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Synthesis and reactivity of water-soluble platinum(II) complexes containing nitrogen ligands

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Abstract

A series of water-soluble platinum(II) complexes containing bidentate imino pyridine ligands L of the general formula $LPtX_2$ (X = Cl or Me) have been prepared. The dichloro complexes are very stable in water or dimethyl sulfoxide (DMSO), even at elevated temperatures, whereas the dimethyl complexes are less stable in these strongly polar solvents. In DMSO, an equilibrium between the complex $LPtMe_2$ and $(DMSO)_2PtMe_2$ is observed, whereas in water decomposition is observed within 1 day at room temperature.
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1. Introduction

Organic transformations catalysed by transition metals in aqueous media have become increasingly attractive due to the benign nature of water and the cost benefits [1]. Much work has been done in recent years to develop water-soluble phosphine ligands for transition metals, and sulfonated phosphines such as TPPTS are now quite common [2–5]. Some of these water-soluble phosphine ligands have even found industrial application, for example in the Rhône–Poulenc/Ruhrchemie hydroformylation process of propylene to butyraldehyde [4]. Other transformations of alkenes such as hydrogenation, alkylation, isomerisation and oxidation to form ketones or epoxides have also been reported [1] and, more recently, the hydration of alkynes [6,7]. Although sulfonate substituents ($-SO_3^-$) have been most popular, a number of other substituents such as carboxylate ($-CO_2^-$), phosphonate ($-PO_3^{2-}$) and polyhydroxy groups, have also been employed to increase the hydrophilicity of ligands and their metal complexes [5].

Whereas a considerable amount of research has been devoted to the development of water-soluble phosphines, nitrogen based ligands have received comparatively little attention so far. In the limited number of examples, the hydrophilicity has been introduced either through an ionic substituent (cationic or anionic) or a polyhydroxy substituent (as in carbohydrates). Sulfonated bipyridine ligands of type **A** were among the first examples of nitrogen ligands developed for applications in aqueous solution (see Fig. 1) [8–11]. Subsequently, several other monodentate [12] and bidentate ligands, either with ionic (**B** and **C**) [13–15] or polyhydroxy (**D**) [16–19] substituents have been developed. Examples of multidentate ligands are the tridentate tris(pyrazolyl)methane (**E**) [20] and the tris(pyridyl)amine [21] derivatives as well as tetradentate porphyrin ligands [22]. An additional class of water-soluble nitrogen ligands worth mentioning in this context are amino acids, which have been studied extensively in combination with platinum [23].

We have recently embarked on a research program towards the synthesis of water-soluble complexes based

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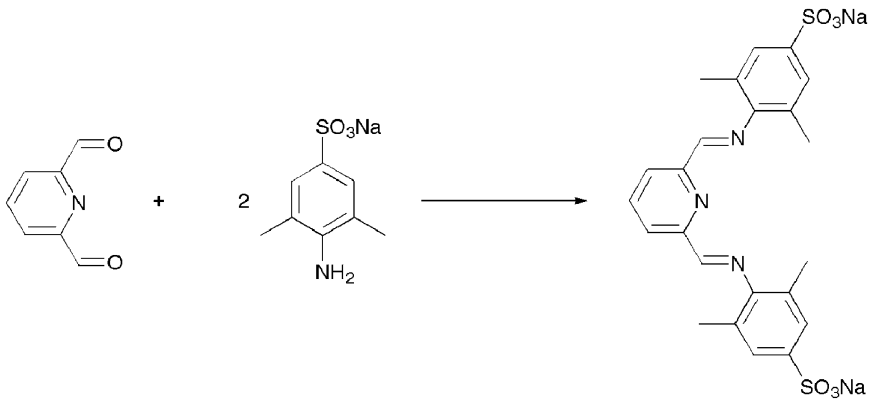


2e (1)

on nitrogen ligands. These complexes have potential applications in catalysis, for example C–H activation in water (Shilov chemistry) [24] or as anti-cancer agents [25,26]. Here we present our initial studies on the synthesis and characterization of platinum(II) dihalide and dialkyl complexes containing sulfonated imino pyridine ligands and their stability in strongly polar solvents such as H_2O and dimethyl sulfoxide (DMSO).

2. Results and discussion

Sulfonated iminopyridine ligands **2a**–**c** were prepared by condensation of pyridine carboxaldehyde and the sodium salt of the appropriate sulfanilic acid via a method recently described by Buffin (Scheme 1) [14]. It should be noted that for all preparations strictly anhydrous solvents and a nitrogen atmosphere are required; sulfonated iminopyridines are very moisture-sensitive. 2,6-Dialkyl sulfanilic acids **1c**–**d** were prepared from the corresponding aniline and H_2SO_4 [27]. Under the conditions used for the successful preparation of **1a**–**c**, the reaction of the bulkier 2,6-diisopropylphenyl derivative **1d** with pyridine carboxaldehyde gave repeatedly a mixture of product and starting materials, which could not be separated. In addition to the series of bidentate ligands, we also prepared a potentially tridentate ligand **2e** from pyridine dicarboxaldehyde and **1c**, as shown in Eq. (1). The same procedure affords the bis(imino)pyridine derivative **2e** in good yield.

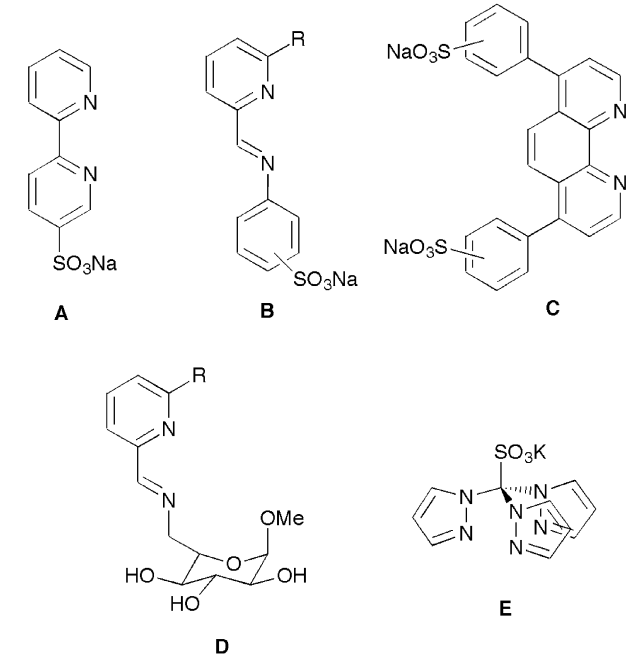
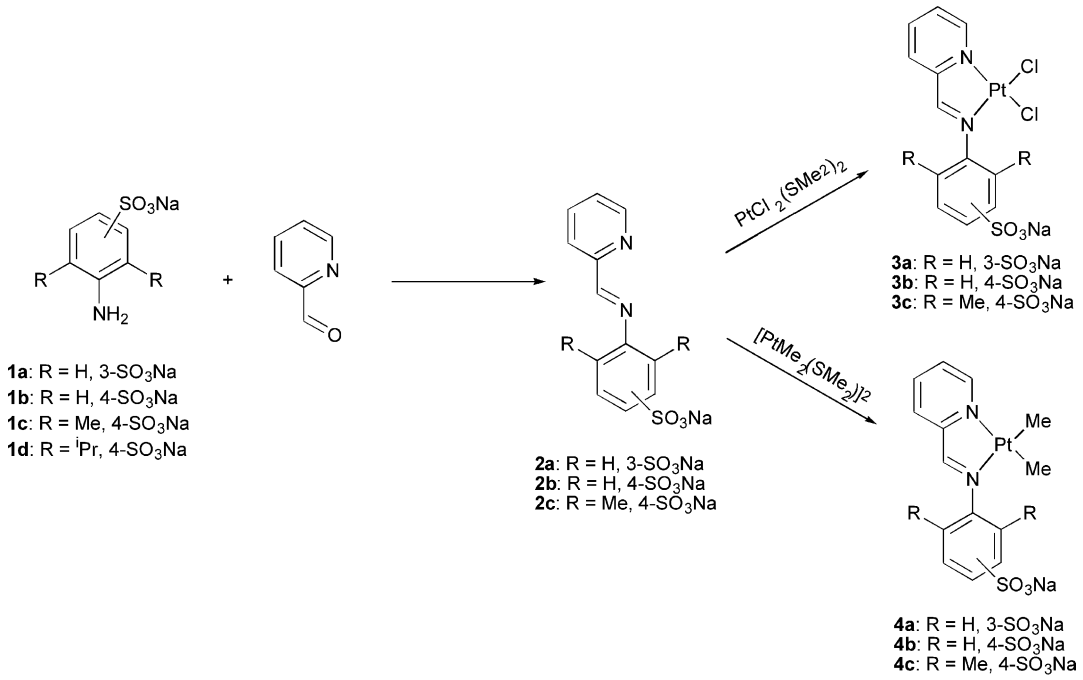


Fig. 1. Examples of water-soluble nitrogen ligands.

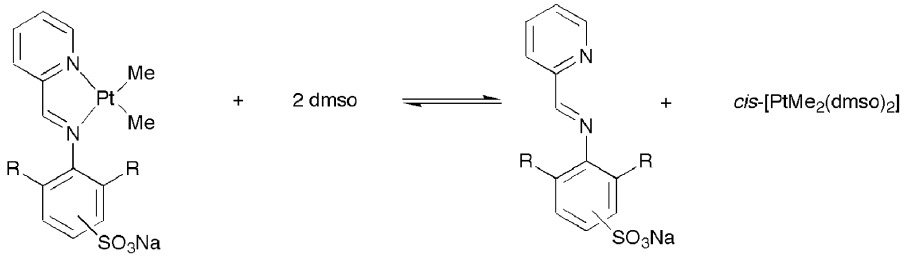
Platinum(II) dihalide complexes **3a**–**c** (see Scheme 1) are prepared by the addition of the iminopyridine ligand, dissolved in a minimal amount of DMSO, to $PtCl_2(SMe_2)_2$ (mixture of *cis* and *trans*). Precipitation of the product with dichloromethane affords the dichloro complexes **3a**–**c** in good yield and purity, which can be freed from residual DMSO by dissolving in methanol and precipitation with diethyl ether. It should be noted that these Pt(II) complexes are insoluble in common organic solvents such as dichloromethane, thf or toluene, but very soluble in polar solvents such as water, DMSO or DMF and, unlike the free ligands, are very stable in water. For example, a solution of **3b** in D_2O, heated at 80 °C for 24 h, did not show any change or signs of decomposition. Reaction of the potentially tridentate ligand **2e** with $PtCl_2(SMe_2)_2$ in DMSO at room temperature for 2 days resulted in a dark orange solution, which upon addition of DCM yielded an orange product. However, ^{1}H-NMR in d_6-DMSO revealed only the presence of starting materials. The same reaction in methanol at room temperature also only yielded the starting materials back after workup. Similar difficulties have been encountered with the tridentate ligand terpyridine (terpy) [28].



Scheme 1.

Platinum(II) dimethyl complexes **4a**–**c** are prepared by a similar procedure, using $[PtMe_2(\mu\text{-}SMe_2)]_2$ as the Pt precursor (see Scheme 1). The reactions were carried out in a small amount of DMSO as the solvent and the products were precipitated by the addition of toluene, washed with toluene and dichloromethane to afford the pure dark-red complexes. When the reaction was carried out in methanol, a complex mixture of products was obtained, which was not further investigated.

The dimethyl complexes **4a**–**c** have been characterized by ^{1}H-NMR and microanalysis. Noteworthy are the ^{195}Pt satellites on the imine proton ($J_{Pt-H} \approx 33$ Hz) and the two different Pt-methyl signals ($J_{Pt-H} \approx 85$ Hz), confirming the complex formation. ^{1}H-NMR spectra have been recorded in d_6-DMSO and D_2O. ^{13}C-NMR spectra could not be obtained due to decomposition in these solvents (*vide infra*). Freshly prepared samples in either solvent show a clean ^{1}H-NMR spectrum of the complex. However, typically within a day, decomposition is observed to occur for all complexes **4a**–**c** in both solvents, giving rise to a mixture of products. Besides the signals for the starting complex, the decomposition products in d_6-DMSO can be readily identified as free ligand and *cis*-$[PtMe_2(d_6\text{-}Me_2SO)_2]$ based on the known chemicals shifts of the ligand and *cis*-$[PtMe_2(Me_2SO)_2]$ which has been prepared previously [29]. These observations reveal that the bidentate ligand is being displaced from the metal by the DMSO solvent, according to Eq. (2).



(2)

Similar reactions to the reverse reaction of Eq. (2), where the DMSO ligands in *cis*-$[PtR_2(Me_2SO)_2]$ (R = methyl or phenyl) are displaced by bidentate nitrogen ligands such as bipyridine or phenanthroline, have been studied previously in benzene and in acetonitrile solu-

tion [30–32]. It appears that, due to the presence of the large excess of DMSO, in the case of complexes **4a**–**c** the sulfonated iminopyridine ligands are competing for coordination with the DMSO solvent, resulting in an equilibrium. Similar observations have been made for *cis*-[$PtMe_2(Me_2SO)_2$] in D_2O and CD_3CN as the solvent, which results in an equilibrium between the starting complex, the solvento species *cis*-[$PtMe_2(Me_2SO)(D_2O)$] or *cis*-[$PtMe_2(Me_2SO)(CD_3CN)$], respectively, and free DMSO [32,33]. The equilibrium (Eq. (2)) can be reversed by the addition of toluene or DCM, resulting in the precipitation of the Pt(II) complexes. This strategy is successfully exploited in the synthesis of complexes **4a**–**c** from *cis*-[$PtMe_2(Me_2S)]_2$ and the ligand in DMSO.

In D_2O, decomposition of **4a**–**c** is also observed, but in this case a more complex mixture of products is obtained which could not be analysed. Considering that D_2O easily displaces a DMSO ligand in the complex *cis*-[$PtMe_2(Me_2SO)_2$] [33], and that DMSO can displace the nitrogen ligand, we believe that in this case the sulfonated iminopyridine ligands are displaced by D_2O, followed by deuterolysis of the ligand and further degradation of the resulting aqua alkyl platinum complexes. Traces of methane are also observed, but no formation of Pt(0). From these observations it is clear that these water-soluble nitrogen ligands provide insufficient stabilization of platinum(II) dialkyl complexes in strong donor solvents such as DMSO or D_2O. The different behaviour of the dialkyl Pt(II) complexes compared to the dichloro complexes is ascribed to the stronger *trans* effect of the methyl ligands, thereby weakening the Pt–N bonds.

In conclusion, we have prepared a series of water-soluble Pt(II) dichloro and dimethyl complexes containing sulfonated iminopyridine ligands. The dichloro complexes are stable in strongly polar solvents such as H_2O and DMSO, whereas the dimethyl complexes slowly decompose in these solvents at room temperature. These studies have shown that for the application of platinum complexes in strongly polar media such as H_2O, in particular where metal carbon bonds are involved (e.g. Shilov chemistry), strong metal ligand interactions will be required to prevent catalyst degradation. We are currently investigating other, more strongly coordinating, water-soluble nitrogen and oxygen ligands, with the aim to generate Pt(II) complexes that show greater stability in such strongly polar environments.

3. Experimental

3.1. General

All moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk or cannula techniques, or in a conventional nitrogen-filled glove box. NMR spectra were recorded on a Bruker AC-250 spectrometer at 250 MHz (^1H) and 62.9 MHz (^{13}C) at 293 K; chemical shifts for ^1H and ^{13}C-NMR are referenced to the residual protio impurity and to the ^{13}C-NMR signal of the deuterated solvent. Mass spectra were recorded on either a VG Autospec or a VG Platform II spectrometer. Elemental analyses were performed by the Science Technical Support Unit at the London Metropolitan University.

3.2. Solvents and reagents

Toluene and pentane were dried by passing through a column, filled with commercially available Q-5 reagent (13 wt.% CuO on alumina) and activated alumina (pellets, 3 mm). Benzene and DMSO were dried by prolonged reflux over a suitable drying agent (Na and CaH_2, respectively) under an atmosphere of nitrogen, and distilled prior to use. DMF was dried and distilled over molecular sieves (4 Å). Methanol and ethanol were dried by heating under reflux with sodium metal and then distilled under nitrogen. Diethyl ether and tetrahydrofuran were dried over sodium metal with a benzophenone ketyl indicator, whereas dichloromethane was dried over CaH_2. $PtCl_2(SMe_2)_2$ and [$PtMe_2(\mu$-$SMe_2)]_2$ were prepared according to literature procedures [34,35]. Ligands **2a** and **2b** were prepared according to the procedure described by Buffin [14]. 2,6-dimethylsulfanilic acid **1c** was prepared according to a literature procedure [27]. All other chemicals and NMR solvents were obtained commercially and used as received.

3.3. 2,6-Diisopropyl sulfanilic acid

In a 250 ml round-bottomed flask, concentrated H_2SO_4 (12.25 g, 0.125 mol) was added to water (23 ml). To this mixture, 2,6-diisopropylaniline (22.15, 0.125 mol) was added dropwise over 20 min via a dropping funnel. Water was then removed by distillation under vacuum (water pump) and the reaction mixture was heated to 260 °C for 3 h. NaOH solution (7.5 g, 120 ml H_2O) was added to the cooled reaction mixture. This mixture was heated again and filtered hot. The filtrate was acidified with concentrated HCl to pH 2.5 and then cooled to initiate precipitation. To this suspension, water (175 ml) was added and then heated to 90 °C, during which 20% Na_2CO_3 was added to obtain pH 8. Charcoal (2.5 g) was added to the mixture, after which it was filtered hot. NaCl (20 g) was added to the filtrate and HCl was added dropwise to initiate product precipitation. The resulting precipitate was isolated by filtration to afford 2,6-diisopropyl sulfanilic acid as a white solid.

Yield: 10.3 g (32%). ^{1}H-NMR (250 MHz, d_6-DMSO): δ 7.41 (s, 2H, Ar-*H*), 3.15 (sept, 2H, C*H*(CH_3)$_2$), 1.16 (d, 12H, CH(C*H*$_3$)$_2$). ^{13}C-NMR (62.9 MHz, D_2O): δ 146.6, 140.08, 127.70, 121.20, 27.04 (*C*H), 23.35 (*C*H$_3$). EI mass spectrum (*m*/*z*): 257 (40, [M]$^+$), 242 (100, [M−Me]$^+$).

3.4. General synthesis of sodium 2,6-dialkylsulfanilate *1c* and *1d*

In a 100 ml round-bottom-flask, NaOMe was dissolved in dry methanol (30 ml), after which one equivalent of the dialkylsulfanilic acid was added. The solution was stirred for 30 min during which the sodium salt precipitates. Methanol was evaporated, affording the sodium salt as a white solid, which was pure by NMR.

1c: Yield 93%. ^{1}H-NMR (250 MHz, D_2O): δ 7.33 (s, 2H, Ar-*H*), 2.16 (s, 6H, C*H*$_3$). ^{13}C-NMR (62.9 MHz, D_2O): δ 147.21, 135.10, 127.84, 126.37, 19.45 (*C*H$_3$).

1d: Yield 81%. ^{1}H-NMR (250 MHz, D_2O): δ 7.43 (s, 2H, Ar-*H*), 2.90 (sept, 2H, C*H*(CH_3)$_2$), 1.13 (d, 12H, CH(C*H*$_3$)$_2$). ^{13}C-NMR (62.9 MHz, D_2O): δ 145.51, 136.79, 135.38, 123.06, 29.94 (*C*H), 24.35 (*C*H$_3$).

3.5. 2-((2,6-Dimethyl-4-sulfonyl-phenylimino)methyl)pyridine *2c*

In a 3-necked 250 ml round-bottom flask equipped with a reflux condenser and a nitrogen inlet, sodium 2,6-dimethylsulfanilate (2 g, 8.97 mmol) was added to a solution of dry ethanol (100 ml) and dry benzene (20 ml) under an atmosphere of nitrogen. The resulting mixture was heated to reflux and anhydrous methanol was added until all of the salt had dissolved. 2-pyridinecarboxaldehyde (0.85 ml, 8.97 mmol) was then added dropwise. The solution was heated until approximately half of its original volume remained and then cooled to ambient temperature to initiate product precipitation. After the addition of diethylether (30 ml), the product **2c** was isolated by filtration and washed with diethyl ether.

Yellow solid. Yield: 2.24 g (80%). ^{1}H-NMR (250 MHz, d_6-DMSO): δ 8.69 (d, 1H, py-*H*), 8.25 (s, 1H, *H*C=N), 8.20 (d, 1H, py-*H*), 7.99 (t, 1H, py-*H*), 7.61 (dd, 1H, py-*H*), 7.32 (s, 2H, Ar-*H*), 2.09 (s, 6H, –C*H*$_3$). ^{13}C-NMR (62.9 MHz, d_6-DMSO): δ 163.78 (s, H*C*=N), 153.63, 149.66, 143.89, 137.24, 125.96, 125.36, 120.92, 17.90 (s, –C*H*$_3$). FAB mass spectrum (*m*/*z*): 313 ([M]$^+$, 46). Anal. Calc. for $C_{14}H_{13}N_2SO_3Na$: C, 53.84; H, 4.20; N, 8.97. Found: C, 53.94; H, 4.00; N, 8.84%.

3.6. 2,6-bis((2,6-Dimethyl-4-sulfonyl-phenylimino)methyl)pyridine *2e*

In a 3-necked 250 ml round-bottom flask equipped with a suba seal, reflux condenser and a nitrogen inlet, **1c** (0.99 g, 4.44 mmol) was added to dry ethanol (70 ml). Pyridine dicarboxaldehyde (0.30 g, 2.22 mmol) was dissolved in dry benzene (10 ml) in a separate schlenk flask and then added. A further 10 ml of dry benzene was added to the mixture and then heated under reflux for 2 h. All solvent was distilled off and the yellow residue was washed with dry pentane and dried under vacuum overnight, affording the product as a yellow solid in 78% yield. ^{1}H-NMR (250 MHz, d_6-DMSO): δ 8.40 (d, 2H, py-*H*), 8.38 (s, 2H, *H*C=N), 8.19 (t, 1H, py-*H*), 7.34 (s, 4H, Ar-*H*), 2.09 (s, 12H, C*H*$_3$). ^{13}C-NMR (62.9 MHz, d_6-DMSO): δ 163.1 (*C*H=N), 153.8, 150.0, 143.6, 138.4, 125.4 (ArC_m), 122.9, 120.7, 17.88 (*C*H$_3$). FAB(+) mass spectrum (*m*/*z*): 569 ([M+Na]$^+$, 7), 546 ([M]$^+$, 10). Anal. Calc. for $C_{23}H_{21}N_3S_2O_6Na_2$: C, 50.64; H, 3.88; N, 7.70. Found: C, 50.49; H, 3.68; N, 7.50%.

3.7. 2-((3-Sulfonyl-phenylimino)methyl)pyridine platinum(II) dichloride *3a*

The sulfonated imino pyridine ligand **2a** (191 mg, 0.67 mmol) was dissolved in a small amount of DMSO (1 ml). This solution was transferred to a separate Schlenk flask containing $PtCl_2(SMe_2)_2$ (262 mg, 0.67 mmol). The yellow colour changed to orange-red within 15 min. After stirring overnight, dichloromethane was added to precipitate the product, which was filtered and washed with DCM. In order to remove small residues of DMSO, the complex was dissolved in methanol, precipitated with diethyl ether and dried under vacuum. Complexes **3b** and **3c** were prepared by the same procedure.

3a: Brown solid. Yield: 218 mg (59%). ^{1}H-NMR (250 MHz, d_6-DMSO): δ 9.47 (d, 1H, py-*H*), 9.33 (s, 1H, *H*C=N), 8.44 (t, 1H, py-*H*), 8.25 (d, 1H, py-*H*), 7.99 (t, 1H, py-*H*), 7.65 (m, 2H, Ar-*H*), 7.40 (m, 2H, Ar-*H*). ^{13}C-NMR (62.9 MHz, d_6-DMSO): δ 172.8, 167.0, 158.3, 149.0, 147.6, 140.5, 134.3, 129.4, 127.4, 125.9, 126.7, 120.5. FAB(+) mass spectrum (*m*/*z*): 551 ([M]$^+$, 15). Anal. Calc. for $C_{12}H_9N_2SO_3NaPtCl_2$: C, 26.19; H, 1.65; N, 5.09. Found: C, 26.27; H, 1.69; N, 4.91%.

3b: Orange solid. Yield: 360 mg (69%). ^{1}H-NMR (250 MHz, D_2O): δ 9.04 (s, 1H, *H*C=N), 9.01 (d, 1H, py-*H*), 8.16 (t, 1H, py-*H*), 8.06 (d, 1H, py-*H*), 7.72 (d, 2H, Ar-*H*), 7.65 (t, 1H, py-*H*), 7.50 (d, 2H, Ar-*H*). ^{13}C-NMR (62.9 MHz, D_2O): δ 175.7 (s, H*C*=N), 159.1, 152.3, 150.8, 146.1, 143.7, 133.0, 132.8, 128.6, 127.6. FAB(−) mass spectrum (*m*/*z*): 550 ([M]$^-$, 25), 527 ([M−Na]$^-$, 100). Anal. Calc. for $C_{12}H_9N_2SO_3NaPtCl_2$: C, 26.19; H, 1.65; N, 5.09. Found: C, 26.17; H, 1.62; N, 4.92%.

3c: Orange solid. Yield: 0.56 g (76%). ^{1}H-NMR (250 MHz, D_2O): δ 9.31 (d, 1H, py-*H*), 9.04 (s, 1H, *H*C=N), 8.33 (t, 1H, py-*H*), 8.14 (d, 1H, py-*H*), 7.88 (t, 1H, py-*H*), 7.54 (s, 2H, Ar-*H*), 2.27 (s, 6H, C*H*$_3$). ^{13}C-NMR (62.9 MHz, D_2O): δ 176.73 (s, H*C*=N), 158.89, 152.80, 149.58, 144.89, 144.00, 135.22, 132.88, 132.69, 127.56,

19.87 (s, CH_3). FAB(+) mass spectrum (m/z): 579 ($[M]^+$, 14). Anal. Calc. for $C_{14}H_{13}N_2PtCl_2NaSO_3$: C, 29.08; H, 2.27; N, 4.84. Found: C, 28.83; H, 2.24; N, 4.75%.

3.8. 2-((3-Sulfonyl-phenylimino)methyl)pyridine platinum(II) dimethyl **4a**

A mixture of $[PtMe_2(\mu\text{-}SMe_2)]_2$ (130 mg; 0.23 mmol) and the sulfonated iminopyridine ligand **2a** (125 mg; 0.44 mmol) is dissolved in a small amount of DMSO (< 0.5 ml) and stirred at room temperature overnight. After the addition of an excess toluene (ca. 10 ml), the suspension is stirred overnight, filtered, washed with toluene and finally with dichloromethane. Complexes **4b** and **4c** were prepared by the same procedure.

4a: Red/purple solid. Yield: 191 mg (85%). ^{1}H-NMR (250 MHz, D_2O): δ 9.19 (s, 1H, CH=N, $J_{H-Pt} = 30$ Hz), 8.86 (m, 1H, 6-pyr$H$), 7.8–7.0 (m, ArH and pyr$H$), 0.94 (s, 3H, Pt–CH_3, $J_{H-Pt} = 80$ Hz), 0.50 (s, 3H, Pt–CH_3, $J_{H-Pt} = 84$ Hz).

4b: Dark-red solid. Yield: 173 mg (84%). ^{1}H-NMR (250 MHz, D_2O): δ 9.27 (s, 1H, CH=N, $J_{H-Pt} = 31$ Hz), 8.88 (d, 1H, 6-pyr$H$, $J = 5.3$ Hz, $J_{H-Pt} = 20$ Hz), 8.09 (t, 1H, 4-pyr$H$, $J = 7.7$ Hz), 7.90 (d, 1H, 3-pyr$H$, $J = 7.4$ Hz), 7.77 (d, 2H, ArH, $J = 8.4$ Hz), 7.61 (t, 1H, 5-pyr$H$, $J = 6.6$ Hz), 7.18 (d, 2H, ArH, $J = 8.4$ Hz), 0.98 (s, 3H, Pt–CH_3, $J_{H-Pt} = 85$ Hz), 0.52 (s, 3H, Pt–CH_3, $J_{H-Pt} =$ 85 Hz). Anal. Calc. for $C_{14}H_{15}N_2SO_3NaPt$: C, 33.01; H, 2.97; N, 5.50. Found: C, 33.13; H, 3.08; N, 5.38%.

4c: Dark-red solid. Yield: 182 mg (74%). ^{1}H-NMR (250 MHz, D_2O): δ 9.30 (s, 1H, CH=N, $J_{H-Pt} = 36$ Hz), 9.04 (d, 1H, 6-pyr$H$), 8.21 (t, 1H, 4-pyr$H$, $J = 7.8$ Hz), 7.99 (d, 1H, 3-pyr$H$, $J = 7.5$ Hz), 7.76 (t, 1H, 5-pyr$H$, $J = 6.3$ Hz), 7.56 (s, 2H, ArH), 2.13 (s, 6H, ArCH_3), 0.99 (s, 3H, Pt–CH_3, $J_{H-Pt} = 84$ Hz), 0.27 (s, 3H, Pt–CH_3, $J_{H-Pt} = 86$ Hz). Anal. Calc. for $C_{16}H_{19}N_2SO_3$-NaPt: C, 35.76; H, 3.56; N, 5.21. Found: C, 35.86; H, 3.53; N, 5.12%.

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