Nucleophilic and electrophilic platinum compounds for C-H bond activation

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Chapter 5
Platinum(II) (NN) and Platinum(II) (NNO) Complexes for C-H Activation

5.1 Introduction

In 1969 Shilov and co-workers demonstrated that Pt(II) salts are capable of activating alkane C-H bonds.\[^{[1]}\] Some years later, they also reported that catalytic conversion of alkanes (including methane) to mixtures of the corresponding chlorides and alcohols could be achieved by employing aqueous solutions of Pt(II) and Pt(IV) salts.\[^{[2,3]}\]

\[
\begin{align*}
R-\text{H} + \text{Pt}^{\text{IV}} + \text{HX} & \xrightleftharpoons[120 \degree C]{\text{Pt}^{\text{II}} \text{(cat.)}} R-\text{X} + \text{Pt}^{\text{II}} + 2\text{H}^+ \\
X &= \text{OH, Cl}
\end{align*}
\]

Scheme 5.1 Functionalization of alkanes catalyzed by Pt(II)

The Shilov system is clearly unprecedented in many aspects. Firstly, the reaction is performed in aqueous solution and is unaffected by the presence of molecular oxygen. Secondly, the reaction exhibits an unusual chemoselectivity; alkane C-H bonds are activated at equal or even faster rate than the C-H bonds of the produced alcohols or alkyl chlorides. Thirdly, the order of regioselectivity (primary C-H > secondary C-H > tertiary C-H) is the reverse of what is normally found for electrophilic and radical oxidations of hydrocarbons. However, use of expensive Pt(IV) as stoichiometric oxidant, poor turnover numbers and sometimes unsatisfactory selectivity, causes that the Shilov system is not suitable for practical applications.

After the initial report of Shilov, he and other scientists have aimed at understanding this selective conversion of alkanes into alcohols.\[^{[3-17]}\] The C-H activation appears to determine both the rate and selectivity of the alkane oxidation and this subsequently provided significant motivation to understand the details of its mechanism. Unfortunately, the C-H activation step has proven to be the most difficult to study. Currently it is clear that the reaction involves electrophilic displacement of a proton of the alkane by Pt(II).

In 1999 Tilset et al. reported that benzene and also methane C-H bond activation occurs at the aqua complex Pt(CH\text{3})(N^\text{1}\text{-N}^\text{1})(H\text{2}O)^+\text{BF}_4^- (A, N^\text{1}\text{-N}^\text{1} = \text{ArN=CMe-CMe=NAr, Ar} = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3))
under unusually mild conditions (benzene at 25 °C; methane at 45 °C, see Scheme 5.2) in the poorly coordinating solvent 2,2,2-trifluoroethanol (TFE).\[18\]

Scheme 5.2 Hydrocarbon activation at a cationic platinum(II) diimine aqua complex

These C-H activation reactions of benzene and methane appear to occur under the mildest reaction conditions yet reported for such processes at cationic platinum complexes. Since the above described complex A is very reactive towards almost every C-X bond, and because special precautions are required (low temperatures, exclusion of oxygen, special non-reactive solvents), we investigated cationic platinum complexes stabilized in a tridentate fashion by a 2-pyridinecarbaldimine based NNO-ligand.

The idea for the design of these complexes is that these complexes are expected to be more easy to handle than their didentate counterparts, the NN platinum complexes described by Bercaw\[12\] and Tilset,\[18\] but that these tridentate NNO platinum complexes retain the reactivity towards C-H bonds of hydrocarbons described for these didentate NN platinum complexes. So, we set out to investigate the effect of coordination of the oxygen towards the cationic platinum center on the stability of the starting complex and its reactivity towards C-H bonds of hydrocarbons. The NNO ligands could potentially coordinate in a tridentate fashion in such a way that reactivity and stability go together, *i.e.* the ligand provides stabilization in a tridentate mode and enough reactivity in a didentate mode (see Scheme 5.3).

Scheme 5.3 Tridentate NNO ligands with hemi-labile oxygen ligand

For that reason, we designed tridentate 2-pyridinecarbaldimine-based NNO-ligands. The accessibility of NNO ligands is very straightforward; synthesis of such ligands can be done in one
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step from readily available materials. Surprisingly, just a few platinum(NNO)-complexes, or any NNO-complexes with $^{10}\text{d}$-metals for that matter, are known.$^{[19-21]}$

\[
\text{Scheme 5.4 Synthesis of } [\text{Pt(NNO)(Me)}][X]-\text{complexes}
\]

The route towards these platinum(NNO)-complexes is proposed by reaction of tetramethylbis[$\mu$-(dimethylsulfide)]-diplatinum(II) with the NNO-ligand to give a Pt(Me)$_2$(NNO) complex in which only the two nitrogens are coordinated to the platinum center (see Scheme 5.4). Treatment with acids can drive off methane to give cationic [Pt(Me)(NNO)]$^+$ complexes, with coordination of the oxygen.

5.2 Results and Discussion

5.2.1 (NNO)-Ligand Synthesis

The potentially tridentate 2-pyridinecarboxaldimine-based NNO-ligands 3 were prepared by a condensation-reaction of a 2-pyridinecarboxaldehyde with an appropriate amine or aniline (see Scheme 5.5) in reasonable to excellent yields.

The starting compounds 1a,b and 2w-z are commercially available, but the aldehydes 1c-f are not. So, we synthesized PyCa-based NNO-ligands 3cz, 3dz and 3ez from the corresponding aldehydes 1c, 1d and 1e. The synthesis of 6-[(triphenylmethoxy)methyl]-pyridine-2-carboxaldehyde (1c) is known,$^{[22]}$ 2,6-bis(hydroxymethyl)pyridine is reacted with trityl chloride in a mixture of pyridine and a catalytic amount of dimethylaminopyridine (DMAP), to give in moderate isolated yield 2,6-bis(hydroxymethyl)pyridine monotrityl ether (1c'). Attempted conversion of this compound with MnO$_2$ in dichloromethane at room temperature into aldehyde 1c, as described in the patent by Stahl et al.,$^{[22]}$ was not successful, only starting materials were obtained.
Instead, oxidation by SeO$_2$ was attempted, since it is known that methyl-groups of 2-methylpyridine can be selectively oxidized to their corresponding pyridine-2-aldehydes.\textsuperscript{[23]} Treatment of 2,6-bis(hydroxymethyl)pyridine monotrityl ether (1c') with SeO$_2$ in hexanes (instead of 1,4-dioxane)\textsuperscript{[23]} in presence of 3Å molsieves gives overnight at reflux temperature aldehyde 1c in excellent yield (99%). Reaction of 1c with isopropylamine (2c) gave 3cz in quantitative yield.

\[
\begin{array}{ccc}
\text{1} & \text{2} & \text{H}_2\text{O} \\
\text{R}^1 & \text{R}^2-\text{NH}_2 & \text{N-R}^2 \\
\hline
\text{CH}_3 & \alpha\text{-phenol} & \text{3aw} \\
\text{H} & \alpha\text{-phenol} & \text{3bw} \\
\text{H} & \text{C}_2\text{H}_5\text{OCH}_3 & \text{3bx} \\
\text{H} & (4\text{-methyl})\text{-phen-2-ol} & \text{3by} \\
\text{CH}_2\text{OC(Ph)}_3 & \|\text{-propyl} & \text{3cz} \\
\text{CH}_2\text{OCH}_2\text{OCH}_3 & \|\text{-propyl} & \text{3dz} \\
\text{CH}_2\text{OCH}_3 & \|\text{-propyl} & \text{3ez} \\
\text{CH}_2\text{OH} & \|\text{-propyl} & \text{3fz} \\
\end{array}
\]

\textbf{Scheme 5.5 PyCa based NNO ligands}

The synthesis of 6-methoxymethoxymethyl-pyridine-2-carbaldehyde (1d) is also straightforward by reaction of 2,6-pyridinedimethanol with 1 eq. of chloromethyl methyl ether in a mixture of diisopropylethylamine and THF at 0 °C in analogy to the literature,\textsuperscript{[24]} but dichloromethane was replaced by THF. Subsequently, the alcohol 1d' was converted into aldehyde by treatment with SeO$_2$ to give 1d.

Attempts to synthesize 1f, in order to introduce a hydroxymethyl-group by removing the protecting groups of 1c (trityl-group) or of 1d (MOM-group), failed. Treatment of 1c with acetic acid,\textsuperscript{[25]} $p$-toluen sulfonic acid in MeOH,\textsuperscript{[26]} ZnBr$_2$\textsuperscript{[27]} or formic acid in diethyl ether\textsuperscript{[28]} to remove the trityl group, did not result in formation of 1f. Removal of the MOM-group in 1d by acidic procedures (boiling acetic acid/sulfuric acid,\textsuperscript{[29]} THF/water/6M HCl-mixture, concentrated HCl in MeOH\textsuperscript{[30]} ) a mild acidic method (in situ generation of HBr via CBr$_4$ in iPrOH)\textsuperscript{[31]} and an alternative procedure (LiBF$_4$, H$_2$O, CH$_3$CN, 70 °C),\textsuperscript{[24]} did not result in formation of 1f either. This failure is due to the reactivity of the aldehydes 1c or 1d towards the deprotecting agents and other reagents were just not able to remove the protecting groups.
The synthesis of 6-(methoxymethyl)-pyridine-2-carbaldehyde (1e) looks straightforward and consist of deprotonation of 2,6-pyridinedimethanol by one alcohol-group and successive treatment with methyl iodide, producing 2,6-pyridinedimethanol monomethyl ether (1e'). However, this preparation was problematic and mainly bis-methylation was observed. So, the yield of the desired mono-methylated product dropped to 4% (literature: 88%)\[32\], although more solvent was used and the methyl iodide was added dropwise as described.\[32\] Oxidation of the 2,6-pyridinedimethanol monomethyl ether (1e') by SeO$_2$ in hexanes at reflux temperature resulted in quantitative formation of 1e.

5.2.2 PtMe$_2$(NNO) complexes with didentate N,N'-coordinated NNO ligands

For the synthesis of the Pt(Me)$_2$(κ²N,N'-NNO)-complexes, a straightforward approach was used. Addition of the NNO-ligand to ½ equivalent of tetramethylbis[μ-(dimethylsulfide)]-diplatinum(III) in THF or diethylether gives the corresponding Pt(Me)$_2$(κ²N,N'-NNO)-complex 4 in good to excellent isolated yield\[18\] (see Scheme 5.7).
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\[
\begin{align*}
\text{Scheme 5.7 Synthesized } & N,N'-(NNO)Pt(Me)_2\text{-complexes} \\
\begin{array}{cccc}
\text{Compound} & \mathbf{R^1} & \mathbf{R^2} & \text{Yield} \\
4aw & \text{CH}_3 & \text{o-phenol} & 71\% \\
4bw & \text{H} & \text{o-phenol} & 85\% \\
4bx & \text{H} & \text{C}_2\text{H}_4\text{OCH}_3 & 98\% \\
4by & \text{H} & (4\text{-methyl})\text{-phen-2-ol} & 91\% \\
4cz & \text{CH}_2\text{OC}(\text{C}_6\text{H}_5)_3 & \text{i-propyl} & 85\% \\
4dz & \text{CH}_2\text{OCH}_2\text{OCH}_3 & \text{i-propyl} & 94\% \\
4ez & \text{CH}_2\text{OCH}_3 & \text{i-propyl} & 70\% \\
\end{array}
\end{align*}
\]

All compounds 4 are stable as powders for weeks at room temperature. For longer periods, storage at -20 °C is required. Complexes 4aw, 4bw and 4by are not stable in solution at room temperature. While measuring \(^{13}\text{C}\) NMR spectra these complexes slowly degraded to new single compounds, which will be described in the next part.

5.2.3 Platinum(methyl) complexes with tridentate NNO-ligands

As a general method for creation of a cationic [Pt(Me)(κ^3N,N’O-NNO)]BF₄-complex we added HBF₄ to Pt(Me)₂(κ^3N,N’-NNO)-complex, similar to what has been described for [Pt(Me)(NN)]BF₄-complexes.\(^{[18]}\)

\[
\begin{align*}
\text{Scheme 5.8 Didentate coordination of the NNO ligand} \\
\begin{array}{l}
\text{4bx} \quad \text{HBF}_4, \text{-CH}_4, \text{OEt}_2 \rightarrow \text{5bx} \\
\text{4bx} \quad \text{(CD}_3)_2\text{CO, OEt}_2 \rightarrow \text{5bx} \\
\end{array}
\end{align*}
\]

As a first approach, we used 3bx as potential tridentate coordinating NNO-ligand in the platinum complex 4bx. When we treated 4bx with 1 equivalent of HBF₄ in diethyl ether at low temperature (-60 °C), we observed the formation in good yield (89%) of the platinum(methyl)(NNO) species 5bx. According to \(^1\text{H}\) NMR spectroscopy, the ether-oxygen is
coordinating to the cationic platinum center (see Scheme 5.8). We first thought that the NNO ligand was coordinating in a tridentate fashion, but comparison of the integrals of the relevant signals in the $^1$H NMR spectrum showed that diethyl ether was coordinating to the cationic platinum center and that one Pt-CH$_3$ group was missing. Most likely, the methyl-group trans to the imine had reacted to give methane, hence coordination of the oxygen of the NNO-ligand was not possible.

For the assessment of the exact geometry of the metal complex, we used the i-propylpyridinecarbaldimine (iPrPyCa, 3bz) as the ligand, which enabled to determine which methyl is consumed in the selective elimination of methane.

![Scheme 5.9 Thermodynamic product trans towards imine in (PyCa)Pt$^+$ (Me) complexes](image)

In order to capture the product of the reaction at room temperature, we added the strong acid HBF$_4$ in a strongly coordinating medium (acetonitrile). The complex [Pt(Me)(NN)]$^+\text{BF}_4^-$ was formed after elimination of methane, which directly reacts with acetonitrile to form [Pt(Me)(NN)(CH$_3$CN)]$^+\text{BF}_4^-$ (6bz). When we react (iPrPyCa)Pt(Me)$_2$ (4bz) with HBF$_4$ (54% solution in diethyl ether) in acetonitrile, we observed the formation of complex 6bz with 100% selectivity, its geometry was proved by $^1$H NMR NOE experiments. In this case, the thermodynamic product consists of a cationic platinum complex 6bz which is stabilized by acetonitrile trans to the imine group (see Scheme 5.9). However, we cannot exclude that the initial kinetic product is the cis-product (elimination of methyl group cis to the imine), which rearranges to the thermodynamic trans-product.[33] This possibility was underscored by showing that internal protonation by the mildly acidic phenol-based NNO-ligands 3aw, 3bw and 3by led to trapping of the kinetic product.

![Scheme 5.10 Reductive elimination of methane to give a neutral (NNO)Pt(Me) complex](image)

When the dimethylplatinum(NNO) complexes 4aw, 4bw or 4by are heated in benzene overnight, green solutions result. Analysis of the product revealed that methane has reductively
eliminated and the phenoxy-oxygen is coordinating (see Scheme 5.10). After cooling to room temperature a dark green compound was isolated as the main product according to $^1$H NMR spectroscopy. The thermally stable green compounds 5aw, 5bw and 5by are barely soluble in most organic solvents. Addition of a drop of 2,2,2-trifluoroethanol did improve the solubility of 5aw and 5by sufficiently to obtain $^1$H and $^{195}$Pt NMR spectral data.

![Scheme 5.11 Attempt to methylate 5by](image)

Because of the strong coordination of the phenolic oxygen, no other reactivity was observed. In order to restore the hemi-lability of this oxygen functionality, we tried to methylate the oxygen of 5by in such a way that we obtain a reactive cationic platinum complex, with a coordinated methoxy group. By doing so, we should prevent the rearrangement of the methyl-group *trans* to the imine group to the *cis*-position. A methylation was effected by addition of [Me$_3$O][BF$_4$] in nitromethane to 5by at low temperature (see Scheme 5.11). A color change from green to red was observed, indicating that a (dimethyl)platinum(NN) complex had been formed, and not a cationic platinum complex. However, attempts to characterize this rather reactive compound failed and $^1$H NMR spectroscopy showed several undefined species.

To achieve the formation of a Pt(methyl)(NNO) compound that is easy to handle, yet reactive towards C-H bonds of hydrocarbons, we reasoned that introduction of hemilabile oxygen-containing arms at the other side (at the 6-position of the pyridine) of the PyCa-ligand was needed. For that reason 3cz, 3dz and 3ez and their corresponding dimethylplatinum complexes 4cz, 4dz and 4ez were synthesized.

![Scheme 5.12 Cationic platinum complexes stabilized with a tridentate NNO-ligand](image)
So, when we treated 4dz (red solution) with HBF₄ in diethyl ether at -60 °C, immediately a yellow compound (5dz) precipitated from solution. This compound was filtered off to give a yellow compound that is very reactive towards oxygen. Compound 5dz has been characterized by ¹H and ¹⁹⁵Pt NMR spectroscopy. In the ¹H NMR spectrum, the signal of the imine proton is found at 8.90 with a large ³J_HPt of 116 Hz, suggesting the presence of a weak ligand trans to the imine. A broad singlet is found at 6.93 ppm, indicative of coordinated H₂O.⁸

![Figure 5.1](image)

Figure 5.1 Coordination of oxygen of NNO-ligand of 5dz and oxygen of H₂O visible via ¹H,¹⁹⁵Pt HMQC-spectroscopy (CD₂Cl₂, -20 °C).

¹H,¹⁹⁵Pt HMQC-spectroscopy (see Figure 5.1) gave more information about the structure of 5dz. Correlation peaks are found at δ_H = 8.90 ppm (a), 6.93 ppm (b), 4.78 ppm (c), 4.45 ppm (d), 3.91 ppm (e), 1.19 (f) at δ_Pt = -3072. From these correlations, the conclusion can be drawn that despite coordination of H₂O (b, 6.93 ppm) also the oxygen (CH₂OCH₂OCH₃) of the NNO ligand is coordinating, as appears from correlation peaks at 4.78 ppm (c, ³J_HPt = 25.2 Hz), and 3.91 ppm (e, ³J_HPt = 22.2 Hz). The large ³J_HPt couplings point to ³J_HPt couplings. The CH₂-group c only has correlation if the oxygen is coordinated, in principle CH₂-atom e could have a ⁴J_HPt via the

⁸ ¹³C-¹H correlation spectroscopy showed no correlation peak at δ_H = 6.93 ppm. Johansson et al. found in a cationic aqua platinum(II)-complex the signal of coordinated H₂O also in this region.¹⁸
coordinated pyridine nitrogen, but this should then be in the range of 0-5 Hz due to strong trans-influence of the methyl group. This implies that the cationic platinum center is stabilized by at least two oxygen-atoms (CH$_2$OCH$_2$OCH$_3$ and H$_2$O). Furthermore the $^{195}$Pt chemical shift of -3072 ppm for 5dz confirms the oxygen-coordination compared to the C-coordination in (NN)Pt(Me)$_2$-complex 4dz that was observed at -3427 ppm. This straightforward differentiation of different donor-atoms by means of the $^{195}$Pt-chemical shift is known.$^{[34]}$

One of the goals was to use these cationic (NNO) platinum(II) complexes for the activation of C-H bonds of hydrocarbons. In order to investigate the propensity of 5dz to activate C-H bonds, we dissolved, following a previously employed method,$^{[18]}$ 5dz in 2,2,2-trifluoroethanol (TFE) and added benzene to the mixture. The reaction mixture was subsequently stirred at room temperature for 5 days and then quenched with acetonitrile.

The $^1$H NMR data, after removing the volatiles, showed minor signals at 7.14 and 7.66 ppm indicating the presence of a benzene derivate, possibly a phenyl-platinum complex.$^{[18,35]}$ However, the majority of the peaks in the spectrum is due to various other platinum-containing products, because several peaks with platinum satellites were visible. Most parts of the spectrum are the same as the spectrum taken when the Pt-complex was dissolved in an inert$^{**}$ solvent (TFE, blank reaction). This indicates that intramolecular C-H activation of the ligand has occurred, but identification of these compounds was not possible.

5.3 Conclusions

The obtained neutral Pt$^{II}$(Me)(NNO) and cationic [Pt$^{II}$(Me)(NNO)]$^{+}$BF$_4$ complexes are not suitable for performing C-H bond activation reactions of hydrocarbons, as the neutral Pt$^{II}$(Me)(NNO) complexes are too stable to display any reactivity, whereas the catonic [Pt$^{II}$(Me)(NNO)]$^{+}$BF$_4$ complexes are too reactive, so that activation reactions do not exhibit any selectivity towards specific C-H bonds. Nevertheless, these neutral and cationic platinum complexes are very interesting compounds and can be compared to other tridentate ligand systems$^{[20,36]}$ in the field of their coordination and organometalloid chemistry.

$^{**}$ The inert solvent TFE (2,2,2-trifluoroethanol) has no reactive C-H bonds. Therefore, this solvent is very suitable as solvent for studying C-H bond activation reactions by metal complexes.$^{[18]}$
5.4 Experimental Section

5.4.1 General

All reactions were carried out under nitrogen atmosphere in dry solvents. Diethyl ether, tetrahydrofuran (THF), benzene and hexanes were distilled from sodium metal/benzophenone, dichloromethane and dichloromethane-d$_2$ were distilled from CaH$_2$. Acetone-d$_6$ was distilled from B$_2$O$_3$ and 2,2,2-trifluoroethanol (TFE) was distilled from CaSO$_4$. Chemicals were purchased from Acros Chimica, Aldrich and Fluka. 2-pyridinecarboxaldehyde and 2-methoxyethylamine were distilled before use. 2-[(2-pyridinylmethylene)amino]-ethanol,$^{[37]}$ 6-(methyloxymethyl)-2(hydroxymethyl)-pyridine,$^{[32]}$ $\text{PtCl}_2\text{(SMe}_2\text{)}_2,$$^{[38]}$ and tetramethylbis[µ-(dimethylsulfide)]-diplatinum(II)$^{[38]}$ were synthesized via published methods. The $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded at appropriate frequencies on Varian Mercury 300 ($^1$H: 300.13 MHz, $^{13}$C: 75.47 MHz) and Inova 500 ($^1$H: 499.88 MHz, $^{13}$C: 125.70 MHz) spectrometers. $^{195}$Pt NMR spectra were measured by $^1$H,$^{195}$Pt HMBC spectroscopy$^{[39]}$ at 298K on a Bruker DRX300 spectrometer ($^{195}$Pt: 64.13 MHz).

5.4.2 Synthesis

2-[(6-methyl-2-pyridinyl)methylene]amino]-phenol (3aw)

An amount of 4.03 g (33.3 mmol) 6-methylpyridine-2-aldehyde and 3.63 g (33.3 mmol) 2-aminophenol were dissolved in 50 ml ethanol. 3Å molsieves were added to the solution and the mixture was stirred overnight. The mixture was then filtered over Celite filter aid and the filter was washed furthermore with 10 ml ethanol. The filtrate was reduced in volume to 10 ml and 50 ml hexane was added. The precipitate was collected on a glass filter and dried further in vacuo to yield 3.62 g (53%) of a yellow powder. $^1$H NMR (300.13 MHz, CD$_2$Cl$_2$, δ(ppm)): 8.79 (s, 1H, N=CH), 8.00 (d, $^3$J$_{HH}$ = 7.8 Hz, 1H, pyH), 7.71 (t, $^3$J$_{HH}$ = 7.5 Hz, 1H, pyH), 7.51 (br s, 1H, OH), 7.41 (dd, $^3$J$_{HH}$ = 7.8 Hz, $^4$J$_{HH}$ = 1.5 Hz ,1H, ArH), 7.24 (m, 2H, ArH), 7.01 (dd, $^3$J$_{HH}$ = 8.1 Hz, $^4$J$_{HH}$ = 1.5 Hz ,1H, ArH), 6.94 (dt, $^3$J$_{HH}$ = 7.8 Hz, $^4$J$_{HH}$ = 1.2 Hz, 1H, ArH), 2.60 (s, 3H, CH$_3$). $^{13}$C NMR (75.47 MHz, acetone-d$_6$, δ (ppm)): 159.0, 158.7, 154.6, 153.2, 138.3, 137.8, 137.2, 136.2, 129.5, 125.0, 120.3, 119.1, 117.6, 116.1, 23.8.

2-[(2-pyridinylmethylene)amino]-phenol (3bw)

An amount of 3.49 g (32.6 mmol) 2-pyridinecarboxaldehyde and 3.56 g (32.6 mmol) 2-aminophenol were dissolved in 50 ml methanol. 3Å molsieves were added to the solution and the
mixture was stirred overnight. The solids were filtered off and were extracted twice with 150 ml methanol. The volatiles of the combined filtrates were removed by rotary evaporation yielding 7.0 g of a brown oil. This oil was dissolved in 15 ml methanol, and 200 ml ether was added to precipitate the product. The yellow solid was filtered off on a glass filter and was washed with ether (3x 20 ml). The solid was dried further in vacuo to yield 2.48 g (38%) of a yellow powder. 

1H NMR (300.13 MHz, CD2Cl2, δ(ppm)): 8.85 (s, 1H, N=CH), 8.71 (m, 1H, pyH), 8.23 (d, JHH = 8.1 Hz, 1H, pyH), 7.85 (dt, JHH = 7.8 Hz, JHH = 1.5 Hz, 1H, pyH), 7.43 (dt, JHH = 7.5 Hz, JHH = 1.2 Hz, 1H, ArH), 7.40 (dd, JHH = 7.5 Hz, JHH = 1.2 Hz, 1H, ArH), 7.38 (br s, 1H, OH), 7.25 (dt, JHH = 7.8 Hz, JHH = 1.5 Hz, 1H, ArH), 7.01 (dd, JHH = 8.4 Hz, JHH = 1.5 Hz, 1H, ArH), 6.95 (dt, JHH = 7.7 Hz, JHH = 1.2 Hz, 1H, ArH).

13C NMR (75.47 MHz, aceton-d6, δ (ppm)): 158.7, 155.2, 153.2, 150.0, 137.0, 136.2, 129.6, 125.7, 122.0, 120.3, 117.7, 116.2.

1-methoxy-2-[(2-pyridinylmethylene)amino]-ethane (3bx)

To 5 ml (53 mmol) of 2-pyridinecarboxaldehyde and 10 ml (115 mmol) 2-methoxyethylamine, 3Å molsieves were added in a round-bottomed flask at room temperature. After stirring this mixture for 30 minutes, the molsieves were filtered off and the molsieves were washed with hexane. The volatiles of the filtrate were removed in vacuo to yield a yellow oil (8.5 g, 98%). 

1H NMR (300.13 MHz, CDCl3, δ(ppm)): 8.30 (d, 1H, pyH), 8.09 (s, 1H, imH), 7.67 (d, JHH = 7.5 Hz, 1H, pyH), 7.37 (t, JHH = 7.5 Hz, 1H, pyH), 6.94 ("t", JHH = 4.8 Hz, 1H, pyH), 3.52 (t, JHH = 5.4 Hz, NCH2), 3.38, t, JHH = 5.4 Hz, 1H, OCH2), 7.03 (s, 3H, CH3).

13C NMR (75.47 MHz, CDCl3, δ (ppm)): 163.3, 154.4, 149.3, 124.7, 121.3, 71.8, 60.8, 58.7.

4-methyl-2-[(2-pyridinylmethylene)amino]-phenol (3by)

An amount of 2.56 g (20.8 mmol) 2-amino-p-cresol and 2.31 g (21.6 mmol) 2-pyridinecarboxaldehyde and 3Å molsieves were suspended in 50 ml toluene. This mixture was stirred for 1.5 hours at 100 °C. The molsieves were filtered off and washed with 20 ml toluene. The volatiles of the filtrate were removed by rotary evaporation to yield 5.10 g of a red-brown oil. The oil was crystallized from THF/hexane to yield 1.38 g (39%) yellow needles. 

1H NMR (300.13 MHz, CDCl3, δ(ppm)): 8.81 (s, 1H, imH), 8.72 (d, JHH = 4.8 Hz, 1H, pyH), 8.19 (d, JHH = 7.8 Hz, 1H, pyH), 7.82 (dt, JHH = 7.5 Hz, JHH = 1.2 Hz, 1H, pyH), 7.37 (ddd, JHH = 7.2 Hz, JHH = 4.5 Hz, JHH = 0.9 Hz, 1H, pyH), 7.20 (br s, 1H, ArH), 7.05, dd, JHH = 8.4 Hz, JHH = 1.2 Hz, 1H, ArH),
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6.92 (d, $^3J_{HH} = 8.4$ Hz, 1H, ArH), 2.32 (s, 3H, CH$_3$). $^{13}$C NMR (75.47 MHz, CDCl$_3$, δ (ppm)): 156.9, 154.5, 150.8, 149.9, 136.9, 134.7, 130.7, 129.7, 125.4, 122.0, 117.1, 115.5, 21.0.

2,6-di(hydroxymethyl)pyridine monotrityl ether (1c")

An amount of 2.44 g (17.5 mmol) 2,6-pyridinedimethanol and 0.03 g 4-dimethylaminopyridine (DMAP) were dissolved in 20 ml pyridine. Then 4.89 g (17.5 mmol) trityl chloride was added and the solution was stirred for 1 hour at room temperature. The solution was stirred for another hour at 60 °C. The volatiles were removed by rotary evaporation yielding a yellow oil. The oil was partly dissolved in 50 ml methanol. The mixture was filtrated over 1 cm layer of Celite and the volatiles of the filtrate were removed by rotary evaporation. The remaining oil was dissolved in dichloromethane and brought into a separatory funnel. The organic layer was washed with 10 ml of a saturated solution of K$_2$CO$_3$ in water. The water layer was extracted once with 20 ml dichloromethane and the combined organic layers were dried on MgSO$_4$. The volatiles were removed by rotary evaporation yielding a yellow oil (4.76 g, 71%). The raw product was purified by column chromatography (SiO$_2$, gradient elution with dichloromethane (100% to 80% and ethyl acetate 0 to 20%, $R_f = 0.29$ with eluents dichloromethane). For removal of the last traces of pyridine and ethyl acetate, 200 ml hexane was added to the oil. The volatiles were removed by rotary evaporation yielding 2.83 g (42%) of a white solid. $^1$H NMR (300.13 MHz, CD$_2$Cl$_2$, δ(ppm)): 7.74 (t, $^3J_{HH} = 7.8$ Hz, 1H, pyH), 7.62 (d, $^3J_{HH} = 7.8$ Hz, 1H, pyH), 7.50 (m, 6H, ArH), 7.29 (m, 9H, ArH), 7.10 (d, $^3J_{HH} = 7.5$ Hz, 1H, pyH), 4.62 (d, $^3J_{HH} = 4.5$ Hz, 2H, CH$_2$OH), 4.27 (s, 2H, CH$_2$OCH$_3$), 3.57 (t, 4.5 Hz, 1H, OH). $^{13}$C NMR (75.47 MHz, CDCl$_3$, δ (ppm)): 158.4, 158.0, 144.1, 138.4, 129.1, 128.4, 127.7, 120.1, 119.4, 87.8, 66.7, 64.0.

6-[(triphenylmethoxy)methyl]-pyridine-2-carboxaldehyde (1c)

To 2.01 g (5.3 mmol) 2,6-pyridinedimethanol monotrityl ether, 0.60 g (5.4 mmol) SeO$_2$ and 3Å molsieves, 150 ml hexane was added. The mixture was refluxed overnight coloring the solution light purple after a few hours. After cooling down to room temperature a TLC was taken of the crude colorless mixture which indicated full conversion ($R_f = 0.69$ with eluens dichloromethane). The solids were filtered off and washed with 10 ml dichloromethane. The volatiles of the filtrate were removed in vacuo yielding a yellow oil (2.40 g, 120%). The oil was dissolved in 50 ml dichloromethane and brought into a separatory funnel and the organic layer was washed with 50 ml of a saturated solution of K$_2$CO$_3$ in water. The organic layer was dried on MgSO$_4$ and the volatiles were removed by rotary evaporation yielding a yellow oil (1.97 g, 99%). $^1$H NMR (300.13 MHz,
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CD$_2$Cl$_2$, $\delta$(ppm)): 9.90 (s, 1H, COH), 7.92 (m, 2H, pyH), 7.80 (m, 1H, pyH), 7.50 (m, 6H, ArH), 7.29 (m, 9H, ArH), 4.38 (s, 2H, CH$_2$OCH$_3$). $^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 193.8, 160.7, 152.2, 144.0, 138.1, 129.1, 128.4, 127.7, 125.6, 120.7, 88.0, 67.0.

6-[(triphenylmethoxy)methyl]-pyridine-2-(isopropylimine) (3cz)

An amount of 0.49 g (1.3 mmol) 1c was dissolved in 40 ml ether. 1 ml isopropylamine and 3Å molsieves were added to this solution. The mixture was stirred for one hour at room temperature after which the solids were filtered off and washed with 10 ml ether. The volatiles of the filtrate were removed by rotary evaporation yielding a yellow oil (0.54 g, 100%). $^1$H NMR (300.13 MHz, CD$_2$Cl$_2$, $\delta$(ppm)): 8.26 (s, 1H, imH), 7.8 (m, 3H, pyH), 7.54 (m, 6H, ArH), 7.30 (m, 9H, ArH), 4.32 (s, 2H, CH$_2$OCH$_3$), 3.59 (sept, $^3$$J_{HH}$ = 6.0 Hz, 1H, CH(CH$_3$)$_2$), 1.23 (d, $^3$$J_{HH}$ = 6.0 Hz, 6H, CH(CH$_3$)$_2$). $^{13}$C NMR (75.47 MHz, CD$_2$Cl$_2$, $\delta$ (ppm)): 159.6, 159.2, 154.6, 144.3, 137.5, 129.0, 128.3, 127.6, 122.1, 119.7, 87.7, 67.3, 61.8, 24.2.

6-[(methoxy) methoxymethyl]-pyridine-2-methanol (1d')

An amount of 9.43 g (67.8 mmol) 2,6-pyridinedimethanol was dissolved in 100 ml THF. 25 ml diethylisopropylamine was added to this mixture and then 5 ml chloromethyl methyl ether at 0 °C. The solution was stirred for one night resulting in a orange solution. Then, 50 ml of hexanes was added and the solvents were removed under reduced pressure. The oil was than dissolved in 30 ml dichloromethane and brought into a separatory funnel and the product was washed with 50 ml of dilute potassium carbonate in water. The water-layer was extracted with 3x 30 ml dichloromethane, and the combined organic layers were dried on MgSO$_4$. The solvent was removed under reduced pressure. The product was purified with column chromatography using 20% ethyl acetate in dichloromethane to start with and after the by-product was eluted, the product was washed off the column with ethyl acetate. R$_f$ (product, 20% EtOAc in dichloromethane) = 0.36. The volatile components were removed under reduced pressure, yielding a colorless oil (6.3 g, 51%). $^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$(ppm)): 7.70 (t, $^3$$J_{HH}$ = 7.5 Hz, 1H, pyH), 7.36 (d, $^3$$J_{HH}$ = 7.8 Hz, 1H, pyH), 7.14 (d, $^3$$J_{HH}$ = 7.5 Hz, 1H, pyH), 4.79 (s, 2H, OCH$_2$O), 4.75 (s, 2H, CH$_2$OH), 4.72 (s, 2H, CH$_2$OCH$_2$), 3.78 (s, 1H, OH), 3.43 (s, 3H, OCH$_3$). $^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 158.9, 158.1, 137.6, 120.5, 137.6, 120.5, 119.3, 94.8, 70.3, 64.2, 59.9.
6-methoxymethoxymethyl-pyridine-2-carbaldehyde (1d)
An amount of 2.09 g 6-[(methoxy)-methoxymethyl]-pyridine-2-methanol was dissolved in 50 ml hexane after which 1.42 g selenium oxide was added. This mixture was refluxed at 80 °C overnight. The solution was filtered and washed with diluted potassium carbonate in water. The product was extracted with 3x 30 ml dichloromethane and dried on MgSO₄. The solvent was removed under reduced pressure yielding a colourless oil (2.06 g, 100%). ¹H NMR (300.13 MHz, CDCl₃, δ(ppm)): 10.06 (s, 1H, ), 7.88 (m, 2H, pyH), 7.90 (m, 1H, pyH), 4.82 (s, 4H, CH₂OCH₂), 3.44 (s, 3H, CH₃). ¹³C NMR (75.47 MHz, CDCl₃, δ (ppm)): 193.7, 160.1, 152.2, 138.0, 125.8, 120.3, 95.0, 71.0, 60.0.

6-[(methoxy)methoxymethyl]-pyridine-2-isopropylimine (3dz)
An amount of 0.83 g 1d was dissolved in isopropylamine and some 3Å molsieves were added. This solution was stirred for 30 minutes at room temperature. The mixture was filtered and solids were washed with ether. The solvent of the filtrate was then removed under reduced pressure yielding a colourless oil (0.91 g, 89%). ¹H NMR (300.13 MHz, CDCl₃, δ(ppm)): 8.35 (s, 1H, imH), 7.79 (d, 3JHH = 7.5 Hz, 1H, pyH), 7.77 (t, 3JHH = 7.5 Hz, 1H, pyH), 7.47 (d, 3JHH = 7.8 Hz, 1H, pyH), 4.78 (s, 2H, OCH₂O), 4.71 (s, 2H, CH₂OCH₂O), 3.61 (sept, 3J=5.4 Hz, 1H, CH(CH₃)₂), 3.42 (s, 3H, OCH₃), 1.26 (d, 3JHH = 6.6 Hz, 6H, CH(CH₃)₂). ¹³C NMR (75.47 MHz, CD₂Cl₂, δ (ppm)): 159.6, 158.4, 154.8, 137.4, 122.6, 120.0, 96.7, 70.4, 61.7, 55.6, 24.1.

6-(methoxymethyl)-pyridine-2-methanol (1e')
The synthesis was done according to a literature procedure,[32] but was slightly changed. 3.52 g (25.3 mmol) 2,6-pyridinedimethanol was dissolved in 60 ml dry 1,4-dioxane. 0.72 g (30 mmol) sodium hydride was added and the mixture was stirred for 45 minutes at room temperature. Then 1.60 ml (25.3 mmol) methyl iodide in 20 ml 1,4-dioxane was slowly added to the mixture. The dropping funnel was washed with another 10 ml 1,4-dioxane and also added to the mixture that was stirred overnight at room temperature. The orange solution was filtered over a glass filter with a 1 cm layer of filter aid. After removal of the volatiles of the filtrate by rotary evaporation, ¹H NMR spectroscopy of the sample showed much starting material. To the remaining solids 10 ml dichloromethane was added, filtered over a glass filter and the volatiles of the filtrate were removed by rotary evaporation to yield an oil. The product was purified by column chromatography (on SiO₂, MeOH/CHCl₃, 10:90 v/v, Rf = 0.34, the published method[32] did not give sufficient separation) yielding after removal of the solvents by rotary evaporation 0.14 g (4%) of a colorless
oil. $^1$H NMR (300.13 MHz, CDCl$_3$, δ(ppm)): 7.72 (t, $^3$J$_{HH}$ = 7.8 Hz, 1H, pyH), 7.36 (d, $^3$J$_{HH}$ = 7.8 Hz, 1H, pyH), 7.16 (t, $^3$J$_{HH}$ = 7.5 Hz, 1H, pyH), 4.76 (s, 2H, CH$_2$OCH$_3$), 4.61 (s, 2H, CH$_2$OH), 3.81 (br s, 1H, OH), 3.49 (s, 3H, CH$_3$). $^{13}$C NMR (75.47 MHz, CDCl$_3$, δ (ppm)): 158.8, 157.5, 137.5, 120.0, 119.4, 75.4, 64.2, 59.0.

6-(methoxymethyl)-pyridine-2-carbaldehyde (1e)
An amount of 0.14 g (0.91 mmol) 6-(methoxymethyl)-pyridine-2-methanol was dissolved in 40 ml hexanes. 0.11 g (0.91 mmol) SeO$_2$ and 3 Å molsieves were added to this solution and the mixture was heated at reflux overnight. The solution was filtered over a glass filter and the insoluble material was extracted with 10 ml dichloromethane and the volatiles of the combined filtrate were removed by rotary evaporation yielding 0.14 g (100%) of a white solid. $^1$H NMR (300.13 MHz, CDCl$_3$, δ(ppm)): 10.07 (s, 1H, (CO)H), 7.89 (m, 2H, pyH), 7.67 (m, pyH), 4.68 (s, 2H, CH$_2$), 3.52 (s, 3H, CH$_3$). $^{13}$C NMR (75.47 MHz, CDCl$_3$, δ (ppm)): 193.6, 159.6, 152.3, 137.8, 125.7, 120.6, 75.2, 59.1.

6-(methoxymethyl)-pyridine-2-isopropylimine (3ez)
An amount of 0.17 g (1.12 mmol) le was dissolved in 10 ml diethyl ether and 1.0 ml (12 mmol) isopropylamine and 3 Å molsieves were added to this solution. After 1 hour stirring at room temperature the mixture was filtered. The volatiles of the filtrate were removed by rotary evaporation yielding 0.16 g (74%) of a colorless oil. $^1$H NMR (300.13 MHz, CD$_2$Cl$_2$, δ(ppm)): 8.31 (s, 1H, imH), 7.84 (d, $^3$J$_{HH}$ = 7.8 Hz, 1H, pyH), 7.73 (t, $^3$J$_{HH}$ = 7.8 Hz, 1H, pyH), 7.40 (d, $^3$J$_{HH}$ = 7.2 Hz, 1H, pyH), 4.54 (s, 2H, CH$_2$), 3.59 (sept, $^3$J$_{HH}$ = 6.3 Hz, 1H, CH(CH$_3$)$_2$), 1.22 (d, $^3$J$_{HH}$ = 6.3 Hz, 1H, CH(CH$_3$)$_2$). $^{13}$C NMR (75.47 MHz, CD$_2$Cl$_2$, δ (ppm)): 159.6, 158.7, 154.9, 137.3, 122.4, 119.9, 75.7, 61.7, 58.9, 24.1.

cis-α,α-dimethyl-[κN,κN-2-[[6-methyl-2-pyridinyl)methylene]amino]-phenol]-platinum(II) (4aw)
An amount of 269.6 mg (0.4697 mmol) tetramethylbis[μ-(dimethylsulfide)]-diplatinum(II) and 201.2 mg (0.9477 mmol) 3aw were dissolved in 10 ml THF. Immediately a purple colored solution was formed and after stirring for 5 minutes at room temperature, 20 ml hexane was added. A red precipitate came out of the solution and the volatiles were removed under reduced pressure until 10 ml remained (by this way the desired compounds slowly precipitated from the solution and the
THF/hexane-mixture was evaporated in a more regulate manner than when pure THF was removed *in vacuo*. Then another 50 ml of hexane was added. The solvent was decanted and the red solids were washed twice with hexane (2x 15 ml) to yield 294.3 mg (71%) of a red solid. $^1$H NMR (300.13 MHz, acetone-$d_6$, $\delta$(ppm)): 9.75 (s, $^3J_{HH} = 30.0$ Hz, 1H, imH), 8.20 (t, $^3J_{HH} = 7.8$ Hz, 1H, pyH), 8.05 (d, $^3J_{HH} = 7.2$ Hz, 1H, pyH), 7.79 (d, $^3J_{HH} = 7.2$ Hz, 1H, pyH), 7.25 (m, 2H, pyH), 7.00 (m, 2H, ArH), 3.76 (br s, 1H, OH), 2.88 (s, 3H, CCH$_3$), 1.23 (s, $^2J_{HH} = 87.7$ Hz, 3H, Pt-CH$_3$), 0.80 (s, $^2J_{HH} = 92.1$ Hz, 3H, Pt-CH$_3$). $^{13}$C NMR (75.47 MHz, acetone-$d_6$, $\delta$(ppm)): 167.4, 163.6, 156.8, 151.1, 148.8, 138.1, 129.9, 129.3, 126.3, 122.4, 120.3, 116.7, 25.7, -15.9 ($^1JC_{Pt} = 817$ Hz), -16.9 ($^1JC_{Pt} = 817$ Hz).

cis-$\sigma,\sigma$-dimethyl-$[\kappa N, \kappa N-2-[4-methyl-2-[(2-pyridinylmethylene)amino]-phenol]platinum(II) (4bw)

An amount of 206 mg (0.35 mmol) tetramethylbis[$\mu$-(dimethylsulfide)]-diplatinum(II) and 0.20 g (0.94 mmol) 3bw were dissolved in 7 ml THF. Immediately a purple colored solution was formed and after stirring for 20 minutes at room temperature 15 ml hexane was added. A red precipitate came out of the solution and the solvent was decanted. The solids were washed with hexane (2x 5 ml) and ether/pentane (v/v=1:3, in total 10 ml) yielding a red solid (260.1 mg, 85%). $^1$H NMR (300.13 MHz, acetone-$d_6$, $\delta$(ppm)): 9.71 (s, $^3J_{HH} = 32.1$ Hz, 1H, imH), 9.26 (d, $^3J_{HH} = 5.7$ Hz, $^3J_{HH} = 19.8$ Hz 1H, pyH), 8.41 (dt, $^3J_{HH} = 7.8$ Hz, $^3J_{HH} = 1.5$ Hz, 1H, pyH), 8.24 (d, $^3J_{HH} = 7.5$ Hz, 1H, pyH), 7.76 (dt, $^3J_{HH} = 6.6$ Hz, $^4J_{HH} = 1.5$ Hz, 1H, pyH), 7.07 (d, $^3J_{HH} = 8.4$ Hz, 1H, ArH), 7.06 (s, 1H, ArH), 6.90 (d, $^3J_{HH} = 8.4$ Hz, 1H, ArH), 2.83 (br s, 1H, OH), 1.20 (s, $^3J_{HH} = 86.4$ Hz, 3H, Pt-CH$_3$), 0.82 (s, $^3J_{HH} = 88.2$ Hz , 3H, Pt-CH$_3$). $^{195}$Pt NMR (64.3 MHz, acetone-$d_6$, $\delta$(ppm)): -3339 ppm.

cis-$\sigma,\sigma$-dimethyl-$[\kappa N, \kappa N-1-methoxy-2-[(2-pyridinylmethylene)amino]-ethane]-platinum(II) (4bx)

An amount of 531.6 mg (0.926 mmol) tetramethylbis[$\mu$-(dimethylsulfide)]-diplatinum(II) and 0.41 g (2.5 mmol) 3bx were dissolved in 5 ml THF. Immediately a purple colored solution was formed and after stirring for 5 minutes at room temperature 20 ml hexane was added. A red precipitate came out of the solution and the volatiles were removed in vacuo. The remaining red solids were washed with pentane (3x 15 ml) to yield 709.7 mg (98%) of a red solid. $^1$H NMR (500 MHz, CDCl$_3$, $\delta$(ppm)): 9.19 (d, $^3J_{HH} = 5.0$ Hz, 1H, pyH), 9.12 (s, $^3J_{HH} = 33.6$ Hz, 1H, imH), 8.07 (dt,
cis-α,α-dimethyl-[κN,κN-4-methyl-2-[(2-pyridinylmethylene)amino]-phenol]-platinum(II) (4by)

An amount of 206 mg (0.359 mmol) tetramethylbis[μ-(dimethylsulfide)]-diplatinum(II) and 0.20 g (2.5 mmol) 3by were dissolved in 7 ml THF. Immediately a purple colored solution was formed and after stirring for 5 minutes at room temperature 15 ml hexane was added. A red precipitate came out of the solution and the volatiles were removed in vacuo. The remaining red solids were washed with hexane (10 ml), ether/pentane (10 ml 1:9 v/v) and pentane (10 ml) to yield 279 mg (91%) of a red solid. 1H NMR (500 MHz, acetone-d6, δ(ppm)): 9.65 (s, 3JHH = 32.0 Hz, 1H, imH), 9.28 (d, 3JHH = 5.5 Hz, 1H, pyH), 8.45 (t, 3JHH = 8.0 Hz, 1H, pyH), 8.24 (d, 3JHH = 8.0 Hz, 1H, pyH), 7.96 (t, 3JHH = 5.5 Hz, 1H, pyH), 7.05 (s, 1H, ArH), 7.00 (d, 3JHH = 8.5 Hz, 1H, ArH), 3.28 (s, 1H, OH), 2.28 (s, 3H, ArCH3), 1.17 (s, 2JHH = 85.0 Hz, 1H, Pt-CH3), 0.82 (s, 2JHH = 85.5 Hz, 1H, Pt-CH3).

13C NMR (125.70 MHz, CDC13, δ (ppm)): 165.0, 156.7, 147.5 (2JCP = 35 Hz), 137.0, 128.2 (2JCP = 15 Hz), 126.4, 70.9, 59.1 (2JCP = 37 Hz), 59.1, -15.4 (2JCP = 789 Hz), -18.2 (2JCP = 806 Hz).

cis-α,α-dimethyl-[κN,κN-6-[(triphenylmethoxy)methyl]-pyridine-2-isopropylimine]-platinum(II) (4cz)

An amount of 0.29 g (0.69 mmol) 3cz and 0.17 g (0.30 mmol) tetramethylbis[μ-(dimethylsulfide)]-diplatinum(II) were dissolved in 7 ml THF. Immediately a dark red colored solution was formed and after stirring for 5 minutes at room temperature 15 ml hexane was added, and the volatiles were removed in vacuo. The remaining red solids were washed with hexane (10 ml) and pentane (10 ml) to yield 280 mg (85%) of a red solid. 1H NMR (500 MHz, CDC13, δ(ppm)): 9.17 (s, 3JHH = 32.4 Hz, 1H, imH), 8.32 (d, 3JHH = 7.8 Hz, 1H, pyH), 8.10 (t, 3JHH = 7.5 Hz, 1H, pyH), 7.55 (d, 3JHH = 7.8 Hz, 1H, pyH), 7.49 (d, 3JHH = 7.2 Hz, 6H, ArH), 7.28 (m, 9H, ArH), 4.73 (s, 2H, CH2), 4.68 (sept, 3JHH = 6.0 Hz, 1H, CH(CH3)2), 1.39 (d, 3JHH = 6.6 Hz, 6H, CH(CH3)2), 1.11 (s, 2JHH = 88.8 Hz, 3H, Pt-CH3), 0.96 (s, 2JHH = 83.7 Hz, 3H, Pt-CH3). 13C NMR (125.70 MHz, acetone-d6, δ (ppm)): 163.6, 161.8, 157.6, 144.1, 138.0, 128.9, 128.2, 127.5, 125.5, 125.3, 88.0, 67.4 (2JCP = 18 Hz), 54.3 (2JCP = 40 Hz), 22.4, -16.0 (1JCP = 868 Hz), -18.0 (1JCP = 805 Hz).
cis-σ-dimethyl-κN,κN-6-(methoxy)methoxymethyl]-pyridine-2-isopropylimine]-platinum(II) (4dz)

An amount of 0.255 g (1.15 mmol) 3dz was added to 0.2847 g (0.495 mmol) tetramethylbis[μ-(dimethylsulfide)]-diplatinum(II) dissolved in 15 ml THF. This solution was stirred for 15 min at room temperature. The solution was filtered over a glass filter filled with 1 cm of Celite filter aid and the residue was extracted with 30 ml THF. 10 ml hexanes was added to the filtrate and all the solvents were removed under reduced pressure. The product was dissolved in 1 ml ether, 20 ml pentane was added. The solvent was decanted from the precipitate and the solid was washed 3x with 20 ml pentane. The red solid was further dried under reduced pressure yielding a red solid (0.43 g, 94%). ¹H NMR (500 MHz, acetone-δ₆, δ(ppm)): 9.60 (s, J₃HH = 33.6 Hz, 1H, imH), 8.26 (t, J₃HH = 7.8 Hz, 1H, pyH), 7.93 (m, 2H, pyH), 5.02 (s, 2H, OCH₂O₂), 4.83 (s, 2H, CH₂OCH₂O₂), 4.67 (sept, J₃HH = 6.3 Hz, 1H, CH(CH₃)₂), 3.40 (s, 3H, OCH₃), 1.42 (d, J₃HH = 6.6 Hz, 6H, CH(CH₃)₂), 1.13 (s, J₂H₂Pt = 84.9 Hz, 3H, Pt-CH₃), 1.08 (s, J₂H₂Pt = 91.5 Hz, 3H, Pt-CH₃). ¹³C NMR (125.70 MHz, acetone-δ₆, δ(ppm)): 163.4, 161.8, 157.7, 137.9, 125.7, 125.5, 96.6, 70.1 (J₃CP = 18 Hz), 55.1, 54.6 (J₂CP = 40 Hz), 22.4, -16.0 (J₁CP = 865 Hz), -18.1 (J₁CP = 806 Hz), ¹⁹⁵Pt NMR (64.3 MHz, acetone-δ₆, δ(ppm)): -3427.

cis-σ-dimethyl-κN,κN-6-(methoxymethyl)-pyridine-2-isopropylimine]-platinum(II) (4ez)

An amount of 82.3 mg (0.143 mmol) tetramethylbis[μ-(dimethylsulfide)]-diplatinum(II) and 68.2 mg (0.35 mmol) 3ez were dissolved in 15 ml THF. Immediately a dark red colored solution was formed and after stirring for 30 minutes at room temperature 15 ml hexane was added. A red precipitate came out of the solution and the volatiles were removed in vacuo. The remaining red solids were washed with pentane (2×15 ml) to yield 41.9 mg (70%) of a red solid. ¹H NMR (500 MHz, CD₂Cl₂, δ(ppm)): 9.21 (s, J₃HH = 35.0 Hz, 1H, imH), 8.06 (t, J₃HH = 8.0 Hz, 1H, pyH), 7.84 (d, J₃HH = 7.5 Hz, 1H, pyH), 7.59 (d, J₃HH = 7.5 Hz, 1H, pyH), 4.89 (s, 2H, CH₂), 4.68 (sept, J₃HH = 6.5 Hz, 1H, CH(CH₃)₂), 3.51 (s, 3H, OCH₃), 1.41 (d, J₃HH = 6.5 Hz, 6H, CH(CH₃)₂), 1.13 (s, J₂H₂Pt = 84.5 Hz, 3H, Pt-CH₃), 1.09 (s, J₂H₂Pt = 90.5 Hz, 3H, Pt-CH₃). ¹³C NMR (125.70 MHz, benzene-δ₆, δ(ppm)): 164.6, 159.5, 157.5, 136.5, 128.2, 124.3, 75.7 (J₃CP = 17.8 Hz), 58.8, 54.9 (J₂CP = 40.9 Hz), 23.0, -13.9 (J₁CP = 861 Hz), -16.1 (J₁CP = 807 Hz).
cis-\(\sigma,\sigma\)-dimethyl-[\(\kappa N,\kappa N\)-i-propylpyridinecarbaldimine]-platinum(II) (4bz)

An amount of 336.7 mg (0.586 mmol) tetramethylbis[\(\mu\)-(dimethylsulfide)]-diplatinum(II) and 185.7 mg (1.25 mmol) \(i\)-propylpyridinecarbaldimine were dissolved in 20 ml THF. Immediately a purple colored solution was formed and after stirring for 90 minutes at room temperature, 15 ml hexane was added and the volatiles were removed \textit{in vacuo}. The remaining red solids were washed with pentane (3x15 ml) to yield 361 mg (83%) of a dark red solid. \(^1\)H NMR (300.13 MHz, CDCl\(_3\), \(\delta\)(ppm)): 9.22 (m, 1H, pyH), 9.13 (s, \(^3J_{HH} = 35.4\) Hz, 1H, imH), 8.08 (dt, \(^3J_{HH} = 7.0\) Hz, \(^4J_{HH} = 1.2\) Hz 1H, pyH), 7.67 (d, \(^3J_{HH} = 7.5\) Hz, 1H, pyH), 7.56 (m, 1H, pyH), 4.75 (sept, \(^3J_{HH} = 6.6\) Hz, 1H, \(CH(CH_3)_2\)), 1.41 (d, \(^3J_{HH} = 6.6\) Hz, 6H, CH(C\(_3\))\(_2\)), 1.24 (s, \(^3J_{HH} = 84.3\) Hz, 3H, Pt-CH\(_3\)), 1.09 (s, \(^2J_{CP} = 87.3\) Hz, 3H, Pt-CH\(_3\)). \(^{13}\)C NMR (75.47 MHz, acetone-\(d_6\), \(\delta\)(ppm)): 161.0, 158.1, 146.8 (\(\nu_{CP} = 36.3\) Hz), 137.3, 128.5, 127.4, 56.6 (\(^2J_{CP} = 37.4\) Hz), 22.6, -15.08 (\(^1J_{CP} = 809\) Hz), -17.6 (\(^1J_{CP} = 830\) Hz).

\(\sigma\)-methyl-[\(\kappa N,\kappa N\)-O-2-[[\(6\)-methyl-2-pyridinyl]methylenelamino]-phenol]-platinum(II) (5aw)

An amount of 19.0 mg 4aw was dissolved in 30 ml benzene. This red solution was stirred overnight at reflux temperature. After cooling down to room temperature the volatiles were removed yielding 18.9 mg (100%) of a green solid. This solid is barely soluble in any solvent. However, \(^1\)H NMR was possible in acetone-\(d_6\) after addition of a drop of 2,2,2-trifluoroethanol. \(^1\)H NMR (300.13 MHz, acetone-\(d_6\), \(\delta\)(ppm)): 8.86 (s, \(^3J_{HP} = 35.4\) Hz, 1H, imH), 7.89 (t, \(^3J_{HH} = 8.1\) Hz, 1H, pyH), 7.40 (d, \(^3J_{HH} = 7.5\) Hz, 2H, ArH), 7.24 (d, \(^3J_{HH} = 8.7\) Hz, 1H, pyH), 6.93 (dd, \(^3J_{HH} = 8.4\) Hz, \(^4J_{HH} = 1.5\) Hz, 1H, pyH), 6.79 (dd, \(^3J_{HH} = 7.8\) Hz, \(^4J_{HH} = 1.8\) Hz, 1H, ArH), 6.38 (dd, \(^3J_{HH} = 6.9\) Hz, \(^4J_{HH} = 1.5\) Hz, 1H, ArH). 2.83 (s, 3H, ArCH\(_3\)), 0.92 (s, \(^2J_{HP} = 76.8\) Hz, 3H, Pt-CH\(_3\)).

cis-\(\sigma\)-methyl-[\(\kappa O\)-diethylether-[\(\kappa N,\kappa N\)-1-methoxy-2-[[2-pyridinylmethylene]amino]-ethane]]-platinum(II) tetrafluoro borate (5bx)

An amount of 70 mg (0.18 mmol) 4bx was dissolved in 60 ml diethyl ether. This red-purple solution was cooled to \(-60\) °C, after which 54% HBF\(_4\) in diethyl ether (24 \(\mu\)l, 0.18 mmol) was added to the solution. A red-brown solid came out of the solution and the mixture was stirred for another 90 minutes at \(-60\) °C. The mixture was filtered over a glass filter P4 and the solids were washed with 10 ml cold diethyl ether. The brown red solid is further dried \textit{in vacuo} for a view hours. Yield: 86 mg (89%). \(^1\)H NMR (300.13 MHz, acetone-\(d_6\), \(\delta\)(ppm)): 9.11 (s, \(^3J_{HP} = 118.9\) Hz, 1H, pyH), 8.86 (s, \(^3J_{HP} = 87.3\) Hz, 1H, imH), 7.89 (t, \(^3J_{HH} = 8.1\) Hz, 1H, pyH), 7.40 (d, \(^3J_{HH} = 7.5\) Hz, 2H, ArH), 7.24 (d, \(^3J_{HH} = 8.7\) Hz, 1H, pyH), 6.93 (dd, \(^3J_{HH} = 8.4\) Hz, \(^4J_{HH} = 1.5\) Hz, 1H, pyH), 6.79 (dd, \(^3J_{HH} = 7.8\) Hz, \(^4J_{HH} = 1.8\) Hz, 1H, ArH), 6.38 (dd, \(^3J_{HH} = 6.9\) Hz, \(^4J_{HH} = 1.5\) Hz, 1H, ArH). 2.83 (s, 3H, ArCH\(_3\)), 0.92 (s, \(^2J_{HP} = 76.8\) Hz, 3H, Pt-CH\(_3\)).
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1H, imH), 8.66 (d, \(^3J_{HH} = 5.1\) Hz, 1H, pyH), 8.45 (dt, \(^3J_{HH} = 7.5\) Hz, \(^4J_{HH} = 1.5\) Hz, pyH), 8.33 (d, \(^3J_{HH} = 7.5\) Hz, 1H, pyH), 8.00 (m, 1H, pyH), 4.17 (t, \(^3J_{HH} = 4.5\) Hz, \(^3J_{HP} = 60.9\) Hz, 2H, \(CH_2CH_2OCH_3\)), 3.76 (t, 2H, \(CH_2CH_2OCH_3\)), 3.33 (s, 3H, OCH\(_3\)), 0.89 (s, \(^2J_{HP} = 75.6\) Hz, 3H, Pt-CH\(_3\)). Diethyl ether was found non-coordinating: 3.38 (q, 6.9 Hz, 4H, OCH\(_2\)CH\(_3\)), 1.08 (t, 6.9 Hz, 6H, OCH\(_2\)CH\(_3\)).

**σ-methyl-[κN,κN-σ-O-4-methyl-2-[(2-pyridinylmethylene)amino]-phenoxy]-platinum(II)**

(5by)

An amount of 7.1 mg 4by was dissolved in 15 ml benzene. This red solution was stirred overnight at reflux temperature. After cooling down to room temperature the volatiles were removed yielding 7.0 mg (100%) of a green solid. This solid is barely soluble in any solvent. However, \(^1H\) NMR was possible in acetone-\(d_6\) after addition of a drop of 2,2,2-trifluoroethanol. \(^1H\) NMR (300.13 MHz, acetone-\(d_6\), δ(ppm)): 8.67 (s, \(^3J_{HPR} = 40.2\) Hz, 1H, imH), 8.48 (d, \(^3J_{HH} = 5.1\) Hz, \(^3J_{HP} = 54.3\) Hz, 1H, ArH), 7.97 (td, \(^3J_{HH} = 7.8\) Hz, \(^4J_{HH} = 1.5\) Hz, 1H, pyH), 7.54 (br d, \(^3J_{HH} = 7.5\) Hz, 1H, ArH), 7.36 (m, 1H, pyH), 7.01 (s, 1H, ArH), 6.79 (dd, \(^3J_{HH} = 8.7\) Hz, \(^4J_{HH} = 1.8\) Hz, 1H, pyH), 6.51 (d, \(^3J_{HH} = 8.4\) Hz, 1H, ArH). 2.83 (s, 3H, ArCH\(_3\)), 0.92 (s, \(^2J_{HP} = 76.8\) Hz, 3H, Pt-CH\(_3\)).

**σ-methyl-[κN,κN-κO-6-[(methoxy)methoxymethyl]-pyridine-2-isopropylimine]-platinum(II)**

tetrafluoro borate (5dz)

An amount of 0.0457 g (mmol) 4dz was dissolved in 100 ml diethyl ether. The solution was cooled to -73 °C and 290 μl of a solution of 2.7% HBF\(_4\) in diethyl ether was slowly added. The solution was stirred for 2 hours at -73 °C, after which most of the solvent was decanted. The remaining solvent was removed under reduced pressure and a yellow solid remained (0.034 g, 77%). \(^1H\) NMR (300.13 MHz, CD\(_2\)Cl\(_2\), -20 °C, δ(ppm)): 8.90 (s, \(^3J_{HPR} = 116\) Hz, 1H, imH), 8.19 (m, 1H, pyH), 7.92 (m, 2H, pyH), 6.93 (br s, 2H, H\(_2\)O), 4.78 (s, \(^3J_{HPR} = 25.2\) Hz, 2H, OCH\(_2\)O), 4.45 (sept, 1H, \(^3J_{HH} = 7.3\) Hz, CH(CH\(_3\))\(_2\)), 3.91 (s, \(^3J_{HP} = 22.2\) Hz, 2H, CH\(_2\)OCH\(_2\)O), 3.38 (s, 3H, OCH\(_3\)), 1.48 (d, \(^3J_{HH} = 6.6\) Hz, 6H, CH(CH\(_3\))\(_2\)), 1.19 (s, \(^3J_{HP} = 77.1\) Hz, 3H, Pt-CH\(_3\)). \(^{195}\)Pt NMR (64.3 MHz, CD\(_2\)Cl\(_2\), -20 °C, δ(ppm)): -3072.

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\(\sigma\)-methyl-\(\kappa\)N-acetonitrile-[\(\kappa\)N,\(\kappa\)N-6-[(methoxy)methoxymethyl]-pyridine-2-isopropylimine]-platinum(II) (6dz)

To 10 mg 5dz, 2 ml acetonitrile was added. The excess acetonitrile was removed under reduced pressure yielding 10 mg of a yellow solid. \(^1\)H NMR (300.13 MHz, acetone-\(d_6\), \(\delta\)(ppm)): 9.06 (s, \(^3J_{HH} = 103\) Hz, 1H, imH), 8.23 (m, 1H, pyH), 8.06 (m, 2H, pyH), 5.31 (s, 2H, CH\(_2\)), 4.85 (s, 2H, CH\(_2\)), 4.61 (1H, sept, \(^3J_{HH} = 6.5\) Hz, CH(CH\(_3\))\(_2\)), 3.42 (s, 3H, OCH\(_3\)), 2.63 (s, \(^4J_{HP} = 14.1\) Hz, NCCH\(_3\)), 1.45 (d, \(^3J_{HH} = 6.6\) Hz, 6H, CH(CH\(_3\))\(_2\)), 1.18 (s, \(^2J_{HP} = 79.2\) Hz, Pt-CH\(_3\)). \(^{19}\)Pt NMR (64.3 MHz, acetone-\(d_6\), \(\delta\)(ppm)): -3599. \(^{19}\)F (acetone-\(d_6\), \(\delta\)(ppm)): -152.

cis-\(\sigma\)-methyl-\(\kappa\)N-acetonitrile-[\(\kappa\)N,\(\kappa\)N-3-propylpyridinecarbaldimine]-platinum(II) (6bz)

An amount of 200 mg (0.536 mmol) 4bz was dissolved in 60 ml acetonitrile and cooled to -30 °C. Then 73 \(\mu\)l 54% HBF\(_4\) in diethyl ether was slowly added to the red solution. The mixture was brought to room temperature and the volatiles were removed by rotary evaporation. The remaining solids were washed twice with diethyl ether (2x 15 ml) to yield a yellow powder (239 mg, 92%). \(^1\)H NMR (500 MHz, acetone-\(d_6\), \(\delta\)(ppm)): 9.39 (\(^3J_{HP} = 105.0\) Hz, 1H, imH), 9.09 (d, \(^3J_{HH} = 5.0\) Hz, 1H, pyH), 8.45 (dt, \(^3J_{HH} = 7.5\) Hz, \(^4J_{HH} = 1.5\) Hz, pyH), 8.30 (d, \(^3J_{HH} = 7.5\) Hz, 1H, pyH), 7.99 (m, 1H, pyH), 4.45 (sept, \(^3J_{HH} = 6.5\) Hz, 1H, CH(CH\(_3\))\(_2\)), 3.80 (br s, 3H, CH\(_3\)CN), 1.50 (d, \(^3J_{HH} = 6.5\) Hz, 6H, CH(CH\(_3\))\(_2\)), 1.00 (s, \(^2J_{HP} = 77.0\) Hz, 3H, Pt-CH\(_3\)). \(^{13}\)C (125.70 MHz, acetone-\(d_6\), \(\delta\)(ppm)): 210.1, 171.4, 154.6, 149.7 (\(^2J_{CP} = 32.2\) Hz), 141.7, 131.4, 129.4, 121.7, 69. 4, 58.6 (\(^2J_{CP} = 67.8\) Hz), 22.7, -16.0 (\(^1J_{CP} = 697\) Hz). \(^{19}\)F (acetonitrile-\(d_3\), \(\delta\)(ppm)): -151.8.

5.4.3 C-H bond activation experiments

An amount of 10 mg 5dz was dissolved in 5 ml 2,2,2-trifluoroethanol and 1 ml benzene was added to this solution. The mixture was stirred at room temperature for 5 days. Then 0.5 ml acetonitrile was added to stop the reaction and the solvents were removed under reduced pressure. In another experiment the same procedure as described above was followed but the reaction time was 2 hours instead of 5 days. Also one experiment was carried out as blank reaction with a sample where only 5dz was dissolved in 2,2,2-trifluoroethanol. After 5 days acetonitrile was added and the solvents were removed under reduced pressure and the products were analyzed by \(^1\)H NMR spectroscopy.
5.5 References


