PLATINUM(II) COMPLEXES WITH BIDENTATE NN AND TRIDENTATE NNO LIGANDS FOR C–H BOND ACTIVATION

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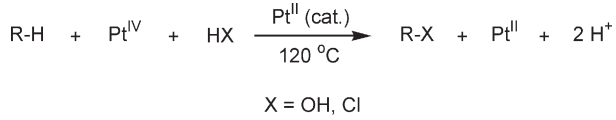
Dedicated to our friend and colleague Dr Karel Mach on the occasion of his 70th birthday, in recognition of his many contributions to organometallic chemistry and of our fruitful collaboration involving René Klein and Peter Witte.

A series of neutral and cationic methylplatinum(II) complexes with bidentate NN and tridentate NNO ligands has been prepared. The complexes involving tridentate NNO ligands were expected to be easier to handle than those with NN ligands, which has indeed been confirmed by the experiments. Nevertheless, the neutral [Pt(Me)(NNO)] and ionic $[Pt(Me)(NNO)]^+BF_4^-$ complexes retain their (non-selective) reactivity to hydrocarbon C–H bonds.

Keywords: N-ligands; Alkyl coplexes; C–H bond activation; ^{195}Pt NMR spectroscopy; Platinum.

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 corresponding chlorides and alcohols could be achieved by employing aqueous solutions of Pt(II) and Pt(IV) salts[2,3] (Scheme 1).



SCHEME 1
Functionalization of alkanes catalyzed by Pt(II)

The Shilov system is clearly unprecedented in many respects. First, the reaction is performed in aqueous solution and is unaffected by the presence

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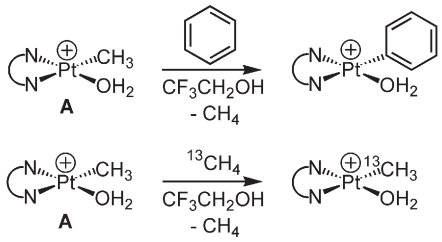
of molecular oxygen. Second, the reaction exhibits an unusual chemoselectivity; alkane C–H bonds are activated at equal or even higher rate than the C–H bonds of the produced alcohols or alkyl chlorides. Third, the order of regioselectivity (primary C–H > secondary C–H > tertiary C–H) is the reverse of what is normally observed for electrophilic and radical-type oxidations of hydrocarbons. However, the use of expensive Pt(IV) as stoichiometric oxidant, poor turnover numbers and sometimes unsatisfactory selectivity make the Shilov system not suited for practical applications.

After the initial report of Shilov, 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 alkane oxidation, and this observation subsequently provided a significant motivation to understand the details of the mechanism. Unfortunately, the C–H activation step has proven to be the most difficult one to study. Currently, it is clear that the reaction involves electrophilic alkane proton displacement by Pt(II).

Tilset et al.[18] have reported that both benzene and methane C–H bonds are activated by the aquo complex $[Pt(CH_3)(H_2O)(N\text{-}N)]BF_4$ (**A**, N-N = ArN=CMe–CMe=NAr, Ar = 3,5-$(CF_3)_2C_6H_3$) under unusually mild conditions (benzene at 25 °C, methane at 45 °C; Scheme 2) in the poorly coordinating solvent 2,2,2-trifluoroethan-1-ol (TFE).

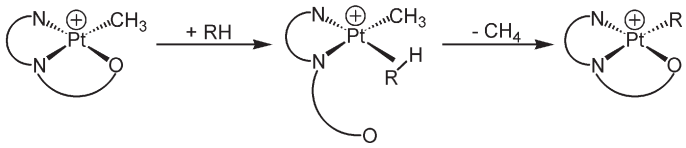


SCHEME 2
Hydrocarbon activation in a cationic aquadiimineplatinum(II) complex

These C–H activation reactions appear to occur under the mildest reaction conditions so far reported for such processes in cationic platinum complexes. As the above described complex **A** is very reactive towards almost every C–X bond, and because special precautions are required (low temperature, exclusion of oxygen, a special non-reactive solvent), we investigated cationic platinum complexes stabilized in a tridentate fashion by a pyridine-2-carbaldimine-based NNO ligand, in which the oxygen donor

moiety is an integral part of the ancillary ligand. The idea behind the design of these complexes is that they are expected to be easier to handle than their bidentate counterparts, the NN platinum(II) complexes described by Bercaw[12] and Tilset[18], at the same time, these tridentate NNO platinum(II) complexes may retain the reactivity towards hydrocarbon C–H bonds as reported for the bidentate NN platinum(II) complexes.

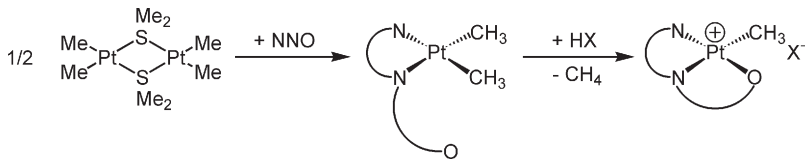
So, we set out to investigate the effect of coordination of the oxygen donor to the cationic platinum(II) center on the stability of the precursor complex, and its reactivity towards hydrocarbon C–H bonds. The NNO ligands might potentially coordinate in a tridentate fashion in such a way that reactivity and stability go together, i.e., the ligand provides stabilization in a tridendate mode and enough reactivity in a bidentate mode (Scheme 3).



SCHEME 3
Tridentate NNO ligands with semilabile oxygen ligand

For this reason, we designed tridentate pyridine-2-carboxaldimine-based NNO ligands. The accessibility of the NNO ligands is simple. Their synthesis can be done in one step from readily available materials. Surprisingly, just a few platinum(II) NNO complexes, or any NNO complexes with other Group 10 metals are known[19–21].

The route towards the platinum(II) NNO complexes is proposed by the reaction of bis[μ-(dimethyl sulfide)]tetramethyldiplatinum(II) with an NNO ligand to give a $[Pt(Me)_2(NNO)]$ complex in which the nitrogen donor atoms are coordinated to the platinum center. Treatment with acids may eliminate methane to give cationic $[Pt(Me)(NNO)]^+$ complexes that coordinate the oxygen-donor side arm (Scheme 4).



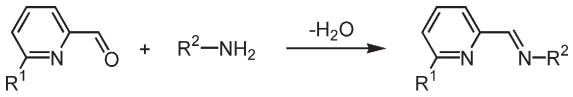
SCHEME 4
Synthesis of [Pt(Me)(NNO)]X complexes

RESULTS AND DISCUSSION

NNO Ligand Syntheses

The potentially tridentate pyridine-2-carbaldimine (PyCa)-based NNO ligands **3** were prepared by a condensation reaction of a pyridine-2-carbaldehyde with an appropriate amine or aniline (Scheme 5) in reasonable to excellent yields. The starting compounds **1a**, **1b** and **2a**–**2d** are commercially available, but not the aldehydes **1c**–**1f**. Therefore, we synthesized PyCa-based NNO ligands **3cd**, **3dd** and **3ed** from the corresponding aldehydes **1c**, **1d** and **1e** as described in Experimental.

The synthesis of 6-[(triphenylmethoxy)methyl]pyridine-2-carbaldehyde (**1c**) is known[22]: 2,6-bis(hydroxymethyl)pyridine was reacted with trityl chloride in a mixture of pyridine and a catalytic amount of 4-(dimethylamino)pyridine, to give a moderate (isolated) yield of 2,6-bis(hydroxymethyl)pyridine monotrityl ether (**1c′**). Attempted conversion of this compound into aldehyde **1c** with MnO_2 in dichloromethane at room temperature, as described in the patent by Stahl et al.[22], was not successful; only starting materials were obtained. Instead, oxidation with SeO_2 was attempted (Scheme 6), since it is known that methyl groups of 2-methyl-



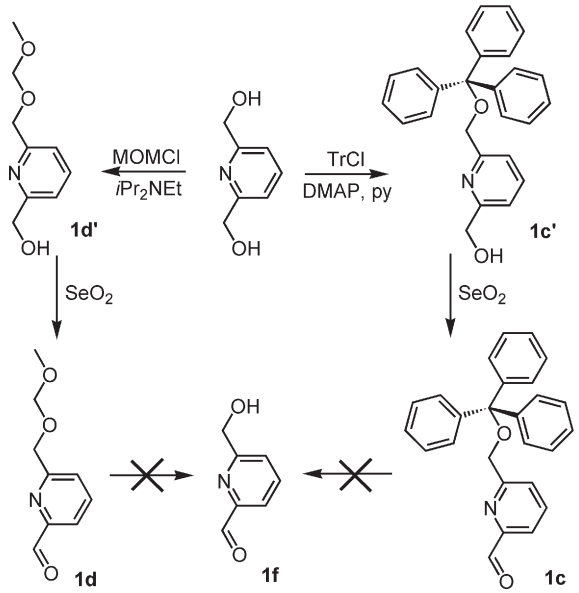
R^1	R^2	Compound	Yield, %
CH_3 **1a**	2-hydroxyphenyl **2a**	**3aa**	53
H **1b**	2-hydroxyphenyl **2a**	**3ba**	38
H **1b**	$C_2H_4OCH_3$ **2b**	**3bb**	98
H **1b**	2-hydroxy-4-methylphenyl **2c**	**3bc**	39
$CH_2OC(C_6H_5)_3$ **1c**	i-Pr **2d**	**3cd**	100
$CH_2OCH_2OCH_3$ **1d**	i-Pr **2d**	**3dd**	91
CH_2OCH_3 **1e**	i-Pr **2d**	**3ed**	100
CH_2OH **1f**	i-Pr **2d**	**3fd**	–

SCHEME 5
PyCa-based NNO ligands

pyridine can be selectively oxidized to their corresponding pyridine-2-carbaldehydes[23]. Treatment of 2,6-bis(hydroxymethyl)pyridine monotrityl ether (**1c′**) with SeO_2 in hexanes (instead of 1,4-dioxane)[23] in the presence of 3 Å molecular sieves under reflux overnight gave aldehyde **1c** in excellent yield (99%). The subsequent reaction of **1c** with isopropylamine (**2d**) gave **3cd** in quantitative yield.

The synthesis of 6-[(methoxy)methoxymethyl]pyridine-2-carbaldehyde (**1d**) is also straightforward: by the reaction of pyridine-2,6-dimethanol with 1 equivalent of chloromethyl methyl ether in a mixture of ethyl(diisospropyl)amine and THF at 0 °C, in analogy to the literature[24], but with dichloromethane replaced by THF. Subsequently, the obtained alcohol **1d′** was converted into aldehyde **1d** by treatment with SeO_2.

Attempts to synthesize **1f**, in order to introduce a hydroxymethyl group by removing the protecting groups in **1c** (trityl group) or **1d** (MOM group), failed. Treatment of **1c** with acetic acid[25], 4-methylbenzene-1-sulfonic acid in MeOH [26], $ZnBr_2$ [27], or formic acid in diethyl ether[28] to remove the trityl group, did not result in formation of **1f**. Removal of the MOM group in **1d** by acid procedures (boiling acetic acid/sulfuric acid[29], THF/water/6 M HCl, concentrated HCl in MeOH [30]), a mild acid method (in situ generation of



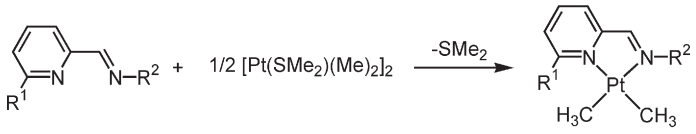
SCHEME 6
Syntheses of **1c** and **1d** and attempted synthesis of **1f**

HBr via CBr_4 in i-PrOH)[31], and by an alternative procedure ($LiBF_4$, H_2O, CH_3CN, 70 °C)[24], did not result in formation of **1f** either. This failure is due to the reactivity of aldehydes **1c** or **1d** towards the deprotecting agents.

The synthesis of 6-(methoxymethyl)pyridine-2-carbaldehyde (**1e**) consists of deprotonation of one OH group in pyridine-2,6-dimethanol and subsequent treatment with methyl iodide, producing pyridine-2,6-dimethanol monomethyl ether (**1e′**)[32]. However, this preparation was problematic and mainly bis-methylation was observed. So, the yield of the desired monomethylated product decreased to 4% (lit.[32] 88%); although, more solvent was used and methyl iodide was added dropwise, as described elsewhere[32]. Oxidation of pyridine-2,6-dimethanol monomethyl ether (**1e′**) with SeO_2 in hexanes at the reflux resulted in quantitative formation of **1e**.

[Pt(Me)$_2$(NNO)] Complexes with BidentateN,N′-Coordinated NNO Ligands

For the syntheses of the Pt(Me)$_2$(κ^2*N*,*N*′-NNO) complexes, a straightforward approach was chosen. Addition of the NNO ligand to 0.5 equivalent of bis[μ-(dimethyl sulfido)]tetramethyldiplatinum(II) in THF or diethyl ether[18] gives the corresponding [Pt(Me)$_2$(κ^2*N*,*N*′-NNO)] complexes **4** in good to excellent isolated yield (Scheme 7).



3 **4**

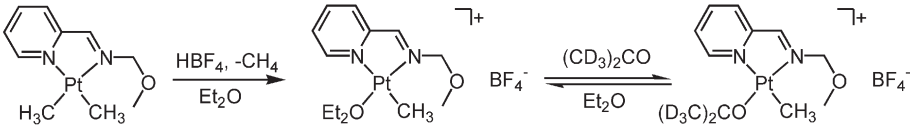
R^1	R^2	Compound	Yield, %
CH_3	2-hydroxyphenyl	**4aa**	71
H	2-hydroxyphenyl	**4ba**	85
H	$C_2H_4OCH_3$	**4bb**	98
H	2-hydroxy-4-methylphenyl	**4bc**	91
$CH_2OC(C_6H_5)_3$	i-Pr	**4cd**	85
$CH_2OCH_2OCH_3$	i-Pr	**4dd**	94
CH_2OCH_3	i-Pr	**4ed**	70

SCHEME 7
Synthesized [Pt(Me)$_2$(κ^2*N*,*N*′-NNO)] complexes

Complexes **4** as powders are stable for weeks at room temperature. For longer periods, storage at –20 °C is required. Complexes **4aa**, **4ba** and **4bc** are not stable in solution at room temperature; the complexes slowly degraded to new compounds while recording their ^{13}C NMR spectra, which will be described in the next part.

Methylplatinum(II) Complexes with Tridentate NNO Ligands

As a general method for the formation of a cationic [Pt(Me)(κ^3*N*,*N*′*O*-NNO)]BF_4 complex, we reacted HBF_4 with [Pt(Me)$_2$(κ^2*N*,*N*′-NNO)], similarly to what has been described for [Pt(Me)(NN)]BF_4 complexes[18].

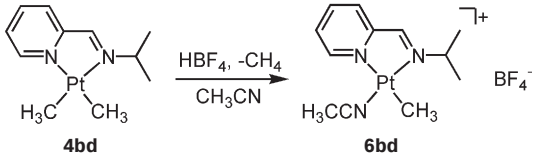


SCHEME 8
Bidentate coordination of the NNO ligand

In a first approach, we used **3bb** as potential tridentate coordinating NNO ligand in the platinum complex **4bb**. When we treated **4bb** with 1 equivalent of HBF_4 in diethyl ether at low temperature (–60 °C), we formed the complex [Pt(Me)(NNO)] **5bb** (Scheme 8) in good yield (89%). According to ^1H NMR spectra, the ether-oxygen coordinates to the cationic Pt center. We first thought that the NNO ligand coordinated in a tridentate fashion. However, comparison of the integrals of the relevant signals in the ^1H NMR spectrum showed that diethyl ether coordinated to the cationic Pt center and that one methyl ligand at Pt was missing. Most probably, the methyl bound trans to the imine group reacted to give methane, hence coordination of the oxygen of the NNO ligand was not possible.

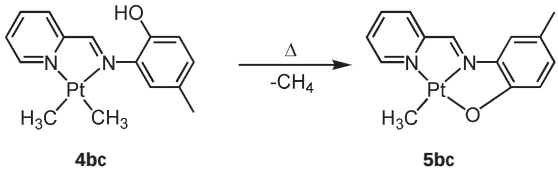
For the assessment of the exact geometry of the metal complex, we used 2-[(isopropylimino)methyl]pyridine (i-PrPyCa, **3bd**) as the ligand, which enabled to determine which methyl is consumed in the selective elimination of methane. In order to capture the product of the reaction at room temperature, we added the strong acid HBF_4 in a strongly coordinating medium (acetonitrile). The complex [Pt(Me)(NN)]BF_4 was formed after elimination of methane, which directly reacted with acetonitrile to form [Pt(CH_3CN)(Me)(NN)]BF_4 (**6bd**). When we reacted [Pt(Me)$_2$(i-PrPyCa)] (**4bd**) with HBF_4 (54% solution in diethyl ether) in acetonitrile, we observed

complex **6bd** was formed with 100% selectivity. Its geometry was proved by ^{1}H NMR NOE experiments. In this case, the thermodynamic product is cationic platinum complex **6bd** stabilized by the acetonitrile ligand trans to the imino group (Scheme 9). However, we cannot exclude that the initial kinetic product is the *cis* isomer (by elimination of the methyl ligand *cis* to the imino group), which rearranges to the thermodynamic trans isomer[33]. This possibility was underscored by showing that internal protonation by the weakly acid phenol-based NNO ligands **3aa**, **3ba** and **3bc** led to trapping of the kinetic product.



SCHEME 9
Thermodynamic product trans to the imino group in the complex [Pt(Me)$_2$(i-PrPyCa)]

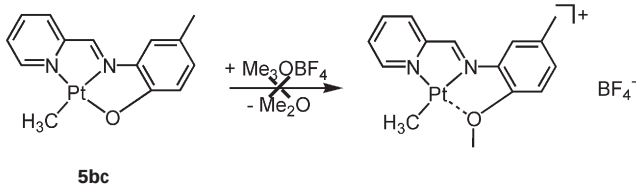
When the [Pt(Me)$_2$(NNO)] complexes **4aa**, **4ba** or **4bc** are heated in benzene overnight, green solutions result. Analyses of the products revealed that methane had been reductively eliminated and the phenolato oxygen coordinated (Scheme 10). After cooling to room temperature, a dark green compound was isolated as the main product according to ^{1}H NMR spectra. The thermally stable green compounds **5aa**, **5ba** and **5bc** are almost insoluble in most organic solvents. Addition of a drop of 2,2,2-trifluoroethan-1-ol improved the solubility of **5aa** and **5bc** sufficiently to obtain ^{1}H and ^{195}Pt NMR spectral data.



SCHEME 10
Reductive elimination of methane to give a neutral [Pt(Me)(NNO)] complex

Due to the strong coordination of the phenolato oxygen, no other reactivity was observed. In order to restore its semilability, we tried to methylate the oxygen of **5bc** 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 imino

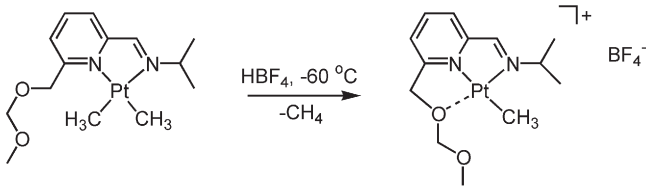
group to the *cis* position. The methylation was effected by addition of Me_3OBF_4 in nitromethane to **5bc** at low temperature (Scheme 11). The color change from green to red indicated that a [Pt(Me)$_2$(NN)] complex, and not a cationic platinum one, was formed. However, attempts to characterize this rather reactive compound failed and ^{1}H NMR spectra showed several undefined species.



5bc

SCHEME 11
Attempt to methylate **5bc**

In order to achieve the formation of a [Pt(Me)(NNO)] compound, which is easy to handle, yet reactive to hydrocarbon C–H bonds, we reasoned that the introduction of semilabile oxygen-containing arms at the other side (at position 6 of pyridine) of the PyCa ligand was needed. For that reason, **3cd**, **3dd** and **3ed** and their corresponding dimethylplatinum complexes **4cd**, **4dd** and **4ed** were synthesized. Hence, on treatment of **4dd** (red solution) with HBF_4 in diethyl ether at –60 °C, a yellow compound **5dd** immediately precipitated from solution (Scheme 12). This compound turned to yellow after filtration and was very reactive towards oxygen. Compound **5dd** was characterized by ^{1}H and ^{195}Pt NMR spectra. In the ^{1}H NMR spectrum, the signal of the imine proton was found at 8.90 ppm, with large $^3J_{HPt}$ of 116 Hz, suggesting the presence of a weak ligand trans to the imino group. A broad singlet was found at 6.93 ppm, indicating coordinated H_2O. (^{13}C-^{1}H correlation NMR spectroscopy showed no correlation peak at δ_H 6.93 ppm. Johansson et al. found in a cationic aquaplatinum(II) complex the signal of coordinated H_2O also in this region[18].)



4dd **5dd**

SCHEME 12
Cationic platinum complexes stabilized with a tridentate NNO ligand

$^{1}H,^{195}Pt$ HMQC spectroscopy (Fig. 1) gave more information about the structure of **5dd**. Correlation peaks were found at δ_H 8.90 (a), 6.93 (b), 4.78 (c), 4.45 (d), 3.91 (e), 1.19 (f) at δ_{Pt} –3072. From these correlations, the conclusion can be drawn that, despite coordination of H_2O (b, 6.93 ppm), also the oxygen ($CH_2OCH_2OCH_3$) of the NNO ligand coordinated, as appears from the correlation peaks at 4.78 (c, $^{3}J_{HPt}$ = 25.2 Hz) and 3.91 (e, $^{3}J_{HPt}$ = 22.2 Hz). The large J_{HPt} couplings suggest $^{3}J_{HPt}$ couplings. The CH_2 group c shows correlation only if the oxygen is coordinated. In principle, CH_2 hydrogen e could show a $^{4}J_{HPt}$ via the coordinated pyridine nitrogen, but this would then lie in the range of 0–5 Hz due to the strong trans influence of the methyl group. This implies that the cationic platinum center is stabilized by at least two oxygen atoms ($CH_2OCH_2OCH_3$ and H_2O). Furthermore, the ^{195}Pt chemical shift at –3072 ppm for **5dd** confirms the oxygen coordination compared to the C-coordination in $[Pt(Me)_2(NN)]$ (**4dd**), which was observed at –3427 ppm. Such straightforward differentiation of donor atoms by the ^{195}Pt chemical shift is known and viable for similar complexes[34].

One of our goals was to use these platinum(II) complexes $[Pt(Me)(NNO)]^+$ for the activation of hydrocarbon C–H bonds. Hence, in order to investigate the propensity of **5dd** to activate C–H bonds, we dissolved this complex in

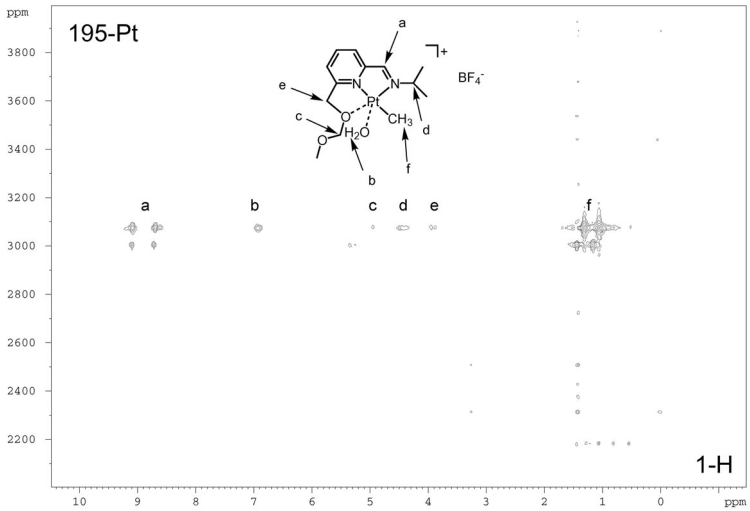


FIG. 1
$^{1}H,^{195}Pt$ HMQC spectrum of **5dd** (CD_2Cl_2, –20 °C)

2,2,2-trifluoroethan-1-ol (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 volatiles, showed minor signals at 7.14 and 7.66 ppm, indicating the presence of a benzene derivative, probably a phenylplatinum complex[18,35]. This indicates that *intramolecular* C–H activation of the ligand has occurred. Besides, several other major peaks in the spectrum suggest the presence of a number of other, unidentified, compounds.

CONCLUSIONS

The obtained neutral [Pt^{II}(Me)(NNO)] and cationic [Pt^{II}(Me)(NNO)]BF_4 complexes are not suitable for performing hydrocarbon C–H bond activation reactions, as the neutral [Pt^{II}(Me)(NNO)] complexes are too stable to display any reactivity. On the other hand, the catonic [Pt^{II}(Me)(NNO)]BF_4 complexes are too reactive, so that the activation reactions do not exhibit any selectivity to specific C–H bonds. Nevertheless, the neutral and cationic platinum complexes are very interesting compounds and they are comparable with other tridentate ligand systems[20,36] in their coordination and organometallic chemistry.

EXPERIMENTAL

General

All reactions were carried out in dry solvents under nitrogen atmosphere. Diethyl ether, tetrahydrofuran (THF), benzene and hexanes were distilled from sodium metal/benzophenone, dichloromethane and dichloromethane-d_2 from CaH_2, acetone-d_6 from B_2O_3 and 2,2,2-trifluoroethan-1-ol (TFE) from anhydrous $CaSO_4$. Chemicals were purchased from Acros Chimica, Aldrich and Fluka. Pyridine-2-carbaldehyde and (2-methoxyethyl)amine were distilled before use. 2-[(2-Pyridinylmethylidene)amino]ethan-1-ol [37], 2-(hydroxymethyl)-6-(methoxymethyl)pyridine[32], [$PtCl_2(Me_2S)_2$] [38], and bis[μ-(dimethyl sulfide)]tetramethyldiplatinum(II) [38] were synthesized via published methods. The ^{1}H and ^{13}C{^{1}H} NMR spectra (δ, ppm; *J*, Hz) were recorded at appropriate frequencies on Varian Mercury 300 (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C) and Inova 500 (499.88 MHz for ^{1}H, 125.70 MHz for ^{13}C) spectrometers. ^{195}Pt NMR was studied by ^{1}H,^{195}Pt HMQC spectroscopy[39] at 298 K on a Bruker DRX300 spectrometer (64.13 MHz).

Syntheses

2-{[(6-Methyl-2-pyridyl)methylidene]amino}phenol (**3aa**)

6-Methylpyridine-2-carbaldehyde (4.03 g, 33.3 mmol) and 2-aminophenol (3.63 g, 33.3 mmol) were dissolved in ethanol (50 ml). 3 Å molecular sieve was added to the solution and the

mixture was stirred overnight. The mixture was then filtered through Celite filter and the filter was washed with ethanol (10 ml). The filtrate was reduced in volume to 10 ml and hexane (50 ml) was added. The precipitate was collected on a glass filter and dried in vacuo to yield 3.62 g (53%) of a yellow powder. ^{1}H NMR (300.13 MHz, CD_2Cl_2): 8.79 (s, 1 H, N=CH), 8.00 (d, $^3J_{HH}$ = 7.8, 1 H, pyH), 7.71 (t, $^3J_{HH}$ = 7.5, 1 H, pyH), 7.51 (br s, 1 H, OH), 7.41 (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.5, 1 H, ArH), 7.24 (m, 2 H, ArH), 7.01 (dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.5, 1 H, ArH), 6.94 (dt, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.2, 1 H, ArH), 2.60 (s, 3 H, CH_3). ^{13}C NMR (75.47 MHz, acetone-d_6): 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-Pyridinylmethylidene)amino]phenol (**3ba**)

Pyridine-2-carbaldehyde (3.49 g, 32.6 mmol) and 2-aminophenol (3.56 g, 32.6 mmol) were dissolved in methanol (50 ml). 3 Å molecular sieve was added to the solution and the mixture was stirred overnight. The solid was filtered off and extracted twice with methanol (150 ml). The volatiles of the combined filtrates were removed by rotary evaporation, yielding 7.0 g of a brown oil. The oil was dissolved in methanol (15 ml), and diethyl ether (200 ml) was added to precipitate the product. The yellow solid was filtered off on a glass filter and washed with diethyl ether (3 × 20 ml). The solid was dried in vacuo to yield 2.48 g (38%) of a yellow powder. ^{1}H NMR (300.13 MHz, CD_2Cl_2): 8.85 (s, 1 H, N=CH), 8.71 (m, 1 H, pyH), 8.23 (d, $^3J_{HH}$ = 8.1, 1 H, pyH), 7.85 (dt, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.5, 1 H, pyH), 7.43 (dt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2, 1 H, ArH), 7.40 (dd, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2, 1 H, ArH), 7.38 (br s, 1 H, OH), 7.25 (dt, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.5, 1 H, ArH), 7.01 (dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.5, 1 H, ArH), 6.95 (dt, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.2, 1 H, ArH). ^{13}C NMR (75.47 MHz, acetone-d_6): 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-pyridylmethylidene)amino]ethane (**3bb**)

Pyridine-2-carbaldehyde (5 ml, 53 mmol) and 2-(methoxyethyl)amine (10 ml, 115 mmol) were placed together with 3 Å molecular sieve in a round-bottom flask at room temperature. After stirring this mixture for 30 min, the sieve was filtered off and washed with hexane. The volatiles were removed in vacuo to yield 8.5 g (98%) of a yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): 8.30 (d, 1 H, pyH), 8.09 (s, 1 H, imH), 7.67 (d, $^3J_{HH}$ = 7.5, 1 H, pyH), 7.37 (t, $^3J_{HH}$ = 7.5, 1 H, pyH), 6.94 ("t", $^3J_{HH}$ = 4.8, 1 H, pyH), 3.52 (t, $^3J_{HH}$ = 5.4, NCH_2), 3.38 (t, $^3J_{HH}$ = 5.4, 1 H, OCH_2), 7.03 (s, 3 H, CH_3). ^{13}C NMR (75.47 MHz, $CDCl_3$): 163.3, 154.4, 149.3, 124.7, 121.3, 71.8, 60.8, 58.7.

4-Methyl-2-[(2-pyridylmethylidene)amino]phenol (**3bc**)

2-Amino-4-methylphenol (2.56 g, 20.8 mmol), pyridine-2-carbaldehyde (2.31 g, 21.6 mmol) and a 3 Å molecular sieve were suspended in toluene (50 ml). This mixture was stirred at 100 °C for 90 min. The molecular sieve was filtered off and washed with toluene (20 ml). The volatiles 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%) of yellow needles. ^{1}H NMR (300.13 MHz, $CDCl_3$): 8.81 (s, 1 H, imH), 8.72 (d, $^3J_{HH}$ = 4.8, 1 H, pyH), 8.19 (d, $^3J_{HH}$ = 7.8, 1 H, pyH), 7.82 (dt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2, 1 H, pyH), 7.37 (ddd, $^3J_{HH}$ = 7.2, $^3J_{HH}$ = 4.5, $^4J_{HH}$ = 0.9, 1 H, pyH), 7.20 (br s, 1 H, ArH), 7.05 (dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.2, 1 H, ArH), 6.92 (d, $^3J_{HH}$ =

8.4, 1 H, ArH), 2.32 (s, 3 H, CH_3). ^{13}C NMR (75.47 MHz, $CDCl_3$): 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-Bis(hydroxymethyl)pyridine Monotrityl Ether (**1c′**)

Pyridine-2,6-dimethanol (2.44 g, 17.5 mmol) and 4-(dimethylamino)pyridine (0.03 g) were dissolved in pyridine (20 ml). Trityl chloride (4.89 g, 17.5 mmol) was then added and the solution was stirred at room temperature for 1 h, and then at 60 °C for another 1 h. The volatiles were removed by rotary evaporation, yielding a yellow oil. The oil was partly dissolved in methanol (50 ml). The mixture was filtered over a 1 cm layer of Celite and the volatiles were removed by rotary evaporation. The remaining oil was dissolved in dichloromethane and the layers formed were separated. The organic layer was washed with a saturated solution of K_2CO_3 in water (10 ml). The water layer was extracted with dichloromethane (20 ml) and the combined organic layers were dried with anhydrous $MgSO_4$. The volatiles were removed by rotary evaporation, yielding a yellow oil (4.76 g, 71%). The crude 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 in dichloromethane). To remove the last traces of pyridine and ethyl acetate, hexane (200 ml) was added to the oil. The volatiles were removed by rotary evaporation, yielding 2.83 g (42%) of a white solid. ^1H NMR (300.13 MHz, CD_2Cl_2): 7.74 (t, $^3J_{HH}$ = 7.8, 1 H, pyH), 7.62 (d, $^3J_{HH}$ = 7.8, 1 H, pyH), 7.50 (m, 6 H, ArH), 7.29 (m, 9 H, ArH), 7.10 (d, $^3J_{HH}$ = 7.5, 1 H, pyH), 4.62 (d, $^3J_{HH}$ = 4.5, 2 H, C**H**$_2$OH), 4.27 (s, 2 H, C**H**$_2$OCH$_3$), 3.57 (t, 4.5, 1 H, OH). ^{13}C NMR (75.47 MHz, $CDCl_3$): 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-[(Trityloxy)methyl]pyridine-2-carbaldehyde (**1c**)

Pyridine-2,6-dimethanol monotrityl ether (2.01 g, 5.3 mmol), SeO_2 (0.60 g, 5.4 mmol) and a 3 Å molecular sieve were mixed with hexane (150 ml). The mixture was refluxed overnight, turning 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 in dichloromethane). The solids were filtered off and washed with dichloromethane (10 ml). The volatiles were removed in vacuo, yielding a yellow oil (2.40 g). The oil was dissolved in dichloromethane (50 ml) and the layers were separated. The organic layer was washed with a saturated solution of K_2CO_3 in water (50 ml). The organic layer was dried with anhydrous $MgSO_4$ and the volatiles were removed by rotary evaporation, yielding a yellow oil (1.97 g, 99%). ^1H NMR (300.13 MHz, CD_2Cl_2): 9.90 (s, 1 H, COH), 7.92 (m, 2 H, pyH), 7.80 (m, 1 H, pyH), 7.50 (m, 6 H, ArH), 7.29 (m, 9 H, ArH), 4.38 (s, 2 H, C**H**$_2$OCH$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): 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-[(Trityloxy)methyl]pyridine-2-[(Isopropylimino)methyl] (**3cd**)

Compound **1cd** (0.49 g, 1.3 mmol) was dissolved in diethyl ether (40 ml). Isopropylamine (1 ml) and a 3 Å molecular sieve were added to this solution. The mixture was stirred at room temperature for 1 h; the solids were then filtered off and washed with diethyl ether (10 ml). The volatiles were removed by rotary evaporation, yielding a yellow oil (0.54 g, 100%). ^1H NMR (300.13 MHz, CD_2Cl_2): 8.26 (s, 1 H, imH), 7.8 (m, 3 H, pyH), 7.54 (m, 6 H, ArH), 7.30 (m, 9 H, ArH), 4.32 (s, 2 H, C**H**$_2$OCH$_3$), 3.59 (sept, $^3J_{HH}$ = 6.0, 1 H, C**H**(CH$_3$)$_2$),

1.23 (d, $^3J_{HH}$ = 6.0, 6 H, CH(C**H**$_3$)$_2$). ^{13}C NMR (75.47 MHz, CD_2Cl_2): 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-[(Methoxymethoxy)methyl]pyridine-2-methanol (**1d′**)

Pyridine-2,6-dimethanol (9.43 g, 67.8 mmol) was dissolved in THF (100 ml). Diethyl(isopropyl)amine (25 ml) was added to this mixture, followed by chloromethyl methyl ether (5 ml) at 0 °C. The solution was stirred overnight, resulting in an orange solution. Hexanes (50 ml) were added and the solvents were removed under reduced pressure. The oil was dissolved in dichloromethane (30 ml) and the product was washed with dilute potassium carbonate in water (50 ml). The water layer was extracted with dichloromethane (3 × 30 ml), and the combined organic layers were dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The product was purified by column chromatography, using 20% ethyl acetate in dichloromethane to start with. After the by-product had been eluted, the product was washed off the column with ethyl acetate. R_F of the product (20% EtOAc in dichloromethane) was 0.36. The volatiles were removed under reduced pressure, yielding a colorless oil (6.3 g, 51%). ^{1}H NMR (300.13 MHz, $CDCl_3$): 7.70 (t, $^3J_{HH}$ = 7.5, 1 H, pyH), 7.36 (d, $^3J_{HH}$ = 7.8, 1 H, pyH), 7.14 (d, $^3J_{HH}$ = 7.5, 1 H, pyH), 4.79 (s, 2 H, OCH_2O), 4.75 (s, 2 H, C**H**$_2$OH), 4.72 (s, 2 H, C**H**$_2$$OCH_2$), 3.78 (s, 1 H, OH), 3.43 (s, 3 H, OCH_3). ^{13}C NMR (75.47 MHz, $CDCl_3$): 158.9, 158.1, 137.6, 120.5, 137.6, 120.5, 119.3, 94.8, 70.3, 64.2, 59.9.

6-[(Methoxymethoxy)methyl]pyridine-2-carbaldehyde (**1d**)

6-[(Methoxymethoxy)methyl]pyridine-2-methanol (2.09 g) was dissolved in hexane (50 ml), followed by addition of SeO_2 (1.42 g). This mixture was refluxed at 80 °C overnight. The solution was filtered and washed with dilute potassium carbonate in water. The product was extracted with dichloromethane (3 × 30 ml) and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, yielding a colorless oil (2.06 g, 100%). ^{1}H NMR (300.13 MHz, $CDCl_3$): 10.06 (s, 1 H), 7.88 (m, 2 H, pyH), 7.90 (m, 1 H, pyH), 4.82 (s, 4 H, CH_2OCH_2), 3.44 (s, 3 H, CH_3). ^{13}C NMR (75.47 MHz, $CDCl_3$): 193.7, 160.1, 152.2, 138.0, 125.8, 120.3, 95.0, 71.0, 60.0.

2-[(Isopropylimino)methyl]-6-[(methoxymethoxy)methyl]pyridine (**3dd**)

Compound **1d** (0.83 g) was dissolved in isopropylamine and a 3 Å molecular sieve was added. This solution was stirred at room temperature for 30 min. The mixture was filtered and solids were washed with diethyl ether. The solvent of the filtrate was then removed under reduced pressure, yielding a colorless oil (0.91 g, 89%). ^{1}H NMR (300.13 MHz, $CDCl_3$): 8.35 (s, 1 H, imH), 7.79 (d, $^3J_{HH}$ = 7.5, 1 H, pyH), 7.77 (t, $^3J_{HH}$ = 7.5, 1 H, pyH), 7.47 (d, $^3J_{HH}$ = 7.8, 1 H, pyH), 4.78 (s, 2 H, OCH_2O), 4.71 (s, 2 H, C**H**$_2$$OCH_2O$), 3.61 (sept, ^3J = 5.4, 1 H, C**H**$(CH_3)_2$), 3.42 (s, 3 H, OCH_3), 1.26 (d, $^3J_{HH}$ = 6.6, 6 H, CH(C**H**$_3$)$_2$). ^{13}C NMR (75.47 MHz, CD_2Cl_2): 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′**)

This compound was synthesized by a modified literature procedure[32]. Pyridine-2,6-dimethanol (3.52 g, 25.3 mmol) was dissolved in dry 1,4-dioxane (60 ml). NaH (0.72 g, 30 mmol) was added and the mixture was stirred at room temperature for 45 min. Then, methyl iodide

(1.60 ml, 25.3 mmol) in 1,4-dioxane (20 ml) was slowly added to the mixture. The mixture was stirred at room temperature overnight. The orange solution was filtered over a glass filter with a 1-cm layer of filter aid. After removal of the volatiles by rotary evaporation, ^{1}H NMR spectra of a sample showed much starting material. To the remaining solids, dichloromethane (10 ml) was added, the solution was filtered over a glass filter and the volatiles were removed by rotary evaporation. The obtained oil was purified by column chromatography (SiO_2, MeOH/$CHCl_3$ (10:90 v/v), R_F 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, $CDCl_3$): 7.72 (t, $^3J_{HH}$ = 7.8, 1 H, pyH), 7.36 (d, $^3J_{HH}$ = 7.8, 1 H, pyH), 7.16 (t, $^3J_{HH}$ = 7.5, 1 H, pyH), 4.76 (s, 2 H, CH_2OCH_3), 4.61 (s, 2 H, CH_2OH), 3.81 (br s, 1 H, OH), 3.49 (s, 3 H, CH_3). ^{13}C NMR (75.47 MHz, $CDCl_3$): 158.8, 157.5, 137.5, 120.0, 119.4, 75.4, 64.2, 59.0.

6-(Methoxymethyl)pyridine-2-carbaldehyde (**1e**)

6-(Methoxymethyl)pyridine-2-methanol (0.14 g, 0.91 mmol) was dissolved in hexanes (40 ml). SeO_2 (0.11 g, 0.91 mmol) and a 3 Å molecular sieve were added to the solution and the mixture was heated to reflux overnight. The solution was filtered over a glass filter, the insoluble material was extracted with dichloromethane (10 ml) 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, $CDCl_3$): 10.07 (s, 1 H, (CO)H), 7.89 (m, 2 H, pyH), 7.67 (m, pyH), 4.68 (s, 2 H, CH_2), 3.52 (s, 3 H, CH_3). ^{13}C NMR (75.47 MHz, $CDCl_3$): 193.6, 159.6, 152.3, 137.8, 125.7, 120.6, 75.2, 59.1.

2-[(Isopropylimino)methyl]-6-(methoxymethyl)pyridine (**3ed**)

Compound **1e** (0.17 g, 1.12 mmol) was dissolved in diethyl ether (10 ml), and isopropylamine (1.0 ml, 12 mmol) and a 3 Å molecular sieve were added to this solution. After stirring at room temperature for 1 h, the mixture was filtered. The volatiles were removed by rotary evaporation, yielding 0.16 g (74%) of a colorless oil. ^{1}H NMR (300.13 MHz, CD_2Cl_2): 8.31 (s, 1 H, imH), 7.84 (d, $^3J_{HH}$ = 7.8, 1 H, pyH), 7.73 (t, $^3J_{HH}$ = 7.8, 1 H, pyH), 7.40 (d, $^3J_{HH}$ = 7.2, 1 H, pyH), 4.54 (s, 2 H, CH_2), 3.59 (sept, $^3J_{HH}$ = 6.3, 1 H, C**H**$(CH_3)_2$), 1.22 (d, $^3J_{HH}$ = 6.3, 1 H, CH(C**H**$_3)_2$). ^{13}C NMR (75.47 MHz, CD_2Cl_2): 159.6, 158.7, 154.9, 137.3, 122.4, 119.9, 75.7, 61.7, 58.9, 24.1.

cis-Dimethyl-(2-{[(6-methyl-2-pyridyl-κ*N*)methylidene]amino-κ*N*}phenol)platinum(II) (**4aa**) (cf. Scheme 7)

Bis[μ-(dimethyl sulfido)]tetramethyldiplatinum(II) (269.6 mg, 0.4697 mmol) and **3aa** (201.2 mg, 0.9477 mmol) were dissolved in THF (10 ml). A purple solution was formed immediately. After stirring at room temperature for 5 min, hexane (20 ml) was added. A red precipitate appeared. The solution volume was reduced to 10 ml in vacuum and another hexane (50 ml) was added. The precipitate was decanted and washed with hexane (2 × 15 ml) to yield 294.3 mg (71%) of the product as a red solid. ^{1}H NMR (300.13 MHz, acetone-d_6): 9.75 (s, $^3J_{HPt}$ = 30.0, 1 H, imH), 8.20 (t, $^3J_{HH}$ = 7.8, 1 H, pyH), 8.05 (d, $^3J_{HH}$ = 7.2, 1 H, pyH), 7.79 (d, $^3J_{HH}$ = 7.2, 1 H, pyH), 7.25 (m, 2 H, pyH), 7.00 (m, 2 H, ArH), 3.76 (br s, 1 H, OH), 2.88 (s, 3 H, CCH_3), 1.23 (s, $^2J_{HPt}$ = 87.7, 3 H, Pt-CH_3), 0.80 (s, $^2J_{HPt}$ = 92.1, 3 H, Pt-CH_3).

^{13}C NMR (75.47 MHz, acetone-d_6): 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 ($^1J_{CPt}$ = 817), –16.9 ($^1J_{CPt}$ = 817).

cis-Dimethyl-(2-{[(4-methyl-2-pyridyl-κ*N*)methylidene]amino-κ*N*}phenol)platinum(II) (**4ba**) (cf. Scheme 7)

Bis[μ-(dimethyl sulfido)]tetramethyldiplatinum(II) (206 mg, 0.35 mmol) and **3ba** (0.20 g, 0.94 mmol) were dissolved in THF (7 ml). A purple solution was formed immediately. After stirring at room temperature for 20 min, hexane (15 ml) was added. A red precipitate was decanted and washed with hexane (2 × 5 ml) and diethyl ether/pentane (1:3 v/v, total 10 ml), yielding a red solid (260.1 mg, 85%). ^{1}H NMR (300.13 MHz, acetone-d_6): 9.71 (s, $^3J_{HPt}$ = 32.1, 1 H, imH), 9.26 (d, $^3J_{HH}$ = 5.7, $^3J_{HPt}$ = 19.8, 1 H, pyH), 8.41 (dt, $^3J_{HH}$ = 7.8, $^3J_{HH}$ = 1.5, 1 H, pyH), 8.24 (d, $^3J_{HH}$ = 7.5, 1 H, pyH), 7.76 (dt, $^3J_{HH}$ = 6.6, $^4J_{HH}$ = 1.5, 1 H, pyH), 7.07 (d, $^3J_{HH}$ = 8.4, 1 H, ArH), 7.06 (s, 1 H, ArH), 6.90 (d, $^3J_{HH}$ = 8.4, 1 H, ArH), 2.83 (br s, 1 H, OH), 1.20 (s, $^3J_{HPt}$ = 86.4, 3 H, Pt-CH_3), 0.82 (s, $^3J_{HPt}$ = 88.2, 3 H, Pt-CH_3). ^{195}Pt NMR (64.3 MHz, acetone-d_6): –3339.

cis-Dimethyl{1-methoxy-2-[(2-pyridylmethylidene-κ*N*)amino-κ*N*]ethane}platinum(II) (**4bb**) (cf. Scheme 7)

Bis[μ-(dimethyl sulfido)]tetramethyldiplatinum(II) (531.6 mg, 0.926 mmol) and **3bb** (0.41 g, 2.5 mmol) were dissolved in THF (5 ml). A purple solution was formed immediately. After stirring at room temperature for 5 min, hexane (20 ml) was added. A red precipitate appeared and the volatiles were removed in vacuo. The red solid was washed with pentane (3 × 15 ml) to yield 709.7 mg (98%) of the product. ^{1}H NMR (500 MHz, $CDCl_3$): 9.19 (d, $^3J_{HH}$ = 5.0, 1 H, pyH), 9.12 (s, $^3J_{HPt}$ = 33.6, 1 H, imH), 8.07 (dt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.5, 1 H, pyH), 7.68 (d, $^3J_{HH}$ = 7.5, 1 H, pyH), 7.58 (dt, $^3J_{HH}$ = 5.5, $^4J_{HH}$ = 1.0, 2 H, pyH), 4.27 (t, $^3J_{HH}$ = 4.7, 2 H, NCH_2), 3.79 (t, $^3J_{HH}$ = 4.7, 2 H, OCH_2), 3.31 (s, 3 H, OCH_3), 1.23 (s, $^2J_{HPt}$ = 84.0, 3 H, Pt-CH_3), 1.12 (s, $^2J_{HPt}$ = 87.5, 3 H, Pt-CH_3). ^{13}C NMR (125.70 MHz, $CDCl_3$): 165.0, 156.7, 147.5 ($^2J_{CPt}$ = 35), 137.0, 128.2 ($^2J_{CPt}$ = 15), 126.4, 70.9, 59.1 ($^2J_{CPt}$ = 37), 59.1, –15.4 ($^1J_{CPt}$ = 789), –18.2 ($^1J_{CPt}$ = 806).

cis-Dimethyl{4-methyl-2-[(2-pyridylmethylidene-κ*N*)amino-κ*N*]phenol}platinum(II) (**4bc**) (cf. Scheme 7)

Bis[μ-(dimethyl sulfido)]tetramethyldiplatinum(II) (206 mg, 0.359 mmol) and **3bc** (0.20 g, 2.5 mmol) were dissolved in THF (7 ml). A purple solution was formed immediately. After stirring at room temperature for 5 min, hexane (15 ml) was added. A red precipitate appeared and the volatiles were removed in vacuo. The red solid was washed with hexane (10 ml), ether/pentane (1:9 v/v, 10 ml) and pentane (10 ml) to yield 279 mg (91%) of the product as a red solid. ^{1}H NMR (500 MHz, acetone-d_6): 9.65 (s, $^3J_{HPt}$ = 32.0, 1 H, imH), 9.28 (d, $^3J_{HH}$ = 5.5, 1 H, pyH), 8.45 (t, $^3J_{HH}$ = 8.0, 1 H, pyH), 8.24 (d, $^3J_{HH}$ = 8.0, 1 H, pyH), 7.96 (t, $^3J_{HH}$ = 5.5, 1 H, pyH), 7.05 (s, 1 H, ArH), 7.00 (d, $^3J_{HH}$ = 8.5, 1 H, ArH), 3.28 (s, 1 H, OH), 2.28 (s, 3 H, $ArCH_3$), 1.17 (s, $^2J_{HPt}$ = 85.0, 3 H, Pt-CH_3), 0.82 (s, $^2J_{HPt}$ = 85.5, 3 H, Pt-CH_3).

cis-Dimethyl{2-[(isopropylimino-κ*N*)methyl]-6-(methoxymethyl)pyridine-κ*N*}-platinum(II) (**4cd**) (cf. Scheme 7)

Compound **3cd** (0.29 g, 0.69 mmol) and bis[μ-(dimethyl sulfido)]tetramethyldiplatinum(II) (0.17 g, 0.30 mmol) were dissolved in THF (7 ml). A dark red solution was formed immediately. After stirring at room temperature for 5 min, hexane (15 ml) was added and the volatiles were removed in vacuo. The red solid was washed with hexane (10 ml) and pentane (10 ml) to yield 280 mg (85%) of the product. ^{1}H NMR (500 MHz, $CDCl_3$): 9.17 (s, $^3J_{HPt}$ = 32.4, 1 H, imH), 8.32 (d, $^3J_{HH}$ = 7.8, 1 H, pyH), 8.10 (t, $^3J_{HH}$ = 7.5, 1 H, pyH), 7.55 (d, $^3J_{HH}$ = 7.8, 1 H, pyH), 7.49 (d, $^3J_{HH}$ = 7.2, 6 H, ArH), 7.28 (m, 9 H, ArH), 4.73 (s, 2 H, CH_2), 4.68 (sept, $^3J_{HH}$ = 6.0, 1 H, C**H**$(CH_3)_2$), 1.39 (d, $^3J_{HH}$ = 6.6, 6 H, CH(C**H**$_3)_2$), 1.11 (s, $^2J_{HPt}$ = 88.8, 3 H, Pt-CH_3), 0.96 (s, $^2J_{HPt}$ = 83.7, 3 H, Pt-CH_3). ^{13}C NMR (125.70 MHz, acetone-d_6): 163.6, 161.8, 157.6, 144.1, 138.0, 128.9, 128.2, 127.5, 125.5, 125.3, 88.0, 67.4 ($^3J_{CPt}$ = 18), 54.3 ($^2J_{CPt}$ = 40), 22.4, –16.0 ($^1J_{CPt}$ = 868), –18.0 ($^1J_{CPt}$ = 805).

cis-Dimethyl{2-isopropylimino-κ*N*)methyl]-6-[(methoxy)methoxymethyl]pyridine-κ*N*}-platinum(II) (**4dd**) (cf. Scheme 7)

Compound **3dd** (0.255 g, 1.15 mmol) was added to bis[μ-(dimethyl sulfido)]tetramethyldiplatinum(II) (0.2847 g, 0.495 mmol) dissolved in THF (15 ml). The solution was stirred at room temperature for 15 min and then filtered through a glass filter filled with 1 cm of Celite. The residue was extracted with THF (30 ml). Hexanes (10 ml) were added to the filtrate and all the solvents were removed under reduced pressure. The product was dissolved in diethyl ether (1 ml) and pentane (20 ml) was added. The precipitate was decanted and washed with pentane (3 × 20 ml). The red solid was further dried under reduced pressure, yielding 0.43 g (94%) of the product. ^{1}H NMR (500 MHz, acetone-d_6): 9.60 (s, $^3J_{HPt}$ = 33.6, 1 H, imH), 8.26 (t, $^3J_{HH}$ = 7.8, 1 H, pyH), 7.93 (m, 2 H, pyH), 5.02 (s, 2 H, OCH_2O), 4.83 (s, 2 H, C**H**$_2$$OCH_2O$), 4.67 (sept, $^3J_{HH}$ = 6.3, 1 H, C**H**$(CH_3)_2$), 3.40 (s, 3 H, OCH_3), 1.42 (d, $^3J_{HH}$ = 6.6, 6 H, CH(C**H**$_3)_2$), 1.13 (s, $^2J_{HPt}$ = 84.9, 3 H, Pt-CH_3), 1.08 (s, $^2J_{HPt}$ = 91.5, 3 H, Pt-CH_3). ^{13}C NMR (125.70 MHz, acetone-d_6): 163.4, 161.8, 157.7, 137.9, 125.7, 125.5, 96.6, 70.1 ($^3J_{CPt}$ = 18), 55.1, 54.6 ($^2J_{CPt}$ = 40), 22.4, –16.0 ($^1J_{CPt}$ = 865), –18.1 ($^1J_{CPt}$ = 806). ^{195}Pt NMR (64.3 MHz, acetone-d_6): –3427.

cis-Dimethyl{2-[(isopropylimino-κ*N*)methyl]-6-(methoxymethyl)pyridine-κ*N*}-platinum(II) (**4ed**) (cf. Scheme 7)

Bis[μ-(dimethyl sulfido)]diplatinum(II) (82.3 mg, 0.143 mmol) and **3ed** (68.2 mg, 0.35 mmol) were dissolved in THF (15 ml). A dark red solution was formed immediately. After stirring at room temperature for 30 min, hexane (15 ml) was added. A red precipitate appeared and the volatiles were removed in vacuo. The red solid was washed with pentane (2 × 15 ml) to yield 41.9 mg (70%) of the product. ^{1}H NMR (500 MHz, CD_2Cl_2): 9.21 (s, $^3J_{HPt}$ = 35.0, 1 H, imH), 8.06 (t, $^3J_{HH}$ = 8.0, 1 H, pyH), 7.84 (d, $^3J_{HH}$ = 7.5, 1 H, pyH), 7.59 (d, $^3J_{HH}$ = 7.5, 1 H, pyH), 4.89 (s, 2 H, CH_2), 4.68 (sept, $^3J_{HH}$ = 6.5, 1 H, C**H**$(CH_3)_2$), 3.51 (s, 3 H, OCH_3), 1.41 (d, $^3J_{HH}$ = 6.5, 6 H, CH(C**H**$_3)_2$), 1.13 (s, $^2J_{HPt}$ = 84.5, 3 H, Pt-CH_3), 1.09 (s, $^2J_{HPt}$ = 90.5, 3 H, Pt-CH_3). ^{13}C NMR (125.70 MHz, benzene-d_6): 164.6, 159.5, 157.5, 136.5, 128.2, 124.3, 75.7 ($^3J_{CPt}$ = 17.8), 58.8, 54.9 ($^2J_{CPt}$ = 40.9), 23.0, –13.9 ($^1J_{CPt}$ = 861), –16.1 ($^1J_{CPt}$ = 807).

cis-{2-[(Isopropylimino-κ*N*)methyl]pyridine-κ*N*}dimethylplatinum(II) (**4bd**) (cf. Scheme 9)

Bis[μ-(dimethyl sulfido)]tetramethyldiplatinum(II) (336.7 mg, 0.586 mmol) and 2-[(isopropylimino)methyl]pyridine (185.7 mg, 1.25 mmol) were dissolved in THF (20 ml). A purple solution was formed immediately. After stirring at room temperature for 90 min, hexane (15 ml) was added. The volatiles were removed in vacuo. The red solid was washed with pentane (3 × 15 ml) to yield 361 mg (83%) of the product. ^{1}H NMR (300.13 MHz, $CDCl_3$): 9.22 (m, 1 H, pyH), 9.13 (s, $^3J_{HPt}$ = 35.4, 1 H, imH), 8.08 (dt, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.2 1 H, pyH), 7.67 (d, $^3J_{HH}$ = 7.5, 1 H, pyH), 7.56 (m, 1 H, pyH), 4.75 (sept, $^3J_{HH}$ = 6.6, 1 H, C**H**$(CH_3)_2$), 1.41 (d, $^3J_{HH}$ = 6.6, 6 H, CH(C**H**$_3)_2$), 1.24 (s, $^2J_{HPt}$ = 84.3, 3 H, Pt-CH_3), 1.09 (s, $^2J_{HPt}$ = 87.3, 3 H, Pt-CH_3). ^{13}C NMR (75.47 MHz, acetone-d_6): 161.0, 158.1, 146.8 ($^2J_{CPt}$ = 36.3), 137.3, 128.5, 127.4, 56.6 ($^2J_{CPt}$ = 37.4), 22.6, –15.08 ($^1J_{CPt}$ = 809), –17.6 ($^1J_{CPt}$ = 830).

Methyl(2-{[(6-methyl-2-pyridyl-κ*N*)methylidene]amino-κ*N*}phenolato)platinum(II) (**5aa**) (cf. Schemes 7 and 10)

Complex **4aa** (19.0 mg) was dissolved in benzene (30 ml). The red solution was stirred at reflux temperature overnight. After cooling to room temperature the volatiles were removed, yielding 18.9 mg (100%) of the product as a green solid, barely soluble in any solvent. However, ^{1}H NMR was possible in acetone-d_6 after addition of a drop of 2,2,2-trifluoroethan-1-ol. ^{1}H NMR (300.13 MHz, acetone-d_6): 8.86 (s, $^3J_{HPt}$ = 35.4, 1 H, imH), 7.89 (t, $^3J_{HH}$ = 8.1, 1 H, pyH), 7.40 (d, $^3J_{HH}$ = 7.5, 2 H, ArH), 7.24 (d, $^3J_{HH}$ = 8.7, 1 H, pyH), 6.93 (td, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.5, 1 H, pyH), 6.79 (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.8, 1 H, ArH), 6.38 (td, $^3J_{HH}$ = 6.9, $^4J_{HH}$ = 1.5, 1 H, ArH), 2.83 (s, 3 H, $ArCH_3$), 0.92 (s, $^2J_{HPt}$ = 76.8, 3 H, Pt-CH_3).

(Diethyl ether){1-methoxy-2-[(2-pyridylmethylidene-κ*N*)amino-κ*N*]ethane}-methylplatinum(II) Tetrafluoroborate (**5bb**) (cf. Schemes 7 and 8)

Complex **4bb** (70 mg, 0.18 mmol) was dissolved in diethyl ether (60 ml). The red-purple solution was cooled to –60 °C, after which 54% HBF_4 in diethyl ether (24 μl, 0.18 mmol) was added. A red-brown solid appeared. The mixture was stirred at –60 °C for another 90 min and then filtered through a glass filter P4. The solid was washed with cold diethyl ether (10 ml). The brown-red solid was further dried in vacuo for several hours. Yield 86 mg (89%). ^{1}H NMR (300.13 MHz, acetone-d_6): 9.11 (s, $^3J_{HPt}$ = 118.9, 1 H, imH), 8.66 (d, $^3J_{HH}$ = 5.1, 1 H, pyH), 8.45 (dt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.5, pyH), 8.33 (d, $^3J_{HH}$ = 7.5, 1 H, pyH), 8.00 (m, 1 H, pyH), 4.17 (t, $^3J_{HH}$ = 4.5, $^3J_{HPt}$ = 60.9, 2 H, C**H**$_2CH_2OCH_3$), 3.76 (t, 2 H, CH_2C**H**$_2OCH_3$), 3.33 (s, 3 H, OCH_3), 0.89 (s, $^2J_{HPt}$ = 75.6, 3 H, Pt-CH_3). Diethyl ether was found noncoordinating in the acetone-d_6 solution: 3.38 (q, 6.9, 4 H, OC**H**$_2CH_3$), 1.08 (t, 6.9, 6 H, OCH_2C**H**$_3$).

Methyl{4-methyl-2-[(2-pyridylmethylidene-κ*N*)amino]phenolato}platinum(II) (**5bc**) (cf. Scheme 10)

Complex **4bc** (7.1 mg) was dissolved in benzene (15 ml). The red solution was stirred at reflux temperature overnight. After cooling to room temperature, the volatiles were removed, yielding 7.0 mg (100%) of the product as a green solid, barely soluble in any solvent. However, ^{1}H NMR was possible in acetone-d_6 after addition of a drop of 2,2,2-trifluoroethan-1-ol.

^{1}H NMR (300.13 MHz, acetone-d_6): 8.67 (s, $^3J_{HPt}$ = 40.2, 1 H, imH), 8.48 (d, $^3J_{HH}$ = 5.1, $^3J_{HPt}$ = 54.3, 1 H, ArH), 7.97 (td, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.5, 1 H, pyH), 7.54 (br d, $^3J_{HH}$ = 7.5, 1 H, ArH), 7.36 (m, 1 H, pyH), 7.01 (s, 1 H, ArH), 6.79 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 1.8, 1 H, pyH), 6.51 (d, $^3J_{HH}$ = 8.4, 1 H, ArH), 2.83 (s, 3 H, $ArCH_3$), 0.92 (s, $^2J_{HPt}$ = 76.8, 3 H, Pt-CH_3).

{2-[(Isopropylimino-κ*N*)methyl]-6-[(methoxymethoxy)methyl]pyridine-κ*N*}-methylplatinum(II) Tetrafluoroborate (**5dd**)

Complex **4dd** (0.0457 g) was dissolved in diethyl ether (100 ml). The solution was cooled to –73 °C and a solution of 2.7% HBF_4 in diethyl ether (290 µl) was slowly added. The solution was stirred at –73 °C for 2 h. After decantation, the remaining solvent was removed under reduced pressure to give 0.034 g (77%) of the product as a yellow solid. ^{1}H NMR (300.13 MHz, CD_2Cl_2, –20 °C): 8.90 (s, $^3J_{HPt}$ = 116, 1 H, imH), 8.19 (m, 1 H, pyH), 7.92 (m, 2 H, pyH), 6.93 (br s, 2 H, H_2O), 4.78 (s, $^3J_{HPt}$ = 25.2, 2 H, O**C**$\mathbf{H}_2$O), 4.45 (sept, 1 H, $^3J_{HH}$ = 7.3, C**H**$(CH_3)_2$), 3.91 (s, $^3J_{HPt}$ = 22.2, 2 H, C$\mathbf{H}_2$$OCH_2$O), 3.38 (s, 3 H, OCH_3), 1.48 (d, $^3J_{HH}$ = 6.6, 6 H, CH(C$\mathbf{H}_3$)$_2$), 1.19 (s, $^3J_{HPt}$ = 77.1, 3 H, Pt-CH_3). ^{195}Pt NMR (64.3 MHz, CD_2Cl_2, –20 °C): –3072.

(Acetonitrile){2-[(isopropylimino-κ*N*)methyl]-6-[(methoxymethoxy)methyl]pyridine-κ*N*}-platinum(II) Tetrafluoroborate (**6dd**)

Complex **5dd** (10 mg) was dissolved in acetonitrile (2 ml). Excess acetonitrile was removed under reduced pressure, yielding 10 mg of the product as a yellow solid. ^{1}H NMR (300.13 MHz, acetone-d_6): 9.06 (s, $^3J_{HPt}$ = 103, 1 H, imH), 8.23 (m, 1 H, pyH), 8.06 (m, 2 H, pyH), 5.31 (s, 2 H, CH_2), 4.85 (s, 2 H, CH_2), 4.61 (1 H, sept, $^3J_{HH}$ = 6.5, C**H**$(CH_3)_2$), 3.42 (s, 3 H, OCH_3), 2.63 (s, $^4J_{HPt}$ = 14.1, CH_3CN), 1.45 (d, $^3J_{HH}$ = 6.6, 6 H, CH(C$\mathbf{H}_3$)$_2$), 1.18 (s, $^2J_{HPt}$ = 79.2, Pt-CH_3). ^{195}Pt NMR (64.3 MHz, acetone-d_6): –3599. ^{19}F NMR (acetone-d_6): –152 (BF_4^-).

(Acetonitrile){2-[(isopropylimino-κ*N*)methyl]pyridine-κ*N*}methylplatinum(II) Tetrafluoroborate (**6bd**)

Complex **4bd** (200 mg, 0.536 mmol) was dissolved in acetonitrile (60 ml) and cooled to –30 °C. Then 54% HBF_4 in diethyl ether (73 µl) was slowly added to the red solution. The mixture was brought to room temperature and the volatiles were removed by rotary evaporation. The remaining solid was washed with diethyl ether (2 × 15 ml) to yield 239 mg (92%) of the product as a yellow powder. ^{1}H NMR (500 MHz, acetone-d_6): 9.39 ($^3J_{HPt}$ = 105.0, 1 H, imH), 9.09 (d, $^3J_{HH}$ = 5.0, 1 H, pyH), 8.45 (dt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.5, pyH), 8.30 (d, $^3J_{HH}$ = 7.5, 1 H, pyH), 7.99 (m, 1 H, pyH), 4.45 (sept, $^3J_{HH}$ = 6.5, 1 H, C**H**$(CH_3)_2$), 3.80 (br s, 3 H, CH_3CN), 1.50 (d, $^3J_{HH}$ = 6.5, 6 H, CH(C$\mathbf{H}_3$)$_2$), 1.00 (s, $^2J_{HPt}$ = 77.0, 3 H, Pt-CH_3). ^{13}C (125.70 MHz, acetone-d_6): 210.1, 171.4, 154.6, 149.7 ($^2J_{CPt}$ = 32.2), 141.7, 131.4, 129.4, 121.7, 69.4, 58.6 ($^2J_{CPt}$ = 67.8), 22.7, –16.0 ($^1J_{CPt}$ = 697). ^{19}F NMR (acetonitrile-d_3): –151.8 (BF_4^-).

C–H Bond Activation Experiments

Complex **5dd** (10 mg) was dissolved in 2,2,2-trifluoroethan-1-ol (5 ml) and benzene (1 ml) was added. The mixture was stirred at room temperature for 5 days. Then, acetonitrile (0.5 ml) was added to stop the reaction and the solvents were removed under reduced pressure. In another experiment, the same procedure was followed but the reaction time was 2 h. A blank

experiment was carried out using a sample where only **5dd** was dissolved in 2,2,2-trifluoroethan-1-ol. After 5 days, acetonitrile was added, the solvents were removed under reduced pressure and the products were analyzed by ^{1}H NMR spectroscopy.

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