. This is probably due to steric hindrance between the platinum bound methyl group and the isopropyl groups of the imine substituent. In the crystal of 3m there are no special features in the packing.

3.4 Reactivity of diorganoplatinum compounds towards additional ligands

To investigate the coordination strength of the imine moieties in 3m in more detail, it was subjected to additional ligands, e.g. pyridine and carbon monoxide which may result in the displacement of one or of both coordinating imine moieties. Displacement of a chelating nitrogen in a square planar platinum [N-C-N] compound by an additional monodentate ligand has not often been studied.30

3.4.1 Pyridine

When the trans-isophthalaldimine platinum(II) methyl compound 3m was subjected to a reaction in C₆D₆ with a large excess of pyridine, it was concluded, based on the ¹H NMR spectrum of the reaction mixture, that one imine moiety was displaced by a pyridine molecule, see Scheme 3-4. The chemical shift of the proton of the coordinating imine was 8.74 ppm. It is noteworthy that the ²J(¹H,¹⁹⁵Pt) of this imine proton decreases from 125 Hz (in 3m) to 101 Hz (in 4m) due to the stronger trans influence of pyridine, compared to an imine moiety. For compound 4m, the Pt-methyl resonance appears at 0.33 ppm (²J(¹H,¹⁹⁵Pt) = 52 Hz), which is appreciably lower than in 3m (0.67 ppm, ³J(¹H,¹⁹⁵Pt) = 53 Hz). The signal of the proton of the dissociated imine moiety was not observed, it was obscured by the aromatic signals, since it was shifted to lower frequency due to the shielding of the aromatic pyridine ring. In the ¹⁹⁵Pt NMR spectrum, the ¹⁹⁵Pt chemical shift changes from -3074 ppm for 3m to -3216 ppm for 4m. These features are in concert with the higher basicity of pyridine compared to an imine.

Then, before the reaction of 3m and pyridine was complete, 4m slowly isomerizes to the cis arylplatinum(II) methyl pyridine complex 5m, as was concluded from ¹H and ¹⁹⁵Pt NMR
spectroscopy (see Scheme 3-4). The conversions of 3m to 4m and of 4m to 5m at room temperature were completed by heating the reaction mixture in the NMR tube over night to 80°C. For 5m, in the 1H NMR spectrum the proton of the dissociated imine was now found at 9.25 ppm, the proton of the coordinating imine at 8.33 ppm ($^3J(1^H,^{195}\text{Pt}) = 52$ Hz). The decrease of the coupling constant compared to 3m (125 Hz) and 4m (101 Hz) is consistent with the much larger trans influence of the methyl group compared to an imine and a pyridine, respectively. The $^3J(1^H,^{195}\text{Pt})$ of 80 Hz observed for the Pt-methyl group at 1.61 in 5m is much larger then observed in 3m and 4m (52 - 53 Hz), which corresponds with the decreased trans influence of the imine moiety compared to the aryl group. The $^1\delta^{195}\text{Pt}$ of 5m was -3550 ppm. The isomerization of 4m to 5m is thermodynamically favorable, due to the more stable cis configuration of the aryl and the methyl group in 5m, both having a strong trans influence, compared to the trans configuration in 4m.41,42

3.4.2 Carbon monoxide

3.4.2.1 Substitution of an imine moiety for carbon monoxide

When carbon monoxide was bubbled through a solution of 3m in C$_6$D$_6$ one imine moiety was displaced by the CO ligand and a trans-isophthalaldimin e platinum(II)methyl carbon monoxide complex 6m was obtained, see Scheme 3-5, analogously to the reaction of 3m

![Scheme 3-5.](image)

with pyridine. In the 1H NMR spectrum of 6m, the chemical shift of the proton on the dissociated imine moiety is found at 8.86 ppm, for the coordinating imine the signal was found at 7.79 ppm ($^3J(1^H,^{195}\text{Pt}) = 86$ Hz), the chemical shift of the Pt-methyl protons was 0.50 ppm ($^3J(1^H,^{195}\text{Pt}) = 44$ Hz) and $^1\delta^{195}\text{Pt} = -4000$. Proof of the coordination of CO stems from the 13C NMR spectrum of 13CO labeled compound 6m*, which showed a $^1J(13^C,^{195}\text{Pt})$ of 1895 Hz and the infrared spectrum (in C$_6$D$_6$) of 6m in which the CO vibration was observed at 2058 cm$^{-1}$.

3.4.2.2 Photoisomerization

In contrast to the observed thermal isomerization of 4m to 5m, it was found that at room temperature compound 6m can only isomerize photochemically to the cis isophthalaldimin e platinum(II) methyl carbon monoxide complex 7m. For 7m, the chemical shift of the
dissociated imine was 8.97 ppm, and 7.92 ppm ($^3J(^1H,^{195}Pt) = 54 \text{ Hz}$) for the coordinating imine. The Pt-methyl resonance was observed at 1.50 ppm ($^3J(^1H,^{195}Pt) = 84 \text{ Hz}$), $\delta^{^{195}Pt} = -3902 \text{ ppm}$. For 7m the CO vibration was observed at 2064 cm$^{-1}$, which is only slightly different from 6m ($v_{CO} = 2058 \text{ cm}^{-1}$). At room temperature, no migration insertion to give a Pt-acyl species was observed.$^{38,43}$

The photoisomerization could be monitored using UV-Vis spectroscopy. Upon irradiation of 6m with a Xe-lamp, the absorption bands at 330 nm and 405 nm disappear while simultaneously an increase in the absorption of 7m at 370 nm is observed (see Figure 3-6). The photoisomerization is irreversible and, as can be seen from the isosbestic points at 390 nm and 355 nm, a very clean process.

![Figure 3-6](image)

**Figure 3-6.** UV/Vis spectral changes accompanying the photoisomerization of 6m into 7m.

The absorption bands at 405 nm for 6m and at 370 nm for 7m are attributed to metal-to-ligand charge transfer (MLCT) transitions from different Pt(d) orbitals to the isophthalaldimine ligand because of their energies, intensities and solvatochromic behaviour. Both 6m and 7m did not show any emission upon excitation into their MLCT bands, implying a short lifetime of the lowest MLCT state. In order to gain more insight in the mechanism of the photoisomerization, nanosecond time-resolved absorption spectra of a solution of 6m in methanol and pentane were measured; the solution was excited with light of 310 nm and 435 nm. Only a weak, broad transient absorption (500 - 750 nm) was observed with a lifetime of 400-500 nanoseconds. This lifetime is too short to belong to a reactive ground state intermediate and is instead assigned to the MLCT state of the platinum(II) complex.$^{44}$ This assignment is supported by the broadness of the long-wavelength absorption, which is rather specific for metal-to-ligand excited states of complexes containing ligands such as bipyridine or isophtalaldimine.
3.5 Discussion

3.5.1 Photoisomerization

The photochemical isomerization of square planar platinum(II) compounds normally proceeds in the absence of additional ligands.\textsuperscript{45} This in contrast to thermal isomerizations which occur via associative mechanisms in most cases. Via a consecutive ligand exchange (with a cationic intermediate),\textsuperscript{46} or via a pseudorotation (with a five-coordinate intermediate).\textsuperscript{47} Dissociative processes are less common.\textsuperscript{39,45,48} Both the consecutive ligand exchange and the dissociative mechanisms\textsuperscript{49} proceed in organoplatinum halide complexes via halide dissociation, an analogous pathway is not possible in this case, since aryl or methyl loss to yield a cationic intermediate is highly unfavorable. The thermal isomerization of the pyridine complex $4m$ to $5m$ will be associative and involve pseudorotation of an intermediate five coordinated bis-pyridine complex, since the pyridine was present in an excess.

For the isomerization of the carbon monoxide complex $6m$, the isomerization proceeds differently, probably no intermediate five coordinated bis-carbon monoxide complex is formed in the presence of an excess carbon monoxide and therefore the isomerization can only proceed photochemically. The far most commonly proposed pathway for a photochemical isomerization in a square planar complex is an intramolecular twisting mechanism via a tetrahedral transition state.\textsuperscript{50,51} Another possibility is that the photoisomerization is initiated by the photodissociation of a ligand, as a result from the crossing of the unreactive MLCT state with the reactive ligand field energy curve.\textsuperscript{44,50} Its repulsive potential results in the dissociation of one ligand, which can be the CO or the imine moiety. This dissociation is followed by isomerization and re-coordination of the ligand.

![Figure 3-7](image-url)
the dissociative mechanism, a three coordinate intermediate is formed and such an intermediate is expected to have a longer lifetime than that observed for the transient species in the transient absorption measurements. Instead, the results of the transient absorption measurements point to a fast intramolecular twisting mechanism directly from the MLCT excited state of the complex (Figure 3-7).

The intermediate in the twisting mechanism is expected to have a severely distorted tetrahedral surrounding, since the cis N-Pt-C_aryl angle, which is around 79° in 3m, can not reach 109°, the value in a perfect tetrahedron.

3.5.2 Cis and trans aryl platinum(II) methyl compounds

In the known aryl-platinum(II) methyl compounds, the carbon fragments are more often found in a cis configuration than in a trans configuration. In the presence of a cis-coordinating (neutral) didentate ligand (e.g. cyclooctadiene, diphosphines and diazabutadiene), the cis-disposition of the carbon fragments is enforced. However, a cis disposition of the carbon fragments is thermodynamically favored over a trans configuration due to their strong mutual trans influence. Therefore, in trans-diorganoplatinum(II) compounds which contain two monodentate phosphine ligands, isomerization to the more stable cis-diorganoplatinum(II) diphosphine compounds may occur.

In compounds 3h and 3m the configuration of the aryl and the methyl groups is trans, as was found for the related trans-diphosphine [P-C-P] platinum(II) methyl compounds prepared by Venanzi and Hughes (see Figure 3-2). The trans configuration of the carbon fragments is dictated in these compounds by the strong coordination of the chelating imine and phosphine moieties, respectively, in a trans configuration to the platinum center. However, the meridional coordination mode of the ligand in 3m can be discontinued by displacement of an imine moiety by an additional ligand, e.g. pyridine or carbon monoxide, to furnish 4m or 6m, respectively. As a result, the ligand acts as a covalently bound κC,κN-didentate ligand. The trans disposition of the aryl and the methyl groups is not retained and these compounds irreversibly isomerize to the compounds 5m and 7m, respectively, in which the aryl and methyl groups are in a cis configuration. Such a cis disposition of the aryl and the methyl groups is generally thermodynamically more stable and is similar to the configuration in methyl derivatives of related κC,κN-didentate ligands.

The fact that compounds 3h and 3m can be isolated demonstrates that these are stable at ambient temperatures, in contrast to analogous palladium methyl compounds. The latter (if formed) are not thermally stable and give rise to reductive elimination of a C-C bond, as was shown in the previous chapter. The higher thermal stability of the diorganoplatinum, compared to diorganopalladium compounds is a general trend and has been theoretically explained.
3.6 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.\(^5\) NMR measurements were performed on a Bruker AC200 (\(^1\)H: 200.13 MHz), a Bruker AMX300/Varian Mercury300 spectrometer (\(^1\)H: 300.13 MHz, \(^13\)C: 75.47 MHz), a Varian Inova500 spectrometer (\(^1\)H: 499.88 MHz, \(^13\)C: 125.70 MHz) and Bruker DRX300 spectrometer (\(^{195}\)Pt: 64.3 MHz, \(^{15}\)N: 30.42 MHz). \(^{195}\)Pt NMR spectra were measured via a normal HMQC sequence at 298K. \(^{15}\)N NMR spectra were measured by a standard gs-HMQC sequence at 298K. \(^{13}\)C NMR spectra were measured with \(^1\)H decoupling. Positive chemical shifts (\(\delta\)) are denoted for high-frequency shifts relative to a TMS reference (\(^1\)H, \(^13\)C), a Na\(_2\)PtCl\(_6\) reference (\(^{195}\)Pt) and a CH\(_3\)NO\(_2\) reference (\(^{15}\)N). Infrared spectra were measured on a Biorad FTS-7 and a Biorad FTS-60A spectrometer from a 0.2 mm film of a 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. For Electron Impact (EI) mass spectrometry, the samples were introduced via a direct insertion probe into the ion source. During the high resolution FAB-MS and EI-MS measurements a resolving power of 10,000 (10% valley definition) was used.

UV-Vis absorption spectra were recorded on a diode-array HP8453 spectrophotometer at 293 K in a 1 cm quartz Hellma-cuvette. Fluorescence spectra were recorded on a SPEX fluorometer. Samples were measured in a 1 cm quartz Hellma-cuvette, \(\lambda_{exc} = 370\) nm. Nanosecond transient absorption (ns TA) spectra were obtained by irradiating the samples with 2 ns pulses (FWHM) of a continuously tunable (420 - 710 nm) Coherent Infinity XPO laser. Frequency doubling was achieved with a BBO crystal. The output power of the laser was typically less than 5 mJ/pulse at a repetition rate of 10 Hz. Samples in a 1 cm quartz cuvette (Hellma) exhibited an optical density of ca. 0.8 at the excitation wavelength. The probe light from a low-pressure, high-power EG&G FX-504 Xe lamp passed through the sample cell and was dispersed by an Acton Spectra-Pro-150 spectrograph, equipped with 150 g/mm or 600 g/mm grating and a tunable slit (1 - 500 \(\mu\)m), resulting in 6 or 1.2 nm maximum resolution, respectively. The data collection system consisted of a gated intensified CCD detector (Princeton Instruments ICCD-576EMG/RB), a programmable pulse generator (PG-200), and an EG&G Princeton Applied Research Model 9650 digital delay generator. \(I\) and \(I_0\) values are measured simultaneously, using a double kernel 200 \(\mu\)m optical fiber.

**Materials:** Compounds 1b, 1f, 1g, 1k and 1m and 2-bromo-isophthalaldehyde are described in Chapter 2. Pt(dbaf)\(_2\),\(^5\) Pt(dipdbaf)\(_2\)\(^5\) were prepared according to literature procedures. 3Å molecular sieves were activated by heating at 150°C in vacuo over night. All other starting materials were obtained from commercial sources and were used as received.

**Bis-(N-methyl)-2-bromo-isophthalaldimine (1a)**

To a solution of 2-bromo-isophthalaldehyde (0.5 g, 2.3 mmol) in 100 mL of THF were added methylammonium chloride (5 g, 74 mmol), Na\(_2\)CO\(_3\) (8 g, 75 mmol) and activated 3Å molecular sieves and the reaction flask was closed with a CaCl\(_2\)-tube. After the reaction mixture was stirred for one weekend, the reaction was complete (GC-MS). The reaction mixture was filtered and the
volatiles were evaporated under reduced pressure and the residue was dried \textit{in vacuo} to yield 0.44 g (1.8 mmol, 80\%) of a light yellow oil that solidified upon standing, which was identified by $^1$H and $^{13}$C NMR spectroscopy as pure 1a. $^1$H NMR (200 MHz, CDCl$_3$): $\delta = 8.74$ (dq, $^4J_{H,HMe} = 1.7$ Hz, $^5J_{HH,Me} = 0.7$ Hz 2H; $HC=N$), 7.99 (d, $^3J_{HH} = 7.7$ Hz, 2H) 7.36 (tt, $^3J_{HH} = 7.7$ Hz, $^5J_{HH} = 0.7$ Hz, 1H), 3.57 (d, $^4J_{HH} = 1.7$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 152.7$ (C=N), 135.6 (C), 130.8 (CH), 127.8 (CH), 126.9 (C-Br) 48.6 (CH$_3$). GC-MS $m/z$ (relative intensity): 240 (M$^{(18)}$Br$^+$), 57, 240 (M$^{(79)}$Br$^+$, 58), 196 ([M-Me-C=NH]$^+$, 9), 42 (Me-C=NH, 100).

**Bis-(N-tert-butyl)-2-bromo-isophthalaldimine (1c)**

To a solution of 2-bromo-isophthalaldehyde (1.0 g, 4.7 mmol) in 20 mL of THF were added tert-butylamine (5 mL, 3.5 g, 48 mmol) and 3Å molecular sieves. The reaction mixture was stirred overnight at room temperature. $^1$H NMR spectroscopic analysis showed full conversion and the reaction mixture was filtered, the volatiles were removed under reduced pressure and the residue was dried \textit{in vacuo}, which resulted in 1.34 g (4.15 mmol, 88\%) of a white solid which was identified by $^1$H and $^{13}$C NMR spectroscopy as pure 1c. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.70$ (s, 2H; $HC=N$), 8.00 (d, $^3J_{HH} = 7.7$ Hz, 2H) 7.35 (t, $^3J_{HH} = 7.7$ Hz, 1H), 1.32 (2, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 155.1$ (C=N), 136.2 (C), 130.6 (CH), 127.8 (CH), 127.6 (C-Br) 58.4 (C), 29.9 (CH$_3$). HRMS(FAB): $m/z$ calc’d ([M+H]$^+$ C$_{16}$H$_{21}$N$_2$Br 323.1123. Found 323.1121.

**Bis-(N-cyclohexyl)-2-bromo-isophthalaldimine (1d)**

Compound 1d was prepared, analogous to 1c, from 2-bromo-isophthalaldehyde (1.0 g, 4.7 mmol) and freshly distilled cyclohexylamine (1.1 ml, 9.4 mmol), in 25 mL of THF at 60°C. The volatiles were removed under reduced pressure and the residue was dried \textit{in vacuo} which resulted in 1.6 g (4.3 mmol, 92\%) of a white solid which was identified by $^1$H and $^{13}$C NMR spectroscopy as pure 1d. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.75$ (s, 2H; $HC=N$), 8.01 (d, $^3J_{HH} = 7.5$ Hz, 2H) 7.31 (t, $^3J_{HH} = 7.5$ Hz, 1H), 3.25 (m, 2H), 1.70-1.56 (m, 14H), 1.43-1.25 (m, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 157.9$ (C=N), 135.9 (C), 130.9 (CH), 127.7 (CH), 127.0 (C-Br), 70.1 (N-CH), 34.9 (CH$_2$), 25.9 (CH$_2$), 24.9 (CH$_2$). HRMS(FAB): $m/z$ calc’d ([M+H]$^+$ C$_{20}$H$_{28}$N$_2$Br 375.1436. Found 375.1440.

**Bis-(N-phenyl)-2-bromo-isophthalaldimine (1e)**

To 2-bromo-isophthalaldehyde (1.0 g, 4.7 mmol) was added aniline (1.0 mL, 1.0 g, 11 mmol) upon which some heat evolved, subsequently 10 mL of diethyl ether and 10 mL of THF were added and the resulting suspension was stirred for 3 h. $^1$H NMR spectroscopic analysis showed full conversion and the volatiles were evaporated under reduced pressure. Residual water was removed by the azeotropic evaporation with toluene (3 times), the residue was washed with pentane (2 times) and dried \textit{in vacuo} to yield 1.43 g (3.94 mmol, 84\%) of a yellow solid which was identified by $^1$H and $^{13}$C NMR spectroscopy as pure 1e. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 9.03$ (s, 2H; $HC=N$), 8.39 (d, $^3J_{HH} = 7.5$ Hz, 2H) 7.54 (t, $^3J_{HH} = 7.5$ Hz, 1H), 7.48 (m, 4H), 7.34 (m, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 159.2$ (C=N), 151.8 (C), 135.8 (C), 132.1 (CH), 129.5 (CH), 129.3 (C-Br), 128.1 (CH), 126.9 (CH), 121.4 (CH). HRMS(El): $m/z$ calc’d ([M]$^+$ C$_{20}$H$_{13}$N$_2$Br 362.0433. Found 362.0419.
**Bis-(N-2,6-dimethylphenyl)-2-bromo-isophthalalaldimine (1h)**

To a solution of 2-bromo-isophthalaldehyde (1.5 g, 7.0 mmol) in 50 mL of toluene were added 2,6-dimethylaniline (2 mL, 2.1 g, 17.6 mmol) and 3Å molecular sieves. The reaction mixture was stirred over night at 60°C and filtered after which the solvent was evaporated under reduced pressure. The residue was washed with 50 mL of pentane and dried in vacuo to yield 2.45 g (5.8 mmol, 84%) of a yellow solid which was identified by 1H and 13C NMR spectroscopy as pure 1h. 1H NMR (500 MHz, CDCl₃): δ = 8.75 (s, 2H; HCN=N), 8.41 (d, 3J_HH = 7.5 Hz, 2H) 7.58 (t, 3J_HH = 7.5 Hz, 1H), 7.11 (bs, 6H), 2.20 (s, 12H). 13C NMR (126 MHz, CDCl₃): δ = 161.2 (C=N), 151.1 (C), 135.9 (C), 131.7 (CH) 128.7 (C-Br), 128.5 (CH), 128.2 (CH), 127.3 (C), 124.4 (CH), 18.7 (CH₃). HRMS(FAB): m/z calc’d ([M+H]+ C₂₄H₂₄N₂²⁺Br) 419.1123. Found 419.1124. Anal. Calcd for C₂₄H₂₂BrN₂: C, 68.74; H, 5.53; N, 6.68. Found: C, 68.88 H, 5.48 N, 6.65.

**Bis-(N-3,5-dimethylphenyl)-2-bromo-isophthalalaldimine (1i)**

Compound 1i was prepared, analogous to 1h, from 2-bromo-isophthalaldehyde (0.74 g, 3.5 mmol) and 3,5-dimethylaniline (0.87 mL, 0.85 g, 7.0 mmol) yielding 1.2 g (2.8 mmol, 80%) of a yellow solid which was identified by 1H and 13C NMR spectroscopy as pure 1i. 1H NMR (500 MHz, CDCl₃): δ = 9.00 (s, 2H; HCN=N), 8.34 (d, 3J_HH = 7.8 Hz, 2H) 7.53 (t, 3J_HH = 7.8 Hz, 1H), 6.97 (bs, 2H), 6.94 (bs, 4H), 2.39 (s, 12H). 13C NMR (126 MHz, CDCl₃): δ = 158.8 (C=N), 151.9 (C), 139.2 (C), 135.9 (C), 131.9 (CH) 129.2 (C-Br), 128.5 (CH), 128.0 (CH), 119.1 (CH), 21.6 (CH₃). HRMS(EI): m/z calc’d ([M]²⁺ C₂₄H₂₂N₂²⁺ 811Br) 420.1027. Found 420.1024. Anal. Calcd for C₂₄H₂₂BrN₂: C, 68.74; H, 5.53; N, 6.68. Found: C, 68.67; H, 5.47; N, 6.59.

**Bis-(N-3,5-di-(trifluoromethyl)-phenyl)-2-bromo-isophthalalaldimine (1j)**

Compound 1j was prepared, analogous to 1h, from 2-bromo-isophthalaldehyde (1.0 g, 4.7 mmol) and 3,5-di-(trifluoromethyl)-aniline (2.8 mL, 4.2 g, 18.8 mmol). The resulting suspension was dissolved in dichloromethane and filtered. The volatiles were removed under reduced pressure and the residue was washed with 40 mL of diethyl ether and dried in vacuo to yield 1.7 g (2.8 mmol, 60%) of a white solid which was identified by 1H and 13C NMR spectroscopy as pure 1j. 1H NMR (300 MHz, CDCl₃): δ = 9.01 (s, 2H; HCN=N), 8.40 (d, 3J_HH = 7.8 Hz, 2H), 7.80 (bs, 2H), 7.66 (bs, 4H), 7.59 (t, 3J_HH = 7.8 Hz, 1H). 13C NMR (126 MHz, CDCl₃): δ = 161.7 (C=N), 152.9 (C), 135.1 (C), 133.2 (CH), 133.0 (q, C-CF₃, 3J_CF = 33 Hz), 130.0 (C), 123.4 (q, CF₃, 1J_CF = 273 Hz), 121.5 (q, 3J_CF = 3 Hz), 120.1 (septet, 3J_CF = 3 Hz). HRMS(FAB): m/z calc’d ([M+H]+ C₂₄H₁₂N₂²⁺BrF₁₂Pt) 634.9975. Found 634.9995.

**Bis-(N-2,6-diethylphenyl)-2-bromo-isophthalalaldimine (1l)**

Compound 1l was prepared, analogous to 1h, from 2-bromo-isophthalaldehyde (1.0 g, 4.7 mmol) and 2,6-diethylaniline (1.6 mL, 1.4 g, 9.4 mmol) in 40 mL of toluene by refluxing over night. The resulting mixture was filtered and the toluene was evaporated under reduced pressure. The excess aniline was removed by heating (T = 150°C) the residue in vacuo which yielded 2.0 g (4.2 mmol, 92%) of a yellow solid, which was identified by 1H and 13C NMR spectroscopy as pure 1l. 1H NMR (300 MHz, CDCl₃): δ = 8.75 (s, 2H; HCN=N), 8.40 (d, 3J_HH = 7.8 Hz, 2H) 7.59 (t, 3J_HH = 7.8 Hz, 1H), 7.16-7.08 (m, 6H), 2.55 (q, 3J_HH = 7.5 Hz), 1.19 (t, 3J_HH = 7.5 Hz). 13C NMR (126 MHz, CDCl₃): δ
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Conversion of 54% and therefore another portion of Pt(dipdba)_2 (1.0 g, 1.2 mmol) was added. After stirring overnight, the reaction mixture was filtered over Celite and the residue was thoroughly extracted with THF. Upon slow evaporation of the THF under reduced pressure, the product crystallized. The small crystals were collected by filtration and washed with diethyl ether and subsequently with pentane. The product was air dried to yield 0.55 g (1.26 mmol, 76%) of dark red crystals which were identified by ^1^H, ^13^C and ^195^Pt NMR spectroscopy as pure 2a. ^1^H NMR (200 MHz, CDCl₃): δ = 8.27 (q, ^3^J_HH = 14 Hz, ^3^J_HP = 142 Hz, 2H; HCl=N), 7.41 (d, ^3^J_HH = 7.7 Hz, ^4^J_HP = 9 Hz, 2H); 7.36 (t, ^3^J_HH = 7.11 Hz, ^5^J_HP = 3 Hz, 1H), 3.96 (d, ^3^J_HH = 1.4 Hz, ^4^J_HP = 32 Hz, 6H). ^13^C NMR (126 MHz, CDCl₃): δ = 176.9 (C=N), 175.6 (C-Pt), 141.5 (CPt = 114 Hz, C), 126.4 (CPt = 28 Hz, CH), 122.8 (CH), 50.7 (CPt = 28 Hz, CH₃). ^195^Pt NMR (CDCl₃): δ = -3618. HRMS (FAB): m/z calc (M+H)^+ C_{19}H_{12}N₂Br²^6Pt 434.9813 Found 434.9828.

**κC₂κN₂κN’-Bis-(N-methyl)-isophthalaldimine-2-yl-platina(II) bromide (2a)**

To a solution of 1a (0.4 g, 1.67 mmol) in 30 mL of THF was added Pt(dipdba)_2 (1.5 g, 1.8 mmol) and the reaction mixture was stirred overnight at 60°C. ^1^H NMR spectroscopic analysis showed a conversion of 54% and therefore another portion of Pt(dipdba)_2 (1.0 g, 1.2 mmol) was added. After stirring overnight, the reaction mixture was filtered over Celite and the residue was thoroughly extracted with THF. Upon slow evaporation of the THF under reduced pressure, the product crystallized. The small crystals were collected by filtration and washed with diethyl ether and subsequently with pentane. The product was air dried to yield 0.55 g (1.26 mmol, 76%) of dark red crystals which were identified by ^1^H, ^13^C and ^195^Pt NMR spectroscopy as pure 2a. ^1^H NMR (200 MHz, CDCl₃): δ = 8.27 (q, ^3^J_HH = 14 Hz, ^3^J_HP = 142 Hz, 2H; HCl=N), 7.41 (d, ^3^J_HH = 7.7 Hz, ^4^J_HP = 9 Hz, 2H); 7.36 (t, ^3^J_HH = 7.11 Hz, ^5^J_HP = 3 Hz, 1H), 3.96 (d, ^3^J_HH = 1.4 Hz, ^4^J_HP = 32 Hz, 6H). ^13^C NMR (126 MHz, CDCl₃): δ = 176.9 (C=N), 175.6 (C-Pt), 141.5 (CPt = 114 Hz, C), 126.4 (CPt = 28 Hz, CH), 122.8 (CH), 50.7 (CPt = 28 Hz, CH₃). ^195^Pt NMR (CDCl₃): δ = -3618. HRMS (FAB): m/z calc (M+H)^+ C_{19}H_{12}N₂Br²^6Pt 434.9813 Found 434.9828.

**κC₂κN₂κN’-Bis-(N-isopropyl)-isophthalaldimine-2-yl-platina(II) bromide (2b)**

Compound 2b was prepared analogous to 2a from 1b (0.74 g, 2.5 mmol) and Pt(dipdba)_2 (1.79 + 0.5 g = 2.29 g, 3.45 mmol) in 30 mL of THF at 50°C. After the filtration over Celite, the solvent was evaporated under reduced pressure, the residue was dissolved in toluene, filtered over Celite and the toluene was evaporated under reduced pressure. The dark residue was washed with diethyl ether and dissolved in THF. The dark impurity was precipitated by adding pentane. The mother liquor contained pure 2b which was isolated by evaporation of the solvents under reduced pressure. The light orange residue was dried in vacuo and was identified by ^1^H and ^13^C NMR spectroscopy as pure 2b (0.44 g, 0.9 mmol, 36%). ^1^H NMR (300 MHz, CDCl₃): δ = 8.35 (s, ^3^J_HH = 147 Hz, 2H; HCl=N), 7.40 (d, ^3^J_HH = 7.7 Hz, 2H), 7.11 (t, ^3^J_HH = 7.7 Hz, 1H), 4.74 (septet, ^3^J_HH = 6.6 Hz, 2H), 1.49 (d, ^3^J_HH = 6.6 Hz, 12H). ^13^C NMR (126 MHz, CDCl₃): δ = 172.7 (CPt = 926 Hz, C-Pt), 172.2 (CPt = 123 Hz, HC=N), 141.7 (CPt = 119 Hz, C), 126.4 (CPt = 27 Hz, CH), 122.5 (CH), 60.2 (CPt = 22 Hz, CH₃CHCH₃), 22.9 (CH₃CHCH₃).

**κC₂κN₂κN’-Bis-(N-tert-butyl)-isophthalaldimine-2-yl-platina(II) bromide (2c)**

Compound 2c was prepared analogous to 2b from 1c (0.51 g, 1.58 mmol) and Pt(dipdba)_2 (1.41 + 1.0 g = 2.41 g, 2.9 mmol) in 30 mL of THF at 60°C. After the filtration over Celite, the solvent was evaporated under reduced pressure and the residue was extensively washed with petroleum ether (boiling range 40-65°C) to remove the dipdba. The residue was dissolved in toluene and filtered over Celite, the product was precipitated from the concentrated filtrate by the addition of petroleum ether (boiling range 100-140°C). The product was collected by filtration and washed with pentane and air dried to yield 0.46 g (0.89 mmol, 56%) of a yellowish/brown powder which was identified by ^1^H, ^13^C and ^195^Pt NMR spectroscopy as pure 2c. ^1^H NMR (500 MHz, CDCl₃): δ = 8.27 (s, ^3^J_HH = 153 Hz, 2H; HC=N), 7.40 (d, ^3^J_HH = 7.8 Hz, 2H), 7.16 (t, ^3^J_HH = 7.8 Hz, 1H), 1.75 (s, 18H). ^13^C NMR...
Compound 2d was prepared, analogously to 2a, from 1d (0.45 g, 1.2 mmol) and Pt(dipdba)
(1.1 + 0.6 g = 1.75 g, 2.1 mmol) in 30 mL of THF at 60°C. After the filtration over Celite, the solvent
was evaporated under reduced pressure and the residue was washed with 400 mL of pentane. The residue
was extracted with hot toluene and filtered over Celite. The volatiles were removed under reduced
pressure and the residue was recrystallized from a THF/pentane mixture, dried in vacuo to yield 0.44
(0.77 mmol, 64%) of orange crystals which were identified by 1H, 13C and 195Pt NMR spectroscopy
as pure 2d. 1H NMR (500 MHz, CDCl3, 318K): δ = 8.31 (s, 3J_HPt = 148 Hz, 2H; HC=N), 7.40 (d, 3J_HH = 8.0 Hz, 2H), 7.10 (t, 3J_HH = 8.0 Hz, 1H), 4.37-4.32 (m, 2H), 2.26 (m, 4H), 1.85 (m, 4H), 1.72 (m, 2H), 1.60-1.45 (m, 8H), 1.29-1.18 (m, 2H). 13C NMR (126 MHz, CDCl3): δ = 173.0 (1J_CPt = 960 Hz, C-Pt), 172.3 (1J_CPt = 121 Hz, HC=N), 142.2 (1J_CPt = 120 Hz, C), 126.5 (1J_CPt = 73 Hz, CH), 122.6 (CH), 68.1 (1J_CPt = 18 Hz, C=C-N=C), 33.9 (1J_CPt = 9 Hz, 25.8 (CH2), 25.7 (CH2). 195Pt NMR (CDCl3): δ = -3648. HRMS(FAB): m/z calc'd ([M+H]+ C16H24N22Br195Pt): 570.1086. Found 570.1049.

Compound 2e was prepared, analogously to 2c, from 1e (0.5 g, 1.38 mmol) and Pt(dipdba)
(1.15 + 0.6 g = 1.75 g, 2.1 mmol) in 30 mL THF at 60°C. After the filtration over Celite, the solvent
was evaporated under reduced pressure and the residue was extensively washed with a petroleum ether
(bubbling range 40-65°C) diethyl ether mixture. The residue was dissolved in hot toluene and filtered
over Celite. The filtrate was concentrated under reduced pressure upon which the product
crystallized. This was collected by filtration, washed with pentane and air dried to yield 0.56 g (1.0
mmol, 73%) of dark red crystals which were identified by 1H, 13C and 195Pt NMR spectroscopy
as pure 2e. 1H NMR (500 MHz, CDCl3): δ = 8.35 (s, 3J_HPt = 140 Hz, 2H; HC=N), 7.38 (d, 3J_HH = 7.5 Hz, 4J_HH = 7.5 Hz, 2H), 7.49 (d, 3J_HH = 7.5 Hz, 4H), 7.42 (t, 3J_HH = 7.5 Hz, 4H), 7.33 (t, 3J_HH = 7.5 Hz, 2H), 7.27 (t, 3J_HH = 7.5 Hz, 1H). 13C NMR (126 MHz, CDCl3): δ = 177.6 (1J_CPt = 110 Hz, HC=N), 176.7 (1J_CPt = 929 Hz, C-Pt), 149.4 (1J_CPt = 16 Hz, C=N=C), 142.2 (1J_CPt = 111 Hz, C), 128.6 (CH), 124.6 (1J_CPt = 13 Hz, CH), 123.3 (CH). 195Pt NMR (CDCl3): δ = -3606. HRMS(FAB): m/z calc'd ([M+H]+ C20H28N22BrPt): 558.0147. Found 558.0121.

Compound 2f was prepared analogously to 2c from 1f (0.5 g, 1.28 mmol) and Pt(dipdba)
(1.1 + 1 g = 2.1 g, 2.5 mmol) in 30 mL of THF at 60°C. The yield was 0.47 g (0.8 mmol, 63%) of an orange/brown
powder which was identified by 1H, 13C and 195Pt NMR spectroscopy as pure 2f. 1H NMR (500 MHz, CDCl3): δ = 8.41 (s, 3J_HPt = 140 Hz, 2H; HC=N), 7.58 (d, 3J_HH = 7.5 Hz, 2H), 7.36 (d, 3J_HH = 8.0 Hz, 2H), 7.19 (t, 3J_HH = 7.5 Hz, 1H) 7.15 (d, 3J_HH = 8.0 Hz, 4H). 13C NMR (126 MHz, CDCl3): δ = 177.1 (1J_CPt = 110 Hz, HC=N), 176.1 (1J_CPt = 935 Hz, C-Pt), 147.1 (1J_CPt = 16 Hz, C-N=C), 142.2 (1J_CPt = 110 Hz, C), 138.4 (CCH2), 129.2 (CH), 128.3 (1J_CPt = 12 Hz, CH), 124.5 (CH) 123.1 (CH), 21.4 (CH3). 195Pt NMR (CDCl3): δ = -3611. HRMS(FAB): m/z calc'd ([M+H]+ C22H20N22BrPt): 586.0460. Found 586.0415.
Chapter 3

κC₅κN,κN'-Bis-(N-4-methoxyphenyl)-isophthalalidimine-2-yl-platina(II) bromide (2g)

Compound 2g was prepared analogous to 2e from 1g (1.0 g, 2.36 mmol) and Pt(dipdba)₂ (4.15 g, 5.0 mmol) in 40 mL THF at 50°C. The reddish-brown precipitate in toluene was collected on a G3 glass filter, washed with Et₂O and pentane and air dried to yield 0.94 g (1.5 mmol, 64%) of a reddish-brown solid which was identified by ₁H, ¹³C and ₁⁹⁵Pt NMR spectroscopy as pure 2g. M.p. 226-228°C. ¹H NMR (300 MHz, CDCl₃) δ = 7.65 (s, 3J_HH = 7.7 Hz, 2H), 7.21 (t, 3J_HH = 7.7 Hz, 1H), 7.45 (d, 3J_HH = 8.9 Hz, 4H), 6.89 (d, 3J_HH = 8.9 Hz, 4H), 3.81 (s, 6H; OCH₃). ¹³C NMR (126 MHz, CDCl₃) δ = 176.1 (2J_CPt = 113 Hz, C=N-C), 175.4 (C-Pt, 1J_CPt = 938 Hz), 159.4 (COCH₃), 142.6 (C=N-C), 141.9 (3J_CPt = 111 Hz, C), 127.7 (3J_CPt = 23 Hz, CH), 125.6 (CH) 122.8 (CH), 113.3 (CH), 55.4 (OCH₃). ₁⁹⁵Pt NMR (CDCl₃): δ = -3608. HRMS(FAB): m/z calc'd ([M-H-Br]+ C₂₂H₂₀N₂O₂Pt): 539.1175. Found 539.1166.

κC₅κN,κN'-Bis-(N-2,6-dimethylphenyl)-isophthalalidimine-2-yl-platina(II) bromide (2h)

Compound 2h was prepared analogous to 2a from 1h (1.0 g, 2.4 mmol) and Pt(dipdba)₂ (2.5 + 1.1 g = 3.6 g, 4.4 mmol) in 30 mL of THF at 60°C. When the reaction was complete (¹H NMR spectroscopy), the reaction mixture was cooled to room temperature upon which the product crystallized. The reaction mixture was filtered over Celite and the product was extracted from the residue with dichloromethane. The solvent was evaporated under reduced pressure and the product was dried in vacuo to yield 1.3 g (2.1 mmol, 88%) of a bright orange solid which was identified by ¹H, ¹³C and ₁⁹⁵Pt NMR spectroscopy as pure 2h. ¹H NMR (300 MHz, CDCl₃) δ = 7.64 (s, 3J_HH = 144 Hz, 2H; HCN), 7.71 (d, 3J_HH = 7.5 Hz, 2H), 7.32 (t, 3J_HH = 7.5 Hz, 1H), 7.10 (bs, 6H), 2.27 (s, 12H; CH₃). ¹³C NMR (126 MHz, CDCl₃) δ = 179.1 (2J_CPt = 106 Hz, C=N-C), 178.4 (C-Pt, 1J_CPt = 935 Hz), 148.1 (C=N-C), 142.1 (3J_CPt = 116 Hz, C), 131.3 (3J_CPt = 10 Hz, C), 128.1 (CH), 128.0 (CH), 127.5 (CH), 123.0 (CH), 18.5 (CH₂). ₁⁹⁵Pt NMR (CDCl₃): δ = -3562. Single crystals suitable for an X-ray structure determination were obtained by slow diffusion of pentane into a THF solution of 2h at -20°C. HRMS(FAB): m/z calc'd ([M+H]+ C₂₄H₂₄N₂BrPt): 614.0773. Found 614.0714.

κC₅κN,κN'-Bis-(N-3,5-dimethylphenyl)-isophthalalidimine-2-yl-platina(II) bromide (2i)

Compound 2i was prepared analogous to 2c from 1i (0.5 g, 1.2 mmol) and Pt(dipdba)₂ (1.2 + 1.5 g = 2.7 g, 4.3 mmol) in 30 mL of THF at 60°C. The yield was 0.3 g (0.5 mmol, 41%) of a orange solid which was identified by ¹H, ¹³C and ₁⁹⁵Pt NMR spectroscopy as pure 2i. ¹H NMR (500 MHz, CDCl₃) δ = 8.53 (s, 3J_HH = 139 Hz, 2H; H-CN), 7.66 (d, 3J_HH = 7.5 Hz, 2H), 7.28 (obscured by solvent), 7.11 (bs, 4H), 6.98 (bs, 2H), 2.37 (s, 12H; CH₃). ¹³C NMR (126 MHz, CDCl₃) δ = 171.7 (2J_CPt = 112 Hz, C=N-C), 171.2 (C-Pt), 144.2 (C), 137.1 (C), 133.1 (C), 125.1 (CH), 122.8 (CH), 117.9 (CH), 117.2 (CH), 16.3 (CH₂). ₁⁹⁵Pt NMR (CDCl₃): δ = -3599. HRMS(FAB): m/z calc'd ([M+H]+ C₂₄H₂₄N₂Br₂Pt): 614.0773. Found 614.0769.

κC₅κN,κN'-Bis-(N-3,5-di-(trifluoromethyl)-phenyl)-isophthalalidimine-2-yl-platina(II) bromide (2j)

Compound 2j was prepared, analogous to 2d, from 1j (0.5 g, 0.8 mmol) and Pt(dipdba)₂ (1.3 g + 0.9 g = 2.2 g, 2.7 mmol) in 30 mL of THF at 60°C. The yield was 0.2 g (0.3 mmol, 34%) of red
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crystals which were identified by $^1$H, $^{13}$C and $^{195}$Pt NMR spectroscopy as pure 2j. $^1$H NMR (500 MHz, CDCl$_3$) $\delta =$ 8.71 (s, $^3$J$_{HH}$ = 139 Hz, 2H; $HC$=N), 8.01 (bs, 4H), 7.88 (bs, 2H), 7.84 (d, $^3$J$_{HH}$ = 7.7 Hz, 2H), 7.39 (t, $^3$J$_{HH}$ = 7.7 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta =$ 179.7 ($^2$J$_{CP}$ = 112 Hz, C=N-C), 179.2 ($^1$J$_{CP}$ = 915 Hz, C-Pt), 149.6 ($^2$J$_{CP}$ = 17 Hz, C=N-C), 141.9 ($^2$J$_{CP}$ = 109 Hz), 132.4 (q, C-CF$_3$, $^2$J$_{CP}$ = 34 Hz), 130.4 ($^3$J$_{CP}$ = 20 Hz, CH), 125.4 (broad, CH) 124.0 (CH), 123.0 (q, CF$_3$, $^1$J$_{CP}$ = 273 Hz), 122.5 (broad, CH). $^{195}$Pt NMR (CDCl$_3$): $\delta =$ -3637. HRMS(FAB): $m/z$ calc $([M+H]^+ + C_{28}H_{12}N_2BrF_{12}Pt):$ 829.9642. Found 829.9641.

$\kappa C, \kappa N, \kappa N'$-Bis-(N-2,4,6-trimethylphenyl)-isophthalaldimine-2-yl-platina(II) bromide (2k)

Compound 2k was prepared, analogous to 2c, from 1k (0.5 g, 1.1 mmol) and Pt(dipba)$_2$ (1.2 g, 1.57 mmol) in 30 mL of THF at 60°C. The THF was evaporated under reduced pressure and the residue was thoroughly washed with petroleum ether (boiling range 40-65°C). The residue was extracted with hot toluene and filtered over Celite. When the toluene solution was concentrated under reduced pressure the product precipitated, which was collected on a P3 glass filter, washed with pentane and air dried to yield 0.56 g (0.87 mmol, 79%) of a bright orange solid which was identified by $^1$H, $^{13}$C and $^{195}$Pt NMR spectroscopy as pure 2k. $^1$H NMR (500 MHz, CDCl$_3$) $\delta =$ 8.33 (s, $^3$J$_{HH}$ = 144 Hz, 2H; $HC$=N), 7.68 (d, $^3$J$_{HH}$ = 7.5 Hz, 2H), 7.31 (t, $^3$J$_{HH}$ = 7.5 Hz, 1H) 6.93 (s, 4H), 2.33 (s, 6H), 2.26 (s, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta =$ 179.3 ($^2$J$_{CP}$ = 108 Hz, C=N-C), 178.3 ($^1$J$_{CP}$ = 942 Hz, C-Pt), 146.0 (C), 142.0 ($^2$J$_{CP}$ = 116 Hz), 136.9 (C), 131.0 (C), 128.8 (CH) 128.1 (CH, $^3$J$_{CP}$ = 26 Hz), 123.0 (CH), 21.3 (CH$_3$), 18.7 (CH$_3$). $^{195}$Pt NMR (CDCl$_3$): $\delta =$ -3557. HRMS(FAB): $m/z$ calc $([M+H]^+ + C_{26}H_{12}N_2BrPt):$ 642.1086. Found 642.1067.

$\kappa C, \kappa N, \kappa N'$-Bis-(N-2,6-diethylphenyl)-isophthalaldimine-2-yl-platina(II) bromide (2l)

Compound 2l was prepared, analogous to 2c, from 1l (0.5 g, 1.1 mmol) and Pt(dipba)$_2$ (1.0 g + 1.0 g = 2.0 g, 2.7 mmol) in 40 mL THF at 60°C. The THF was evaporated under reduced pressure and the greenish residue was washed with 250 mL of diethyl ether. The residue was dissolved in hot toluene and filtered over Celite. The filtrate was concentrated under reduced pressure and upon cooling the product crystallized and was isolated by filtration, washed with pentane and air dried to yield 0.50 g (0.75 mmol, 71%) of orange crystals which were identified by $^1$H, $^{13}$C and $^{195}$Pt NMR spectroscopy as pure 2j. $^1$H NMR (500 MHz, CDCl$_3$, 318K) $\delta =$ 8.39 (s, $^3$J$_{HH}$ = 144 Hz, 2H; $HC$=N), 7.74 (d, $^3$J$_{HH}$ = 7.5 Hz, 2H), 7.34 (t, $^3$J$_{HH}$ = 7.5 Hz, 1H), 7.23-7.15 (m, 6H), 2.77 (m, 4H; CH$_2$CH$_3$), 2.65 (m, 4H; CH$_2$CH$_3$) 1.25 (t, $^3$J$_{HH}$ = 7.8 Hz, 12H; CH$_2$CH$_3$). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta =$ 178.9 ($^2$J$_{CP}$ = 107 Hz, C=N-C), 178.7 ($^1$J$_{CP}$ = 932±2 Hz, C-Pt), 147.1 (C=N-C), 142.0 ($^2$J$_{CP}$ = 116 Hz, C), 137.0 (C), 128.1 (CH, $^3$J$_{CP}$ = 26 Hz), 127.9 (CH), 126.1 (CH), 123.0 (CH), 24.6 (CH$_2$CH$_3$), 14.5 (CH$_2$CH$_3$). $^{195}$Pt NMR (CDCl$_3$): $\delta =$ -3527. HRMS(FAB): $m/z$ calc $([M+H]^+ + C_{28}H_{32}N_2BrPt):$ 671.1384. Found 671.1389.

$\kappa C, \kappa N, \kappa N'$-Bis-(N-2,6-diisopropyl)-isophthalaldimine-2-yl-platina(II) bromide (2m)

Compound 2m was prepared analogous to 2c from 1m (1.0 g, 1.88 mmol) and Pt(dipba)$_2$ (2.34 g + 0.8 g = 3.14 g, 4.2 mmol) in 70 mL of THF at 50°C. The yield was 0.86 g (1.18 mmol, 63%) of bright orange needles which were identified by $^1$H, $^{13}$C and $^{195}$Pt NMR spectroscopy as pure 2m. M.p. >280°C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta =$ 8.38 (s, $^3$J$_{HH}$ = 144 Hz, 2H; $HC$=N), 7.77 (d, $^3$J$_{HH}$ = 8.0 Hz)
Hz, 2H), 7.35 (t, $^3J_{HH} = 8.0$ Hz, 1H), 7.26 (t, $^3J_{HH} = 7.6$ Hz, 2H), 7.21 (d, $^3J_{HH} = 7.6$ Hz, 4H), 3.19 (septet, $^3J_{HH} = 6.5$ Hz, 4H; CH$_2$CHCH$_3$), 1.30 (d, $^3J_{HH} = 6.5$ Hz, 12H; CH$_2$CHCH$_3$), 1.19 (d, $^3J_{HH} = 6.5$ Hz, 12H; CH$_3$CHCH$_3$). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta = 178.6$ ($^1J_{CP} = 927$ Hz, C-Pt), 178.3 ($^2J_{CP} = 108$ Hz, C=C-N), 145.6 (C=C-N), 142.0 ($^2J_{CP} = 114$ Hz, C), 141.7 (C), 128.3 (CH), 128.2 (CH), 128.0 (CH), 28.1 (CH) , 123.0 (CH$_2$CHCH$_3$), 24.6 (CH$_2$CHCH$_3$), 23.0 (CH$_3$CHCH$_3$). $^{195}$Pt NMR (CDCl$_3$): $\delta = -3517$. $^{15}$N NMR (30.4 MHz, CDCl$_3$; $\delta = -148$ ($^1J_{PN} = 477$ Hz). HRMS(FAB): $m/z$ calc ([(M+Br)$^+$ C$_{32}$H$_{38}$N$_2$Pt]: C, 52.89; H, 5.41; N, 3.86. Found: C, 53.08; H, 5.48; N, 3.91.

Methyl-κC,κN,κN',bis-(N-2,6-dimethylphenyl)-isophthalaldimine-2-yl-platina(II) (3h)

To a solution of 2h (159.1 mg, 0.259 mmol) in 20 mL of THF was added dimethylzinc (2 mL of a 2.0M solution in toluene, 4 mmol). In 10 min the orange reaction mixture turned red, and the reaction was very gently quenched with water. Most of the THF was evaporated under reduced pressure and the mixture was extracted three times with 30 mL of hexane. The organic layer was washed subsequently with water, a concentrated NaHCO$_3$ solution and dried on MgSO$_4$. After filtration the solvents were evaporated in vacuo. The residue was extracted with 200 mL of hexane. The hexane was removed under reduced pressure and the residue was washed twice with a small amount of pentane and dried in vacuo to yield 114 mg (0.21 mmol, 80%) of an orange/red solid which was identified by $^1$H, $^{13}$C and $^{195}$Pt NMR spectroscopy as pure 3h. The work-up has to be performed quickly, since otherwise an increasing amount of a decomposition product, which is insoluble in hexane, is formed. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta = 7.63$ (s, $^3J_{HH} = 125$ Hz, 2H; HC=C=N), 7.42 (d, $^3J_{HH} = 7.5$ Hz, 2H), 6.95 (t, $^3J_{HH} = 7.5$ Hz, 1H), 6.86 (br. s, 6H), 2.07 (s, 12H), 0.66 (s, $^3J_{HH} = 53$ Hz, Pt-CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) $\delta = 204.0$ ($^1J_{CP} = 591$ Hz, C-Pt), 180.6 ($^2J_{CP} = 52$ Hz, C=C-N), 149.2, 143.4 ($^2J_{CP} = 91$ Hz), 131.1, 129.3, 126.6, 126.5, 121.6, 18.4 (Ar-CH$_3$), 8.7 ($^1J_{CP} = 604$ Hz, Pt-CH$_3$). $^{195}$Pt NMR (C$_6$D$_6$): $\delta = -3096$. HRMS(FAB): $m/z$ calc ([(M-CH$_3$)$^+$ C$_{33}$H$_{43}$N$_2$Pt]: C, 52.89; H, 5.41; N, 3.86. Found: C, 53.08; H, 5.48; N, 3.91.

Methyl-κC,κN,κN'-bis-(N-2,6-diisopropylphenyl)-isophthalaldimine-2-yl-platina(II) (3m)

Compound 3m was prepared, analogous to 3h, from 2m (113 mg, 0.16 mmol) and dimethylzinc (2 mL of a 2.0M solution in toluene, 4 mmol). During the workup, pentane was used instead of hexane. The yield was 98 mg (0.15 mmol, 95%) of an orange/red solid which was identified by $^1$H, $^{13}$C and $^{195}$Pt NMR spectroscopy as pure 3m. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta = 8.14$, (s, $^3J_{HH} = 125$ Hz, 2H; HC=C=N), 7.42 (d, $^3J_{HH} = 7.5$ Hz, 2H), 7.07 (m, obscured by solvent), 6.92 (t, $^3J_{HH} = 7.5$ Hz, 1H), 3.31 (septet, $^3J_{HH} = 6.8$ Hz, 4H; CH$_2$CHCH$_3$), 1.28 (d, $^3J_{HH} = 7$ Hz, 12H; CH$_2$CHCH$_3$), 0.98 (d, $^3J_{HH} = 7$ Hz, 12H; CH$_3$CHCH$_3$), 0.67 (s, $^3J_{HH} = 53$ Hz, Pt-CH$_3$). $^{13}$C NMR (126 MHz, C$_6$D$_6$) $\delta = 204.6$ (C-Pt), 180.3 ($^2J_{CP} = 56$ Hz, C=C-N), 146.7 (C), 143.2 ($^2J_{CP} = 89$ Hz, C), 141.4 (C), 127.4 (CH), 126.6 (CH), 123.1 (CH), 121.7 (CH), 27.6 (CH$_2$CHCH$_3$), 24.2 (CH$_2$CHCH$_3$), 22.8 (CH$_3$CHCH$_3$), 10.2 ($^1J_{CP} = 623$ Hz, Pt-CH$_3$). $^{195}$Pt NMR (C$_6$D$_6$): $\delta = -3074$. HRMS(FAB): $m/z$ calc ([(M+H)$^+$ C$_{33}$H$_{43}$N$_2$Pt]: C, 52.89; H, 5.40; N, 4.23. Found: C, 60.09; H, 6.35; N, 4.17. Single crystals suitable for X-ray structure determination were obtained by cooling of a concentrated toluene solution.
Trans-σ-methyl-κC,κN-bis-(N-2,6-diisopropylphenyl)-isophthalaldimine-2-yl-pyridine-platina(II) (4m)

To a solution of 3m in C₆D₆ a large excess of pyridine-d₅ was added. Slowly, the formation of a new compound was observed, which was identified by ¹H and ¹⁵Pt NMR spectroscopy as 4m. ¹H NMR (300 MHz, C₆D₆) δ = 8.09 (1H), 8.90 (s, ®J_HH = 101 Hz, 1H; HC=N), 6.87 (m, 3H) 3.70 (septet, ®J_HH = 7 Hz, 2H), 2.82 (septet, ®J_HH = 7 Hz, 2H), 1.38 (d, ®J_HH = 7 Hz, 6H), 1.03 (d, ®J_HH = 7 Hz, 6H), 0.96 (d, ®J_HH = 7 Hz, 12H), 0.33 (s, ®J_HH = 52 Hz, 3H, Pt-CH₃). Some of the signals were obscured by signals of the starting material and the solvent. ¹⁵Pt NMR (C₆D₆): δ = -3216.

Cis-σ-methyl-κC,κN-bis-(N-2,6-diisopropylphenyl)-isophthalaldimine-2-yl-pyridine-platina(II) (5m)

While there was still some 3m present, the NMR tube containing 3m and 4m was heated to 80°C over night, during which all the 3m was converted to 4m, which was quantitatively converted to a compound which was identified by ¹H, ¹³C and ¹⁵Pt NMR spectroscopy as 5m. ¹H NMR (300 MHz, C₆D₆) δ = 9.25 (s, 1H; HC=N), 8.90 (d, ®J_HH = 7.5 Hz, 1H), 8.33 (s, ®J_HH = 52 Hz, 1H; HC=N), 7.25 - 7.15 (m, 3H), 6.83 - 6.70 (m, 3H), 3.45 (septet, ®J_HH = 7 Hz, 4H), 1.61 (s, ®J_HH = 80 Hz, 3H, Pt-CH₃), 1.23 (d, ®J_HH = 7 Hz, 12H), 0.88 (d, ®J_HH = 7 Hz, 6H), 0.87 (d, ®J_HH = 7 Hz, 6H). ¹³C NMR (126 MHz, C₆D₆) δ = 175.4 (®J_CPt = 72 Hz, C=N), 167.1 (C=N), 155.4 (C-Pt), 150.8, 145.4, 145.3, 141.3, 138.0, 132.3, 130.8, 126.5, 123.7, 123.2, 123.0, 122.9, 28.2, 27.1, 25.7, 23.6, 22.2, -13.6 (Pt-CH₃). ¹⁵Pt NMR (C₆D₆): δ = -3530.

Trans-σ-methyl-κC,κN-bis-(N-2,6-diisopropylphenyl)-isophthalaldimine-2-yl-carbonyl-platina(II) (6m)

Through an orange solution of 3m in C₆D₆ was bubbled carbon monoxide, within 30 seconds, the solution turned yellow. By ¹H and ¹⁵Pt NMR spectroscopy it was found that 3m was converted quantitatively to 6m. ¹H NMR (300 MHz, C₆D₆) δ = 8.86 (s, 1H; HC=N) 8.86 (1H), 7.79 (s, ®J_HH = 86 Hz, 1H; HC=N), 7.07-7.06 (m, 3H), 3.25 (septet, ®J_HH = 7 Hz, 2H), 3.01 (septet, ®J_HH = 7 Hz, 2H), 1.16 (d, ®J_HH = 7 Hz, 12H), 1.08 (d, ®J_HH = 7 Hz, 6H), 0.84 (d, ®J_HH = 7 Hz, 6H), 0.50 (s, ®J_HH = 44 Hz, 3H, Pt-CH₃). Some of the signals were obscured by signals of the solvent. ¹³C NMR (126 MHz, C₆D₆) δ = 209.1 (d, ®J_CC = 4 Hz, ®J_CPt = 902 Hz, C-Pt), 188.5 (CH=CO), 178.6 (C), 176.9 (d, ®J_CC = 4 Hz, C), 173.7 (®J_CPt = 1895 Hz, CO), 168.0 (CH=CO), 164.2 (C), 150.1 (C), 141.8 (C), 137.5 (C), 134.4 (CH), 132.2 (CH), 128.3 (CH), 125.7 (CH), 124.5 (CH), 123.6 (CH), 123.3 (CH), 28.5 (CH), 28.3 (CH), 24.5 (CH), 23.4 (CH), 22.5 (CH), 0.86 (Pt-CH₃). The ¹³CO shift and its ®J_CPt was only observed when ¹³C labeled CO was used. ¹⁵Pt NMR (C₆D₆): δ = -4000. IR: ν_C=O = 2058 cm⁻¹.

Cis-σ-methyl-κC,κN-bis-(N-2,6-diisopropylphenyl)-isophthalaldimine-2-yl-carbonyl-platina(II) (7m)

Irradiation of a solution of 6m in C₆D₆ by a Xe-lamp resulted in a clean photo isomerization to 7m. ¹H NMR (300 MHz, C₆D₆) δ = 8.97 (s, 1H; HC=CO) 8.80 (d, ®J_HH = 7 Hz, 1H), 7.92 (s, ®J_HH = 54 Hz, 1H; HC=CO), 7.18 - 6.93 (m, 3.34 - 3.20 (m, 4H), 1.50 (s, ®J_HH = 84 Hz, 3H, Pt-CH₃), 1.16 (d, ®J_HH = 7 Hz, 12H), 1.12 (d, ®J_HH = 7 Hz, 6H), 0.90 (d, ®J_HH = 7 Hz, 6H). Some of the signals were obscured by signals of the solvent. ¹⁵Pt NMR (C₆D₆): δ = -3902. IR: ν_C=O = 2064 cm⁻¹.
Table 3-4. Crystal data and details of the structure determination of 2h and 3m.

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<tr>
<td>Empirical formula</td>
<td>C_{24}H_{24}BrN_{2}Pt 0.4(C_{4}H_{8}O) + disordered solvent</td>
<td>C_{33}H_{42}N_{2}Pt</td>
</tr>
<tr>
<td>FW</td>
<td>643.29 $^a$</td>
<td>661.78</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.03 x 0.03 x 0.30</td>
<td>0.09 x 0.10 x 0.18</td>
</tr>
<tr>
<td>Crystal color</td>
<td>orange</td>
<td>red</td>
</tr>
<tr>
<td>Crystal system</td>
<td>trigonal</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>R3 (No. 148)</td>
<td>P2_1_2_1 (No. 19)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>26.2133(12)</td>
<td>11.2859(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>26.2133(12)</td>
<td>14.6377(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>21.3964(9)</td>
<td>17.7437(1)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
<td>120</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>12732.5(10)</td>
<td>2931.25(4)</td>
</tr>
<tr>
<td>Z</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td>D_{calc} (g/cm³)</td>
<td>1.510 $^a$</td>
<td>1.500</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>6.385 $^a$</td>
<td>4.810</td>
</tr>
<tr>
<td>sin (θ/λ)max (Å⁻¹)</td>
<td>0.50</td>
<td>0.65</td>
</tr>
<tr>
<td>abs. correction</td>
<td>SortAV$^{63}$</td>
<td>PLATON (ABST)$^{62}$</td>
</tr>
<tr>
<td>transm. range</td>
<td>0.69 - 0.80</td>
<td>0.42 - 0.72</td>
</tr>
<tr>
<td>refl. measd. / unique</td>
<td>26988 / 2961</td>
<td>34018 / 6705</td>
</tr>
<tr>
<td>obsd. refl. (I &gt; 2.0σ(I))</td>
<td>2075</td>
<td>6611</td>
</tr>
<tr>
<td>parameters</td>
<td>273</td>
<td>334</td>
</tr>
<tr>
<td>restraints</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>R₁ (obs. / all refl.)</td>
<td>0.0506 / 0.0774</td>
<td>0.0153, 0.0158</td>
</tr>
<tr>
<td>wR₂ (obs. / all refl.)</td>
<td>0.1405 / 0.1556 $^b$</td>
<td>0.0359 / 0.0361 $^c$</td>
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<tr>
<td>GoF</td>
<td>1.061</td>
<td>1.05</td>
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<tr>
<td>Flack parameter</td>
<td>-0.016(4)</td>
<td></td>
</tr>
<tr>
<td>res. density (e/Å³)</td>
<td>-0.47 &lt; 1.63</td>
<td>-0.67 &lt; 0.57</td>
</tr>
</tbody>
</table>

a. Derived values do not contain the contribution of the disordered solvent.
b. w = 1 / [σ²(F₀)² + (0.0977P)² + 33.318AP] where P = (F₀² + 2F₀P³)/3
c. w = 1 / [σ²(F₀)² + (0.0122P)² + 1.6552P] where P = (F₀² + 2F₀P³)/3

Spectroscopic measurements

Carbon monoxide was bubbled through a solution of 4m in pentane or methanol in the dark to yield a solution of 6m, this solution was used directly or the solvent was evaporated under reduced pressure and the residue was dried in vacuo to remove the excess carbon monoxide, after which the residue was re-dissolved. For 6m the absorption at 405 nm in toluene shifts to 390 nm in methanol.
TATA spectroscopy - Irradiation of the sample containing 6m was performed at $\lambda_{\text{exc}} = 310$ nm and $\lambda_{\text{exc}} = 435$ nm, in toluene, pentane and MeOH.

Crystal structure determinations

Data collection and cell refinement were carried out on a Nonius KappaCCD diffractometer with rotating anode, using graphite-monochromated Mo-K\(\alpha\) radiation ($\lambda = 0.71073$ Å) at a temperature of 150(2) K. The structures were solved by Patterson methods (DIRDIF-97\(^60\)) and refined with SHELXL-97\(^61\) against F\(^2\) of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups in structure 2h. In structure 3m the hydrogens H7 and H8 were refined freely with isotropic displacement parameters, the others as rigid groups. Structure 2h contains large voids with a volume of 1283.5 Å\(^3\)/unit cell. These voids are filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON,\(^62\) amounting to 168 electrons/unit cell. Details of the structure determinations are given in Table 3-4.

3.7 References

2) G.S. Hüll, R.J. Puddephatt Organometallics 1998, 17, 1478-86.
37) D.J. Cárdenas, A.M. Echavarren, M.C. Ramirez de Arellano Organometallics 1999, 18, 3337-41. This compound was prepared via cycloplatination of the parent ligand by potassium tetrachloro platinate in acetic acid.


G.W.V. Cave, P.F. Fanizzi, R.J. Deeth, W. Errington, J.P. Rourke, Organometallics 2000, 19, 1355-64.


