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Water-Soluble Mono- and Dimethyl N-Heterocyclic Carbene Platinum(II) Complexes: Synthesis and Reactivity

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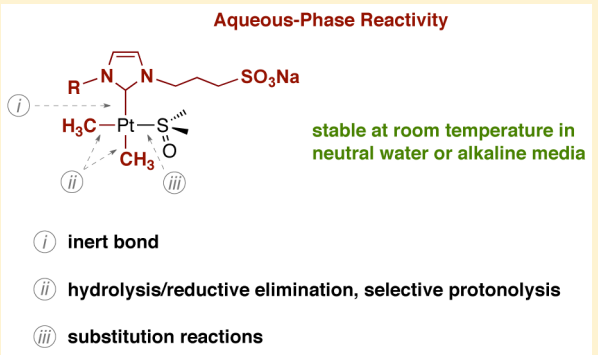
Supporting Information

ABSTRACT: A family of water-soluble dimethyl complexes of formula *cis*-[$PtMe_2$(dmso)(NHC·Na)] (**2**), in which NHC is an anionic N-heterocyclic carbene bearing a sulfonatopropyl chain on one of the nitrogen atoms and a sulfonatopropyl (**a**), methyl (**b**), mesityl (**c**), or 2,6-diisopropylphenyl group (**d**) on the other, have been prepared. The hydrolytic stability of the Pt−C bonds in these complexes under different neutral, alkaline, and acidic aqueous conditions has also been studied. Complexes **2** were found to be quite stable at room temperature in water under neutral or alkaline conditions. Degradation occurred at higher temperatures but involved C sp^3−H activation and C−C reductive elimination processes in addition to Pt−Me bond hydrolysis. Hydrolytic cleavage of the platinum−methyl bonds was favored by good nucleophiles. Thus, the addition of KCN to an aqueous solution of **2** resulted in formation of the monomethyl complexes K[$PtMe(CN)_2$(NHC·Na)] (**9**), whereas the dimethyl complexes K[$PtMe_2$(CNR)(NHC·Na)] (**10**) were formed with the isocyanide $CNCH_2COOK$. The addition of stoichiometric amounts of protic acids to aqueous solutions of **2** resulted in the clean cleavage of one or both platinum(II)−methyl bonds. Thus, the reaction of **2** with HCl afforded the complexes [PtClMe(dmso)(NHC·Na)] (**3**) and [$PtCl_2$(dmso)(NHC·Na)] (**4**), whereas [$PtMe(OH_2)$(dmso)(NHC)] (**5**) and [$Pt(OH_2)_2$(dmso)(NHC)][BF_4] (**7**) were obtained upon treatment with HBF_4. The crystal structure of **9a** is remarkable in light of the longitudinal channels around 6 Å in diameter internally decorated with Pt−Me bonds.



INTRODUCTION

N-Heterocyclic carbenes (NHCs)[1] derived from imidazole are characterized by their versatile substitution and outstanding features as ancillary ligands. Their strong σ-donor capabilities in conjunction with usual imposed steric protection tend to afford robust bonds to metals in fairly stable complexes[2] that are able to catalyze a wide range of homogeneous processes[3] and also have many other major applications.[4] Since water offers exceptional chemical reactivity due to its unique properties, such as its ability to solvate salts and polar compounds or its high dielectric constant, the interest in using water-soluble NHC metal complexes for some of their applications is evident. A convenient way to render NHC metal complexes water-soluble involves the attachment of ionic or nonionic hydrophilic substituents to the NHC ligand.[5] Herrmann and co-workers patented the first examples of such NHC complexes in 1995,[6] which was followed by a report from Özdemir's group describing a water-soluble NHC-based ruthenium catalyst for the synthesis of 2,3-dimethylfuran.[7] In the past few years, the number of new complexes of this type has increased and, subsequently, the range of catalytic processes tested with them in the aqueous phase has widened. For instance, ruthenium complexes have been studied in olefin metathesis,[8] allylic alcohol isomerizations,[9] or acetophenone hydrogenations,[10] with palladium complexes being studied in cross-coupling reactions,[11,12] gold complexes in alkyne hydrations,[13,14] iridium complexes in transfer hydrogenations,[15] and copper complexes in click reactions.[16] The synthesis and application of water-soluble NHC transition-metal complexes in catalysis has recently been reviewed.[17]

Platinum(II) complexes containing more conventional monodentate[18−20] or chelating[20−22] NHC ligands have proven to be useful in a variety of catalytic processes in organic solvents, such as diboration of unsaturated molecules,[23] tandem hydroboration−cross-coupling,[24] or reductive cyclization of diynes and enynes,[25] and also as metal-based chemotherapeutic agents.[26] However, platinum complexes containing hydrophilic NHC ligands were unknown until recently, when we reported the synthesis of water-soluble (NHC)Pt(0)[27] and Pt(II)[28] complexes that could be used as recoverable catalysts for the hydrosilylation of alkynes in water at room temperature in the former case or for the hydration of alkynes in water in the latter.

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Although the applications of water-soluble NHC complexes are progressing rapidly, there is as yet little information available concerning basic aspects of the chemical reactivity of these complexes in water, including the limits of the hydrolytic stability of the metal−NHC bonds. The aim of this work was to gain an understanding of the chemical behavior of water-soluble NHC platinum compounds containing alkyl ligands in the aqueous phase. Thus, herein we disclose the synthesis of methyl complexes of platinum(II) coordinated to sulfonated NHC ligands **a**−**d** (Figure 1) in a study that focuses on the hydrolytic stability of the Pt−C bonds in these complexes.

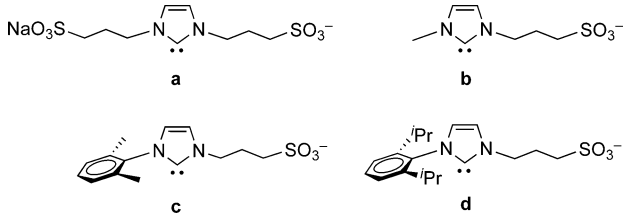
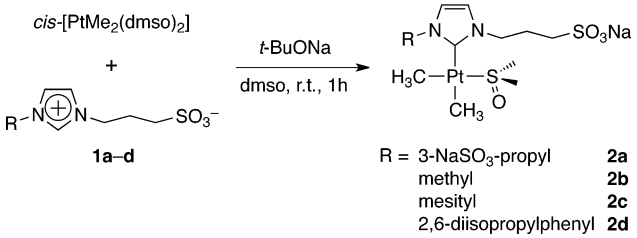


Figure 1. Anionic sulfonated NHC ligands used in this work.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Dimethyl NHC Platinum(II) Complexes 2a−d. The mono(NHC) complexes *cis*-[$PtMe_2$(dmso)(NHC·Na)] (**2a**−**d**) were obtained by treating *cis*-[$PtMe_2$(dmso)$_2$] with a stoichiometric amount of the corresponding imidazolium salt **1a**−**d** using sodium *tert*-butoxide as the deprotonating agent (Scheme 1; the NHCs

Scheme 1. Synthesis of the Complexes *cis*-[$PtMe_2$(dmso)(NHC·Na)] (2)



used in this work are anionic, and the neutral formula unit will be abbreviated for convenience as NHC·Na). The transformations were completed in less than 1 h in dmso at room temperature, and after a simple workup, the complexes were obtained as analytically pure solids in very high yields (>90%).

Complexes **2** were characterized by ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopy, mass spectrometry (ESI-TOF), and elemental analysis, in addition to X-ray diffraction in the case of **2a**. Samples of **2a** and **2b** gave accurate C, H, and N analyses after being dried in a vacuum for 12 h at 90 °C. In the case of **2c** and **2d**, the elemental analyses suggested the presence of water molecules, which were also observed in the ^{1}H NMR spectra obtained upon dissolving the solids in dry dmso-d_6. It should be noted that these compounds are hygroscopic in the solid state and quickly take up water from the air.

The fragments with the highest peaks in the ESI(−) mass spectra of **2** were those arising from the combined loss of a Na^+ cation and the coordinated dmso ([M − Na − dmso]$^-$) and, interestingly, from the additional elimination of methane ([M − Na − dmso − 1 or 2 CH_4]$^-$). The latter was the main fragment for the complexes with aryl substituents (**2c** and **2d**), and its assignment was supported by the excellent agreement found between the experimental and calculated distributions of exact masses (with errors below 8 ppm). Methane evolution likely results from intramolecular C sp^3−H bond activations of the alkyl and aryl NHC substituents similar to those reported by the Nolan[29] and Conejero[30] groups in NHC platinum(II)−methyl complexes. Detection of the ion [M − Na]$^-$ in the mass spectra of **2a** and **2b** confirmed the coordination of the dmso molecule to the Pt center in these *N*-alkyl-substituted complexes. Further confirmation of this coordination was obtained by the observation, in D_2O, of the ^{1}H resonances corresponding to the coordinated dmso in the expected region of 2.7 to 3.0 ppm with $^3J(^1H-^{195}Pt) \approx 13-14$ Hz.

The ^{13}C chemical shifts of the carbene carbons (181 to 183 ppm) and the ^{195}Pt chemical shifts (−4023 to −3980 ppm) were comparable to those reported for other *cis*-[$PtMe_2$(L)(NHC)] complexes (176 to 191 ppm and −4002 to −3905 ppm, respectively, with L = dmso,[31] imine,[32,33] phosphane,[34] NHC, and SMe_2[22]). The ^{195}Pt satellites of the ^{13}C resonances were undetectable, probably due to their broadening in solvents of relatively high viscosity.[48] The methyl groups *trans* to the dmso ligand resonated between 0.2 and 0.3 ppm (^{1}H) and −10 to −7 ppm (^{13}C), whereas those *trans* to NHC appeared in the range from −0.3 to 0.0 ppm (^{1}H) and from −4 to −1 ppm (^{13}C). The ^{195}Pt−^{1}H coupling constants were smaller for the methyl ligands *trans* to the carbene (∼60 Hz compared with ∼80 Hz), as might be expected in light of the larger *trans* influence of this ligand. The *cis* stereochemistry together with the slow rotation of the NHC ligand around the Pt−C bond on the NMR time scale explains the chemical nonequivalence observed in the ^{1}H and ^{13}C NMR spectra between both NCH_2 protons in **2a**−**d** (and both aryl moieties in **2c**−**d**) and between the two dmso methyls in the complexes with asymmetrically substituted NHCs **2b**−**d**.[19,31]

Single crystals of **2a** suitable for X-ray diffraction analysis were obtained as an octahydrate (**2a**·8H_2O) by slow diffusion of acetone into an aqueous solution of the complex. It is worth mentioning that crystal structures containing sulfonated NHC metal complexes are rare.[13,28,35,36] Figure 2a depicts one of the two crystallographically independent *cis*-[$PtMe_2$(dmso)(NHC)]$^{2-}$ moieties found in the crystal structure of **2a** together with a selection of distances and angles. The angles between the *cis* bonds in the square-planar coordination environment of the Pt atom range from 86.0(8)° to 94.0(5)° [from 84.1(7)° to 94.5(4)° for the second independent molecule]. The NHC ligand ring is almost perpendicular to the Pt coordination plane (86°) in both independent units, and the Pt−C_{NHC} distance of 2.09(2) Å [2.04(2) Å] is within the range of those reported for *cis*-[$PtMe_2$(L)(NHC)] complexes with L = imine,[32,33] phosphane,[34] NHC, or SMe_2[22] (2.03−2.09 Å). The *cis*-[$PtMe_2$(dmso)(NHC)]$^{2-}$ units are organized in the form of double layers parallel to the *a*−*b* crystallographic plane in the three-dimensional structure of **2a**·8H_2O, with the methyl groups pointing inward and the sulfonates out of the layer (Figure 2b). These anionic double layers are stacked along the *c* axis and alternate with cationic layers of hydrated Na^+ cations (Figure S23, Supporting Information).

The ^{1}H NMR spectra of complexes **2** remained unaltered 8 days after being dissolved in D_2O under neutral or alkaline conditions (0.1 M NaOD) at room temperature. The stability of these complexes in water resembles that found by Atwood's group for Pt(II) dimethyl complexes with sulfonated

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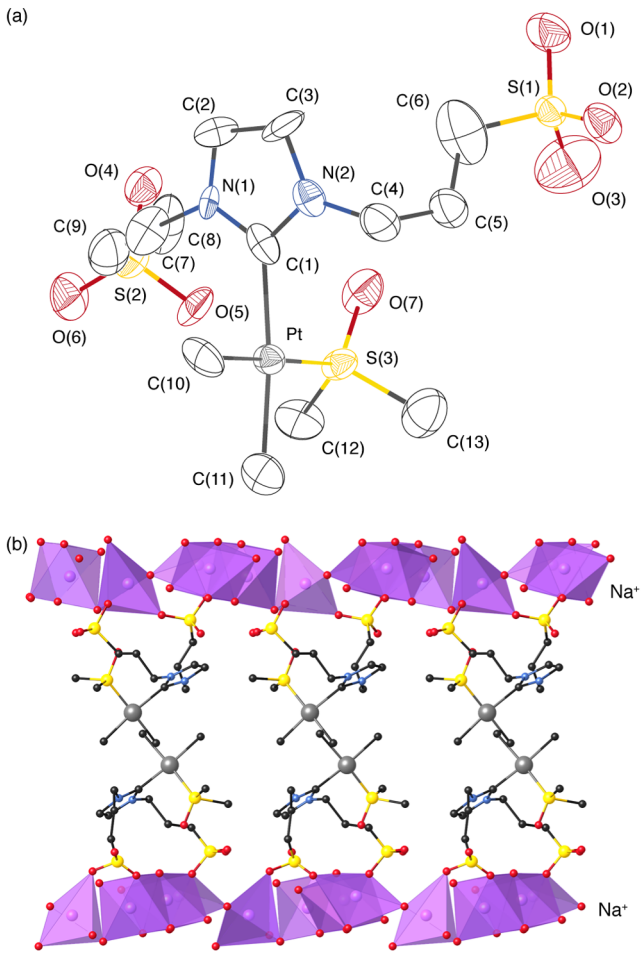
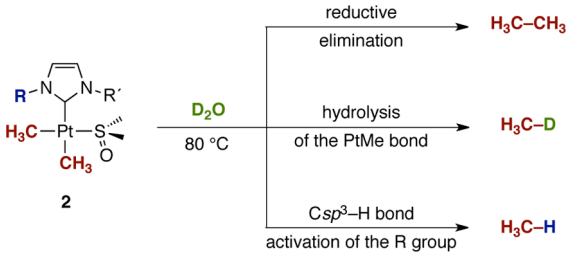


Figure 2. (a) ORTEP diagram (50% probability ellipsoids) of the anionic complex $[PtMe_2(dmso)(NHC)]^{2-}$ (**2a**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) [the corresponding distances and angles for the second independent unit are given in brackets]: Pt−C(1), 2.09(2) [2.040(16)]; Pt−C(10), 2.062(18) [2.142(19)]; Pt−C(11), 2.08(2) [2.159(19)]; Pt−S(3), 2.237(4) [2.254(5)]; C(1)−Pt−C(10), 87.0(7) [84.1(7)]; C(10)−Pt−C(11), 86.0(8) [91.7(8)]; C(11)−Pt−S(3), 92.9(6) [94.5(4)]; C(1)−Pt−S(3), 94.0(5) [89.5(6)]; C(1)−Pt−C(11), 172.7(8) [175.7(8)]; C(10)−Pt−S(3), 178.9(6) [171.2(8)]. (b) View of the crystal structure of **2a** along the crystallographic *b* axis. The hydrated Na^+ cations are represented as polyhedra.

phosphanes.[37] In contrast, it has been reported that $PtMe_2$ complexes with sulfonated iminopyridine ligands are quickly degraded under similar conditions by displacement of the didentate N,N-ligand by water.[38] At 80 °C and under neutral conditions, the decomposition of complexes **2** in D_2O is noticeable within hours, with the solutions darkening and the evolution of gases. These gases were collected in chloroform-d_1, and their analysis by ^1H NMR showed the formation of comparable amounts of ethane, methane, and methane-d_1. In the case of **2a**, for instance, almost 50% of the methyl groups were transformed into ethane, more than 25% into methane, and around 25% into methane-d_1. While the formation of methane-d_1 is easily explained by hydrolysis of the PtMe bonds, nondeuterated methane likely proceeds from the intramolecular C sp^3−H activation of the N-substituents discussed above (Scheme 2).[29,30] This preliminary study shows that hydrolysis of the Pt−Me bonds is only one of the routes involved in the thermally induced decomposition of complexes **2** in water.

Scheme 2. Thermally Induced Decomposition of Complexes 2 in Water



Reactivity of the Dimethyl Complexes 2 with Brønsted Acids in Water. In light of these results, we examined the reactivity of complexes **2** in water with Brønsted acids derived from coordinating and noncoordinating anions (HCl and HBF_4, respectively). The reaction of **2** with hydrochloric acid is very fast at room temperature and occurs chemoselectively at the Pt−Me bonds in a stepwise manner. Thus, the addition of a first equivalent of a titrated hydrochloric acid solution results in protonolysis of only one of the Pt−Me bonds to give the monomethyl complexes [PtClMe(dmso)-(NHC·Na)] (**3**, Scheme 3a), whereas reaction with a second equivalent of HCl affords the already known dichloride complexes *cis*-[$PtCl_2$(dmso)(NHC·Na)] (**4**, Scheme 3b).[28] The inertness of the Pt−NHC bond under these conditions, even when an excess of acid was used, is noteworthy. For instance, monitoring of a solution of **2b** and five equivalents of DCl in D_2O at room temperature by ^1H NMR spectroscopy for 7 days did not show the formation of any detectable amount of imidazolium salt. This resistance may be of interest as regards the application of these complexes under acidic aqueous conditions, for instance in the hydration of alkynes.[39]

In solution, the monomethyl complexes **3** comprise a mixture of *SP*-4−3 and *SP*-4−4 diastereoisomers. These complexes can also be prepared by direct metalation of the corresponding imidazolium **1** with *trans*-[PtClMe(dmso)$_2$], using sodium hydrogen carbonate as the deprotonating base (Scheme 3c). To the best of our knowledge, the synthesis of haloalkyl mono(NHC) platinum(II) complexes has not been reported previously. As may be expected in light of the steric interactions, the isomer with the chlorido and carbene ligands in *cis* position (*SP*-4−4) is favored by the most hindered NHCs (**3c** and **3d**) in both dmso-d_6 and D_2O (see Scheme 3 and the Experimental Section). The composition of the mixture is also dependent on the solvent but independent of the method of preparation, thereby suggesting that both diastereoisomers are interconverting in solution. This isomerization is slow enough in dmso-d_6 at room temperature to observe sharp ^1H NMR resonances for the two isomers in all complexes, although a significant saturation transfer between the methyl ligands of both isomers was observed in a 1D EXSY experiment carried out for **3c** in dmso-d_6. Broadening of resonances was, however, observed in D_2O for **3c** and **3d**. The concurrence of isomerization processes in solution is well known for other square-planar haloalkyl platinum(II) complexes.[37,40]

The reaction of dimethyl complexes **2** with HBF_4 in water at room temperature also occurs rapidly and chemoselectively. After addition of the first equivalent of acid and subsequent

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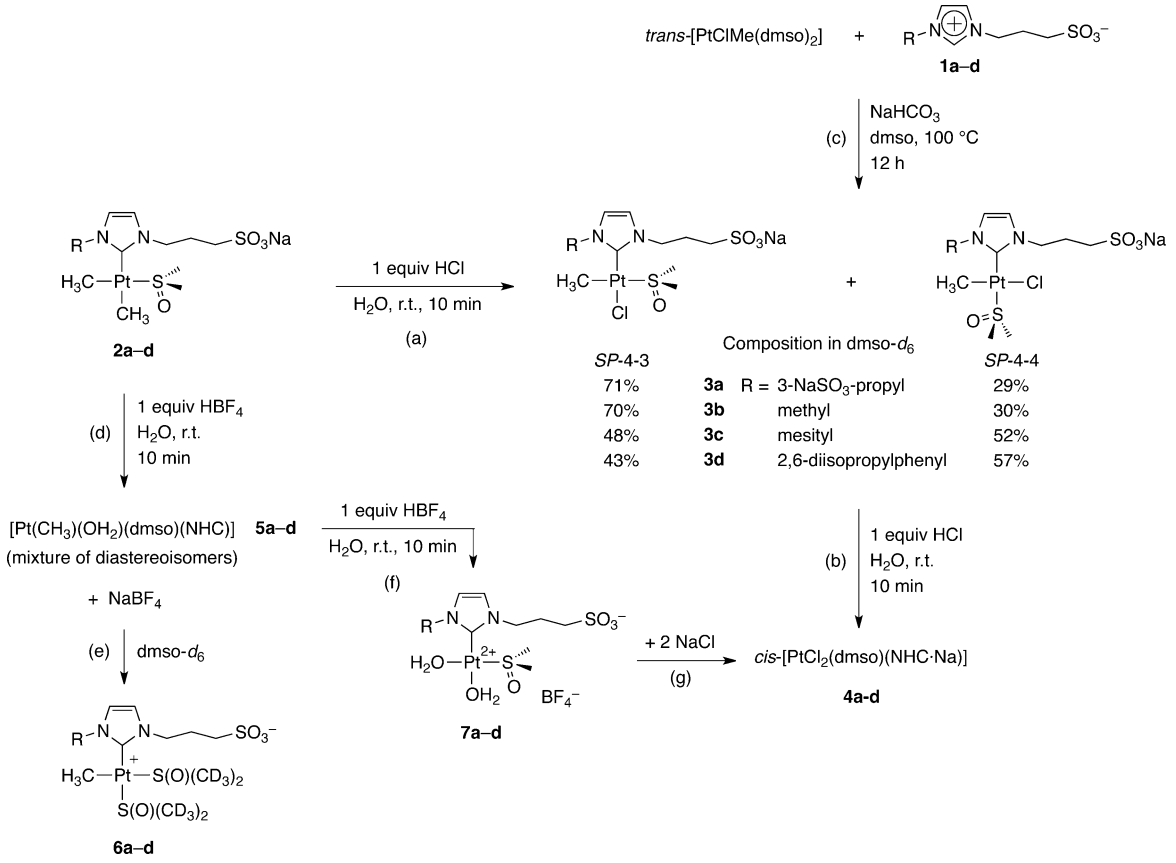
Scheme 3. Reactions of 2 with Hydrochloric and Tetrafluoroboric Acids



removal of the aqueous solvent, the complexity of the ^{1}H NMR spectra obtained in D_2O was attributed to the formation of one major and one or two minor diastereoisomers of the "cationic" (more properly, zwitterionic) aquamethyl complexes [Pt(CH$_3$)(OH$_2$)(dmso)(NHC)] (**5**, Scheme 3d). In contrast, the spectra became drastically simplified in dmso-d_6, where displacement of the coordinated water (and the nondeuterated dmso) by the solvent resulted in formation of the *cis* complex **6** (Scheme 3e). The addition of a second equivalent of HBF_4 to complexes **2** afforded the "dicationic" complexes **7**, essentially as *cis* diastereoisomers (Scheme 3f). The formulation given to these diaqua complexes was supported by their clean transformation into the dichloride complexes **4** upon addition of sodium chloride (Scheme 3g).

Complexes **3**–**7** were obtained as spectroscopically pure solids and were characterized by ESI-TOF mass spectrometry and ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopy. The elemental analyses found for complexes **3** were unsatisfactory, even taking into account the solvation by water molecules. Samples of the monomethyl (**5**, **6**) and diaqua complexes (**7**) were contaminated by the $NaBF_4$ formed as byproduct in the reaction. No purification was attempted. As was observed above for **2**, the most intense peaks detected in the mass spectra of these complexes were those associated with the decoordination of dmso or water ligands followed by the additional loss of methane in the case of the methyl complexes **3** and **5**. Coordination of a dmso molecule to the platinum center in **3** and **7** was confirmed by observation of the corresponding methyl protons in D_2O solution. The *cis* arrangement proposed for **6** and **7** was based on the number of ^{2}H or ^{1}H resonances observed for the methyl groups of the dmso ligands. When required, this assignment was corroborated by NOESY experiments that were also used to establish the stereochemistry of the two diastereoisomers found for **3** (see Experimental Section for details). The NCH_2 protons of the sulfonated chain were made equivalent by fast rotation of the NHC ligand around the Pt–NHC bond at room temperature in the case of some of the complexes bearing less hindered NHC ligands (**a** and **b**). The chemical shifts of the carbenic carbon (C^2) in the monomethyl complexes **3** (around 152 and 162 ppm for the *SP*-4–3 and *SP*-4–4 isomers, respectively) and **6** (156–158 ppm) were intermediate between those found in the dimethyl **2** (181–183 ppm) and dichloride complexes **4** (140–143 ppm). The values found for **6** were in excellent agreement with those previously reported for cationic [PtMeLL′(NHC)][X] complexes (L = L′ = py, X = PF_6;[41] L = imine, L′ = NCMe, X = OTf).[32]

Single crystals of **3a** were obtained in the form of the *SP*-4–3 isomer solvated with water and dmso molecules (*SP*-4–3-**3a**·5H_2O·0.5dmso). Figure 3a depicts one of the two crystallographically independent $[PtMeCl(dmso)(NHC)]^{2-}$ units together with a selection of distances and angles found in both. These units are organized in the form of singly negatively charged layers between layers of sodium cations in the three-dimensional structure, with the sulfonate groups pointing toward the interface of both layers (Figure 3b). The NHC ring is almost perpendicular to the Pt coordination plane in both independent units (85.4° and 81.2°, respectively). The Pt–C_{NHC} distances of 1.945(8) and 1.966(8) Å are toward the low end of the range reported for (NHC)Pt(II) complexes (90% of Pt–C_{NHC} distances between 1.94 and 2.06 Å, mean 2.00 Å). This can be mostly ascribed to the influence of the chloride

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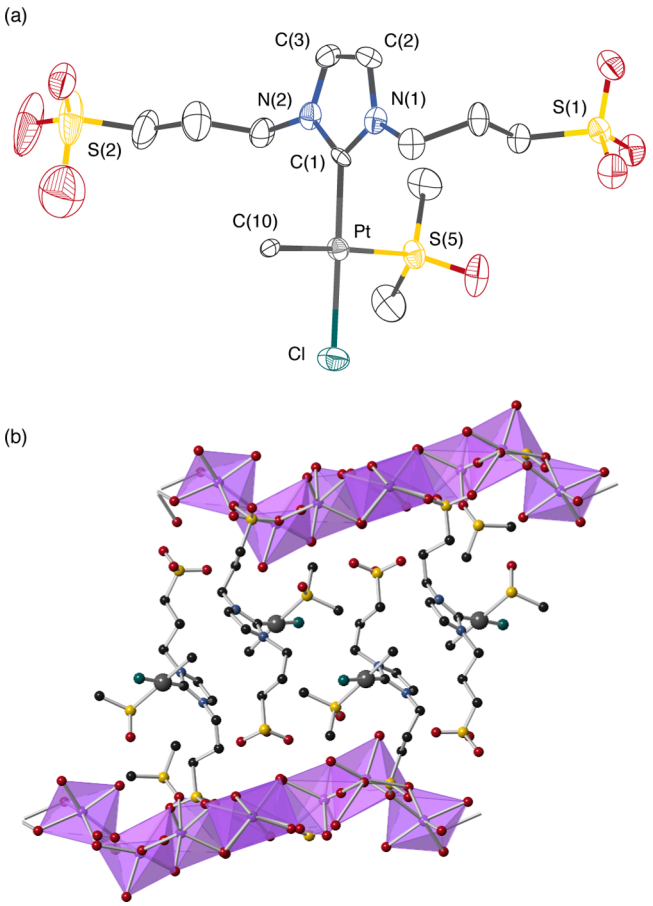
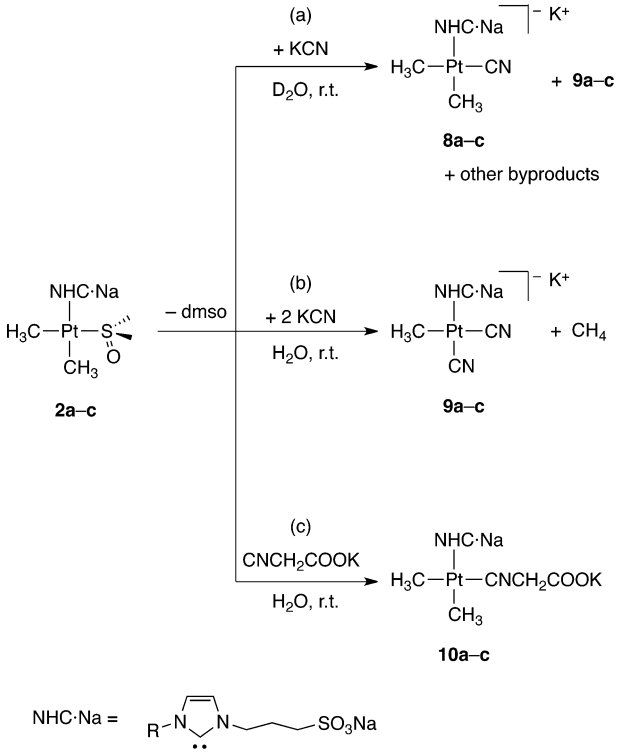


Figure 3. (a) ORTEP diagram (50% probability ellipsoids) of the anionic complex *SP*-4−3-[PtClMe(dmso)(NHC)]$^{2-}$ (*SP*-4−3-**3a**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) [the corresponding distances and angles for the second independent unit are given between brackets]: Pt−C(1), 1.945(8) [1.966(8)]; Pt−C(10), 2.136(6) [2.095(7)]; Pt−Cl, 2.359(2) [2.360(2)]; Pt−S(5), 2.282(2) [2.305(2)]; C(1)−Pt−C(10), 88.7(3) [89.2(3)]; C(10)−Pt−Cl, 90.74(18) [88.5(2)]; Cl−Pt−S(5), 89.79(7) [89.04(8)]; C(1)−Pt−S(5), 90.9(2) [93.2(2)]; C(1)−Pt−Cl, 177.6(2) [177.3(2)]; C(10)−Pt−S(5), 177.06(16) [177.3(2)]. (b) View of the crystal structure of *SP*-4−3-**3a** along the crystallographic *a* axis. The solvated Na^+ cations are represented as polyhedra.

trans ligand, as can be deduced from a comparison with the distances found in the dichloride (**4a**)[28] and dimethyl (**2a**) analogues (1.97(2) and 2.04(2) [2.09(2)] Å, respectively) and with the typical distances for NHC−Pt(II) bonds with chloride in *trans* position (from 1.94 to 2.00 Å, mean 1.97 Å). The Pt−CH_3 (2.095(7) [2.136(6)] Å) and Pt−Cl distances (2.359(2) [2.360(2)] Å) are comparable to those found for the corresponding bonds *trans* to the NHC ligand in **2a** (Pt−CH_3, 2.08(2) [2.16(2)] Å) and **4a** (Pt−Cl, 2.359(5) Å).[28]

Hydrolysis of the Platinum−Methyl Bonds Promoted by Nucleophiles. In the course of our preliminary studies on the reactivity of the dimethyl complexes **2**, we observed that substitution of the coordinated dmso by ligands such as cyanide is accompanied by hydrolysis of the Pt−CH_3 bonds. After addition of one equivalent of potassium cyanide to a solution of **2a−c** in deuterated water, the expected substitution products K[$PtMe_2$(CN)(NHC·Na)] (**8a−c**) were slowly formed in the initial stages of the reaction (Scheme 4a). However, ligand exchange was incomplete (around 40% for **2a** after 4 h of

Scheme 4. Reactions of Dimethyl Complexes 2 with KCN and $CNCH_2COOK$ in Water



reaction) and was accompanied by the formation of other minor byproducts. In addition, complexes **8a−c** evolved over time to give derivatives **9a−c**. Integration of the ^{1}H resonances for these derivatives and the observation of a small 1:1:1 triplet at 0.06 ppm (J_{HD} = 2.1 Hz), corresponding to CH_3D, suggested the involvement of hydrolysis of one of the Pt−CH_3 bonds in the formation of **9**. The formula K[$PtMe(CN)_2$(NHC·Na)] was corroborated when spectroscopically pure samples of **9a−c** were isolated by reaction of **2a−c** with two equivalents of KCN in water (Scheme 4b). Under these conditions, the reaction was almost quantitative in less than 3 h at room temperature. Complexes **9a−c** thus obtained were stable in water at room temperature for at least 8 d.

The notable acceleration of the transformations **2** → **8** → **9** with increasing cyanide concentration (compare the reactions with one and two equivalents of KCN) is to be expected for square-planar Pt(II) complexes involving associative substitution mechanisms. Thus, nucleophilic attack of the cyanide ligand to the platinum(II) center in **2** is followed by dissociation of the dmso ligand, whereas the alternative hydrolytic cleavage of the Pt−CH_3 bond does not occur to any observable extent in this complex. Cleavage of this bond likely involves two steps: nucleophilic attack of the cyanide to the platinum(II) center followed by electrophilic attack by the water protons to the methyl group. The balance between the two steps can tentatively explain the differences observed in the stability of the Pt−CH_3 bonds. The methyl probably becomes a better leaving group in **8** because replacement of the coordinated dmso by cyanide increases the electron-richness of the Pt(II) center, thus making the Pt−CH_3 bond more polar and susceptible to electrophilic attack by the water protons. It has to be assumed that the second cyanide ligand in **9** produces a notable reduction of the susceptibility of the Pt center to nucleophilic attack to explain the water stability of this complex.

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Since hydrolysis of the Pt−Me bond in the above complexes is promoted by nucleophiles, it is reasonable to propose that ligands displaying a lower nucleophilicity versus platinum(II)[42] than cyanide could stabilize the substitution product by inhibiting hydrolysis. The stability shown by complexes **2** under alkaline conditions might actually be considered to be a consequence of the lower nucleophilicity of the hydroxide ion, although substitution was not observed either. Unlike hydroxide, potassium 2-isocyanoacetate is a water-soluble isocyanide ligand that was able to displace the coordinated dmso ligand in **2a−c** to afford the dimethyl complexes **10a−c** in high yields (>90%, Scheme 4c). The reaction occurs in water at room temperature without hydrolysis of the Pt−CH_3 bonds, even in the presence of an additional equivalent of the isocyanide.

The ESI-TOF mass spectra of **9** and **10** showed intense peaks corresponding to the loss of sodium(1+) or potassium(1+) ions from the neutral unit formula, in some instances accompanied by incorporation of a proton from the solvent (water or methanol). Fragments resulting from the additional loss of methane were also observed for all complexes. The coordination of two cyanide ligands in a *cis* disposition in **9** was inferred from observation of two IR absorptions corresponding to CN stretching vibrations (at *ca.* 2120 and 2100 cm^{-1}) and two NMR resonances for the cyanide carbons (at *ca.* 142 and 145 ppm). The carbenic and methyl carbons of **10** showed well-defined ^{195}Pt satellites with coupling constants of around 800 Hz for the carbene, 595 Hz for the methyl *trans* to the isocyanide, and 500 Hz for the methyl *trans* to the NHC. The *trans* influence of the NHC ligand probably causes the weaker coupling to ^{195}Pt of the methyl group *trans* to it.

Single crystals of **9a** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a methanol solution of the complex. The solid-state structure contains two crystallographically independent $[PtMe(CN)_2(NHC)]^{3-}$ units together with their corresponding Na^+ and K^+ counterions, water molecules, and, in addition, methanesulfonic acid of unknown origin (**9a**·1.5H_2O·0.5$MeSO_3H$). Figure 4a depicts one of the anionic organometallic Pt units together with a selection of bond distances and angles. The dihedral angle between the NHC ring and the metal coordination plane is equal to 72.1° in one and 85.8° in the other Pt unit. The average Pt−C_{NHC} (2.02 Å) and Pt−CH_3 distances (2.03 Å) are slightly shorter than the mean values found for (NHC)Pt(II) methyl complexes in the Cambridge Structural Database (2.036 and 2.084 Å, respectively). Nevertheless, the most remarkable feature is the three-dimensional arrangement of the structural units in a columnar honeycomb structure with cells of tetragonal symmetry and channels with an internal diameter of around 6 Å (Figure 4b). These channels are delimited by walls made of Pt complexes with their sulfonated groups pointing toward the Na^+ and K^+ cations arranged in the cell edges. In this way, the Pt−CH_3 bonds are facing the channel interior. This is interesting because activation of such bonds would result in exposure of the Pt centers to the interior of the enlarged channels (Figure 4c).

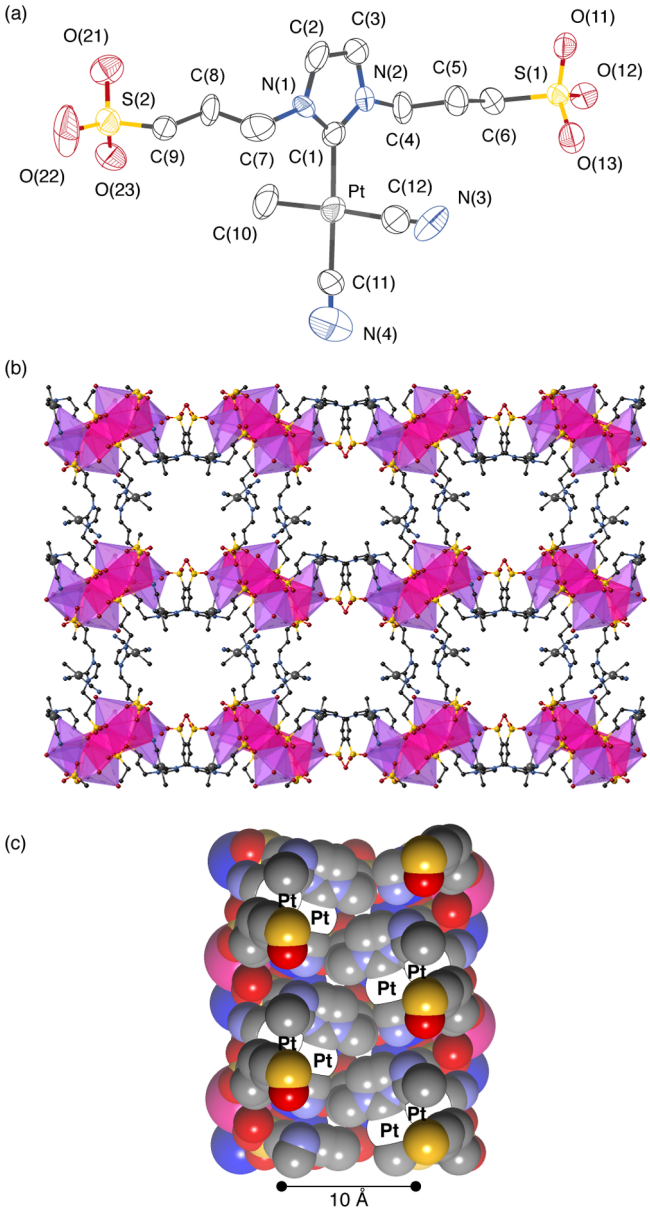

Figure 4. (a) ORTEP diagram (50% probability ellipsoids) for the complex $[PtMe(CN)_2(NHC)]^{3-}$ (**9a**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) [the corresponding distances and angles for the second independent unit are given between brackets]: Pt−C(1), 1.993(16) [2.045(15)]; Pt−C(10), 2.05(2) [2.016(16)]; Pt−C(11), 1.990(19) [1.988(18)]; Pt−C(12), 1.94(2) [1.940(18)]; C(11)−N(4), 1.12(2) [1.117(19)]; C(12)−N(3), 1.13(2) [1.18(2)]; C(1)−Pt−C(10), 89.9(7) [87.3(7)]; C(10)−Pt−C(11), 87.3(8) [87.9(7)]; C(11)−Pt−C(12), 90.5(8) [94.2(6)]; C(1)−Pt−C(12), 92.3(7) [90.7(6)]; C(1)−Pt−C(11), 176.6(7) [174.4(6)]; C(10)−Pt−C(12), 177.6(8) [177.9(7)]; Pt−C(11)−N(4), 171(2) [176.6(17)]; Pt−C(12)−N(3), 174.9(19) [175.6(15)]. (b) View of the crystal structure of **9a** along the crystallographic *c* axis. The coordination spheres of the Na^+ and K^+ cations are represented as polyhedra. (c) Space-filling representation displaying a sectional view of one channel. Methyl groups have been removed to reveal the positions of the Pt center (shown as blank spheres in the picture).

■ CONCLUSIONS

We have developed an efficient method for the preparation of dimethyl derivatives of water-soluble NHC platinum(II) complexes and have studied the hydrolytic stability of their Pt−C bonds under different conditions. The platinum−methyl bonds of these derivatives are stable for days at room temperature in water under neutral or alkaline conditions. The degradation observed for these complexes at higher temperatures involves C−H activation and C−C reductive elimination processes in addition to Pt−Me bond hydrolysis.

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Nevertheless, we have shown that the reactivity of the platinum−methyl bonds with water increases significantly after addition of Lewis bases that are good nucleophiles toward the Pt(II) metal centers. The stoichiometric addition of protic acids to aqueous solutions of the above complexes results in the clean cleavage of one or both platinum(II)−methyl bonds. In contrast, the Pt−NHC bond remains unaltered under the above conditions. We have also shown the synthetic utility of selective protolysis of the Pt−Me bonds under acidic conditions by preparing several new neutral and cationic Pt(II) NHC derivatives. It is important to note that the reactivity trends observed in water for the hydrolysis of Pt−C bonds might be quite different in other solvents. As an example, the ring-opening hydrolysis of noncoordinated NHCs, which has been observed by several authors in organic solvents containing traces of moisture,[43] is disfavored in the presence of larger amounts of water because the solvation reduces the basicity of the hydroxide anion.[44]

In addition, we have reported the crystal structures of three complexes bearing sulfonatopropyl substituents at the nitrogen atoms of the NHC ligand. In these structures, the solvated sodium or potassium cations and the organometallic Pt complexes are arranged in separate domains, with the sulfonated groups of the NHC ligand located at the domain interface. In the case of complex **9a**, the three-dimensional arrangement is of special interest because of the longitudinal channels with a diameter of around 6 Å internally decorated with Pt−Me bonds.

Further efforts are under way in our laboratories with regard to the organometallic reactivity and applications of these water-soluble Pt(II) dimethyl complexes.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed under an argon atmosphere using standard Schlenk techniques. Unless otherwise stated, reagents and solvents were used as received from commercial sources. The complexes *cis*-dimethylbis(dimethyl sulfoxide)platinum(II)[45] and *trans*-chloromethylbis(dimethyl sulfoxide)platinum(II)[46] and the imidazolium salts **1a**,[47] **1b**,[48] **1c**,[35] and **1d**[35] were prepared as described in the literature. All solvents were deoxygenated prior to use. Dimethyl sulfoxide was distilled under argon over calcium hydride. Deionized water (type II quality) was obtained using a Millipore Elix 10 UV water purification system. ^{1}H, ^{13}C, and ^{195}Pt NMR spectra were recorded using a Varian Mercury 300, Unity 300, or Unity 500 Plus spectrometer. Chemical shifts (δ, parts per million) are quoted relative to $SiMe_4$ (^{1}H, ^{13}C) and K_2PtCl_6 in water (^{195}Pt). They were measured by internal referencing to the ^{13}C or residual ^{1}H resonances of the deuterated solvents (39.0 ppm for dmso-d_6 carbons; 2.49 ppm for dmso-d_5 protons, and 4.69 ppm for HDO) or by the substitution method in the case of ^{195}Pt. Coupling constants (J) are given in hertz. When required, two-dimensional ^{1}H−^{13}C HSQC and HMBC experiments were carried out for the unequivocal assignment of ^{1}H and ^{13}C resonances. IR spectra were recorded for KBr pellets over the range 4000−400 cm^{-1} using a Perkin−Elmer Spectrum 2000 spectrophotometer. The Analytical Services of the Universidad de Alcalá performed the C, H, and N analyses using a LECO CHNS-932 microanalyzer, and the mass spectra were obtained using an Agilent G3250AA LC/MSD TOF Multi (MALDI and ESI) mass spectrometer in the electrospray ionization mode. The Analytical Services of the Universidad Autónoma de Madrid performed some of the mass spectra using an ABSciex QSTAR pulsar I QTOF mass spectrometer.

*[PtMe$_2$(dmso)(NHC·Na)] (**2**).* Sodium *tert*-butoxide (0.130 g, 1.35 mmol) was added to a solution of *cis*-[PtMe$_2$(dmso)$_2$] (0.515 g, 1.35 mmol) and the corresponding imidazolium salt (1.35 mmol) in dimethyl sulfoxide (10 mL). The mixture was stirred for 1 h at room temperature and then filtered through a plug of kieselguhr. The solvent was removed under high vacuum at 90 °C to dryness. The powdery solid thus obtained was dried under vacuum for 12 h at 90 °C and 4 mbar of pressure.

*cis-(Dimethyl sulfoxide)[1,3-bis(3-sodium sulfonatopropyl)-imidazol-2-ylidene]dimethylplatinum(II) (**2a**).* Complex **2a** was obtained from **1a** (0.451 g, 1.35 mmol) as a white solid (0.864 g, 97%). ^{1}H NMR (300 MHz, D_2O): δ 7.13 (s, 2H, Imz), 4.31 (m, 2H, NCH_2), 4.14 (m, 2H, NCH_2), 2.95 (s with ^{195}Pt satellites, $^{3}J(^{1}H-^{195}Pt)$ = 13.2, 6H, Me_2SO), 2.82 (m, 4H, CH_2S), 2.17 (m, 4H, $CH_2CH_2CH_2$), 0.36 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 81.2, 3H, Me *cis* to NHC), 0.03 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 61.4, 3H, Me *trans* to NHC). ^{1}H NMR (300 MHz, dmso-d_6): δ 7.24 (s, 2H, Imz), 4.18 (m, 4H, NCH_2), 2.40 (m, 4H, CH_2S), 2.05 (m, 4H, $CH_2CH_2CH_2$), 0.16 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 78.6, 3H, Me *cis* to NHC), −0.06 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 60.0, 3H, Me *trans* to NHC). $^{13}C\{^{1}H\}$ NMR (75 MHz, D_2O): δ 181.5 (s, Imz C^2), 121.1 (s, Imz C^{4-5}), 48.4 (s, CH_2S), 48.4 (s, NCH_2), 43.7 (s, Me_2SO), 25.8 (s, $CH_2CH_2CH_2$), −3.8 (s, PtMe *trans* to NHC), −9.0 (s, PtMe *cis* to NHC). ^{195}Pt NMR (64 MHz, dmso-d_6): δ −4021. ESI-MS (negative ion, MeOH): m/z 636.0408 [M − Na]$^-$ (calcd 636.0453) 5%; 558.0279 [M − Na − dmso]$^-$ (calcd 558.0314) 100%; 541.9974 [M − Na − dmso − CH_4]$^-$ (calcd 542.0001) 44%; 525.9651 [M − Na − dmso − 2CH_4]$^-$ (calcd 525.9688) 31%; 503.9827 [M + H − 2Na − dmso − 2CH_4]$^-$ (calcd 503.9868) 52%. Anal. Calcd (%) for $C_{13}H_{26}N_2Na_2O_7PtS_3$: C, 23.67; H, 3.97; N, 4.25. Found (%): C, 23.45; H, 4.21; N, 4.05.

*cis-(Dimethyl sulfoxide)dimethyl[1-methyl-3-(3-sodium sulfonatopropyl)imidazol-2-ylidene]platinum(II) (**2b**).* Complex **2b** was obtained from **1b** (0.276 g, 1.35 mmol) as a pale yellow solid (0.686 g, 96%). ^{1}H NMR (300 MHz, D_2O): δ 7.08 (d, $^{3}J_{HH}$ = 2.1, 1H, Imz), 7.01 (d, $^{3}J_{HH}$ = 2.1, 1H, Imz), 4.27 (m, 1H, NCH_2), 4.13 (m, 1H, NCH_2), 3.64 (s, 3H, NMe), 2.94 (s with ^{195}Pt satellites, $^{3}J(^{1}H-^{195}Pt)$ = 13.8, 3H, Me_2SO), 2.93 (s with ^{195}Pt satellites, $^{3}J(^{1}H-^{195}Pt)$ = 13.8, 3H, Me_2SO), 2.81 (m, 2H, CH_2S), 2.15 (m, 2H, $CH_2CH_2CH_2$), 0.34 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 81.2, 3H, PtMe *cis* to NHC), 0.04 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 61.0, 3H, PtMe *trans* to NHC). ^{1}H NMR (300 MHz, dmso-d_6): δ 7.24 (d, $^{3}J_{HH}$ = 2.1, 1H, Imz), 7.19 (d, $^{3}J_{HH}$ = 2.1, 1H, Imz), 4.17 (m, 2H, NCH_2), 3.68 (s, 3H, NMe), 2.40 (m, 2H, CH_2S), 2.04 (m, 2H, $CH_2CH_2CH_2$), 0.17 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 82.6, 3H, PtMe *cis* to NHC), −0.04 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{95}Pt)$ = 62.7, 3H, PtMe *trans* to NHC). $^{13}C\{^{1}H\}$ NMR (75 MHz, D_2O): δ 181.3 (s, Imz-C^2), 122.6 (s, Imz-C^5), 120.6 (s, Imz-C^4), 48.4 (s, CH_2S), 48.2 (s, NCH_2), 43.9 (s, Me_2SO), 43.6 (s, Me_2SO), 36.8 (s, NMe), 25.8 (s, $CH_2CH_2CH_2$), −3.9 (s, PtMe *trans* to NHC), −9.7 (s, PtMe *cis* to NHC). ^{195}Pt NMR (64 MHz, dmso-d_6): δ −4023. ESI-MS (negative ion, MeOH): m/z 506.0758 [M − Na]$^-$ (calcd 506.0752) 2%; 428.0613 [M − Na − dmso]$^-$ (calcd 428.0613) 100%; 412.0298 [M − Na − dmso − CH_4]$^-$ (calcd 412.0300) 12%; 395.9987 [M − Na − dmso − 2CH_4]$^-$ (calcd 395.9987) 2%. Anal. Calcd (%) for $C_{11}H_{23}N_2NaO_4PtS_2$: C, 24.95; H, 4.38; N, 5.29. Found (%): C, 24.13; H, 4.54; N, 4.90.

*cis-(Dimethyl sulfoxide)dimethyl[1-(3-sodium sulfonatopropyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]platinum(II) (**2c**).* Complex **2c** was obtained from **1c** (0.416 g, 1.35 mmol) as a pale brown solid (0.796 g, 93%). ^{1}H NMR (300 MHz, D_2O): δ 7.27 (d, $^{3}J_{HH}$ = 1.8, 1H, Imz), 6.93 (d, $^{3}J_{HH}$ = 1.8, 1H, Imz), 6.87 (s, 1H, Ar), 6.85 (s, 1H, Ar), 4.33 (m, 1H, NCH_2), 4.26 (m, 1H, NCH_2), 2.92 (s br, 3H, Me_2SO), 2.83 (m, 2H, CH_2S), 2.56 (s br, 3H, Me_2SO), 2.21 (m, 2H, $CH_2CH_2CH_2$), 2.15 (s, 3H, Ar-*p*-Me), 1.96 (s, 3H, Ar-*o*-Me), 1.90 (s, 3H, Ar-*o*-Me), 0.23 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 81.2, 3H, PtMe *cis* to NHC), −0.31 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 59.4, 3H, PtMe *trans* to NHC). ^{1}H NMR (300 MHz, dmso-d_6): δ 7.49 (d, $^{3}J_{HH}$ = 1.8, 1H, Imz), 7.13 (d, $^{3}J_{HH}$ = 1.8, 1H, Imz), 6.95 (s, 2H, Ar), 4.36 (m, 1H, NCH_2), 4.25 (m, 1H, NCH_2), 2.46 (m, 2H, CH_2S), 2.27 (s, 3H, Ar-*p*-Me), 2.16 (m, 2H, $CH_2CH_2CH_2$), 2.07 (s, 3H, Ar-*o*-Me), 1.99 (s, 3H, Ar-*o*-Me), 0.10 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 81.5, 3H, PtMe *cis* to NHC), −0.35 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 61.0, 3H, PtMe *trans* to NHC). $^{13}C\{^{1}H\}$ NMR (75

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MHz, D_2O): δ 182.8 (s, Imz-C^2), 139.2 (s, Ar-C^4), 136.2 (s, Ar-C^2), 136.1 (s, Ar-C^1), 129.0 (s, Ar-C^3), 123.5 (s, Imz-C^4), 120.8 (s, Imz-C^5), 48.8 (s, NCH_2), 48.5 (s, CH_2S), 43.2 (s, Me_2SO), 42.5 (s, Me_2SO), 25.9 (s, $CH_2CH_2CH_2$), 20.6 (s, Ar-*p*-Me), 18.3 (s, Ar-*o*-Me), 18.2 (s, Ar-*o*-Me), −1.9 (s, PtMe *trans* to NHC), −7.3 (s, PtMe *cis* to NHC). ^{195}Pt NMR (64 MHz, dmso-d_6): δ −3985. ESI-MS (negative ion, MeOH): *m*/*z* 532.1192 [M − Na − dmso]$^-$ (calcd 532.1239) 3%; 516.0885 [M − Na − dmso − CH_4]$^-$ (calcd 516.0926) 100%; 500.0562 [M − Na − dmso − $2CH_4$]$^-$ (calcd 500.0613) 18%. Anal. Calcd (%) for $C_{19}H_{36}N_2NaO_{6.5}PtS_2$ (**2c**·2.5H_2O): C, 33.62; H, 5.35; N, 4.13. Found (%): C, 33.50; H, 4.80; N, 4.36.

*cis-[1-(2,6-Diisopropylphenyl)-3-(3-sodium sulfonatopropyl)-imidazol-2-ylidene](dimethyl sulfoxide)dimethylplatinum(II) (**2d**).* Complex **2d** was obtained from **2d** (0.473 g, 1.35 mmol) as a pale brown solid (0.830 g, 91%). ^{1}H NMR (300 MHz, D_2O): δ 7.37 (t, $^3J_{HH}$ = 6.9, 1H, Ar-H^4), 7.29 (s br, 1H, Imz), 7.24 (d, $^3J_{HH}$ = 6.6, 1H, Ar-H^3), 7.22 (d, $^3J_{HH}$ = 6.6, 1H, Ar-H^3), 7.09 (s br, 1H, Imz), 4.55 (m, 1H, NCH_2), 4.22 (m, 1H, NCH_2), 2.98 (s br, 3H, Me_2SO), 2.87 (m, 2H, CH_2S), 2.72 (s br, 3H, Me_2SO), 2.37 (m, 2H, $CHMe_2$), 2.25 (m, 2H, $CH_2CH_2CH_2$), 1.20 (d, $^3J_{HH}$ = 6.6, 3H, $CHMe_2$), 1.14 (d, $^3J_{HH}$ = 6.6, 3H, $CHMe_2$), 0.92 (d, $^3J_{HH}$ = 6.6, 3H, $CHMe_2$), 0.84 (d, $^3J_{HH}$ = 6.6, 3H, $CHMe_2$), 0.18 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 82.2, 3H, PtMe *cis* to NHC), −0.27 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 59.7, 3H, PtMe *trans* to NHC). ^{1}H NMR (300 MHz, dmso-d_6): δ 7.50 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 7.41 (t, $^3J_{HH}$ = 7.6, 1H, Ar-H^4), 7.26 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 7.25 (d, $^3J_{HH}$ = 7.6, 2H, Ar H^3), 4.45 (m, 1H, NCH_2), 4.30 (m, 1H, NCH_2), 2.97 (m, 1H, $CHMe_2$), 2.59 (m, 1H, $CHMe_2$), 2.48 (m, 2H, CH_2S), 2.17 (m, 2H, $CH_2CH_2CH_2$), 1.23 (d, $^3J_{HH}$ = 6.9, 3H, $CHMe_2$), 1.20 (d, $^3J_{HH}$ = 6.9, 3H, $CHMe_2$), 0.99 (d, $^3J_{HH}$ = 6.9, 3H, $CHMe_2$), 0.92 (d, $^3J_{HH}$ = 6.6, 3H, $CHMe_2$), 0.06 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 80.5, 3H, PtMe *cis* to NHC), −0.34 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 61.4, 3H, PtMe *trans* to NHC). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ 183.1 (s, Imz-C^2), 145.6 (s, Ar-C^2), 145.5 (s, Ar-C^2), 135.7 (s, Ar-C^1), 128.6 (s, Ar-C^4), 123.9 (s, Imz-C^5), 122.9 (s, Ar-C^3), 122.7 (s, Ar-C^3), 119.3 (s, Imz-C^4), 48.5 (s, NCH_2), 48.1 (s, CH_2S), 27.3 (s, $CHMe_2$), 26.8 (s, $CHMe_2$), 26.0 (s, $CH_2CH_2CH_2$), 25.71 (s, $CHMe_2$), 25.67 (s, $CHMe_2$), 22.2 (s, $CHMe_2$), 21.9 (s, $CHMe_2$), −0.9 (s, PtMe *trans* to NHC), −8.4 (s, PtMe *cis* to NHC). ^{195}Pt NMR (64 MHz, dmso-d_6): δ −3980. ESI-MS (negative ion, MeOH): *m*/*z* 574.1738 [M − Na − dmso]$^-$ (calcd 574.1709) 47%; 558.1431 [M − Na − dmso − CH_4]$^-$ (calcd 558.1396) 100%; 542.1131 [M − Na − dmso − $2CH_4$]$^-$ (calcd 542.1083) 12%. Anal. Calcd (%) for $C_{22}H_{45}N_2NaO_8PtS_2$ (**2d**·4H_2O): C, 35.33; H, 6.07; N, 3.75. Found (%): C, 35.17; H, 5.51; N, 3.63.

*[PtClMe(dmso)(NHC·Na)] (**3**). Method a.* A titrated aqueous solution of HCl (0.942 M, 150 μL, 0.141 mmol) was added dropwise to a solution of **2** (0.141 mmol) in water (2 mL). The mixture was stirred at room temperature until methane evolution ceased (ca. 5−10 min). The solvent was then removed under high vacuum at 50 °C, and the solid thus obtained dried for 6 h at 70 °C and 4 mbar of pressure.

Method b. Sodium hydrogen carbonate (0.084 g, 1.0 mmol) was added to a solution of *trans*-[PtMeCl(dmso)$_2$] (0.101 g, 0.251 mmol) and the corresponding imidazolium salt (0.250 mmol) in dimethyl sulfoxide (3 mL). The mixture was stirred for 12 h at 100 °C, cooled back to room temperature, and filtered through a plug of kieselguhr. After complete removal of the solvent, the resulting powdery solids were dried under vacuum (5 h, 90 °C, 4 mbar).

Accurate elemental analyses could not be obtained for complexes **3a−d** probably due to their contamination with water and dmso molecules. They were characterized in solution as a mixture of two diastereoisomers. In the case of **3a**, the stereochemistry of these diastereoisomers was determined with a 2D NOESY experiment performed in D_2O. The methyl protons of both isomers showed cross-peaks with the corresponding *N*-alkyl chain, whereas the correlation between the dmso at 3.2 ppm and the methyl at 0.46 ppm, in one case, and the dmso at 3.0 ppm and one of the *N*-alkyl chains, in the other, served to identify the *SP*-4−3 and *SP*-4−4 isomers, respectively. The assignment of stereoisomers for **3b−d** was based on the $^1H-^{195}Pt$ coupling constants found for the methyl groups in **3a**. Coupling constants of around 80−90 Hz (88 Hz in **3a**) were assigned to the isomer with the methyl and chloride ligands in *trans* position (*SP*-4−4), whereas those around 60−70 Hz (66 Hz in **3a**) were assumed to be characteristic of the isomer with methyl and dmso in *trans* position (*SP*-4−3).

*Chlorido[1,3-bis(3-sodium sulfonatopropyl)imidazol-2-ylidene]-(dimethyl sulfoxide)methylplatinum(II) (**3a**).* Compound **3a** was obtained from **2a** (93.0 mg, 0.141 mmol) as a white, spectroscopically pure solid (93.0 mg, 97%). Ratio of diastereoisomers (*SP*-4−3/*SP*-4−4): 52:48 (D_2O), 71:29 (dmso-d_6). ^{1}H NMR (300 MHz, D_2O): δ [*SP*-4−3 and *SP*-4−4] 7.19 (s, 2H, Imz), 7.17 (s, 2H, Imz), 4.36 (m, 4H, NCH_2), 4.24 (m, 4H, NCH_2), 3.23 (s, 6H, Me_2SO), 3.03 (s, 6H, Me_2SO), 2.86 (t, $^3J_{HH}$ = 7.5, 8H, CH_2S, overlapped for both isomers), 2.25 (m, 8H, $CH_2CH_2CH_2$ overlapped for both isomers), 0.50 (s with ^{195}Pt satellites, 3H, $^2J(^1H-^{195}Pt)$ = 65.9, 3H, PtMe), 0.46 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 88.5, 3H, PtMe). ^{1}H NMR (300 MHz, dmso-d_6): δ [*SP*-4−3] 7.35 (s, 2H, Imz), 4.23 (t, $^3J_{HH}$ = 7.0, 4H, NCH_2), 2.47 (m, 4H, CH_2S), 2.11 (m, 4H, $CH_2CH_2CH_2$), 0.34 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 68.4, 3H, PtMe); [*SP*-4−4] 7.37 (s, 2H, Imz), 4.37 (m, 2H, NCH_2), 4.17 (m, 2H, NCH_2), 2.44 (m, 4H, CH_2S), 2.11 (m, 4H, $CH_2CH_2CH_2$), 0.32 (s, 3H, PtMe). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ [*SP*-4−3] 151.8 (s, Imz-C^2), 120.4 (s, Imz-$C^{4,5}$), 48.5 (s, NCH_2), 47.8 (s, CH_2S), 25.7 (s, $CH_2CH_2CH_2$), −12.3 (s, PtMe); [*SP*-4−4] 161.7 (s, Imz-C^2), 120.6 (s, Imz-$C^{4,5}$), 48.2 (s, NCH_2), 47.8 (s, CH_2S), 25.9 (s, $CH_2CH_2CH_2$), −19.7 (s, PtMe). ^{195}Pt NMR (64 MHz, dmso-d_6): δ [*SP*-4−3] −3954; [*SP*-4−4] −4101. ESI-MS (negative ion, MeOH): *m*/*z* 656.0001 [M − Na]$^-$ (calcd 655.9907) 0.6%; 577.9896 [M − Na − dmso]$^-$ (calcd 577.9767) 21%; 556.0028 [M − 2Na + H − dmso]$^-$ (calcd 555.9948) 13%; 561.9588 [M − Na − dmso − CH_4]$^-$ (calcd 561.9454) 3.4%; 503.9981 [M − 2Na − dmso − CH_4 − Cl]$^-$ (calcd 503.9874) 100%.

*Chlorido(dimethyl sulfoxide)methyl[1-methyl-3-(3-sodium sulfonatopropyl)imidazol-2-ylidene]platinum(II) (**3b**).* Compound **3b** was obtained from **2b** (74.7 mg, 0.141 mmol) as a white, spectroscopically pure solid (71.3 mg, 92%). Ratio of diastereoisomers (*SP*-4−3/*SP*-4−4): 53:47 (D_2O), 70:30 (dmso-d_6). ^{1}H NMR (300 MHz, D_2O): δ [*SP*-4−3 and *SP*-4−4] 7.15 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 7.13 (s, $^3J_{HH}$ = 2.0, 1H, Imz), 7.10 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 7.08 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 4.38 (m, 2H, NCH_2), 4.21 (m, 2H, NCH_2), 3.75 (s, 3H, NMe), 3.73 (s, 3H, NMe), 3.22 (s with ^{195}Pt satellites, $^3J(^1H-^{195}Pt)$ = 16.3, 6H, Me_2SO), 3.01 (s, 3H, Me_2SO), 2.99 (s, 3H, Me_2SO), 2.85 (t, $^3J_{HH}$ = 7.5, 4H, CH_2S overlapped for both isomers), 2.23 (m, 4H, $CH_2CH_2CH_2$ overlapped for both isomers), 0.45 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 70.2, 3H, PtMe), 0.33 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 87.6, 3H, PtMe). ^{1}H NMR (300 MHz, dmso-d_6): δ [*SP*-4−3] 7.35 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 7.31 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 4.22 (t, $^3J_{HH}$ = 6.9, 2H, NCH_2), 3.74 (s, 3H, NMe), 2.98 (s, 6H, Me_2SO), 2.44 (m, 2H, CH_2S), 2.10 (m, 2H, $CH_2CH_2CH_2$), 0.34 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 71.6, 3H, PtMe); [*SP*-4−4] 7.38 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 7.32 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 4.38 (m, 1H, NCH_2), 4.18 (m, 1H, NCH_2), 3.75 (s, 3H, NMe), 2.44 (m, 2H, CH_2S), 2.10 (m, 2H, $CH_2CH_2CH_2$), 0.33 (s, 3H, PtMe). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ [*SP*-4−3] 152.0 (s, Imz-C^2), 121.2 (s, Imz-C^5), 120.0 (s, Imz-C^4), 48.0 (s, NCH_2), 47.5 (s, CH_2S), 41.3 (s, Me_2SO), 36.3 (s, NMe), 25.5 (s, $CH_2CH_2CH_2$), −13.1 (s, PtMe); [*SP*-4−4] 121.3 (s, Imz-C^5), 120.4 (s, Imz-C^4), 47.8 (s, NCH_2), 47.5 (s, CH_2S), 36.1 (s, NMe), 25.8 (s, $CH_2CH_2CH_2$), −20.4 (s, PtMe), Imz-C^2 not observed. ^{195}Pt NMR (64 MHz, dmso-d_6): δ [*SP*-4−3] −3964; [*SP*-4−4] −4104. ESI-MS (negative ion, MeOH): *m*/*z* 526.0146 [M − Na]$^-$ (calcd 526.0206) 2.4%; 448.0091 [M − Na − dmso]$^-$ (calcd 448.0067) 100%; 431.9780 [M − Na − dmso − CH_4]$^-$ (calcd 431.9754) 27%.

*Chlorido(dimethyl sulfoxide)methyl[1-(3-sodium sulfonatopropyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]platinum(II) (**3c**).* Compound **3c** was obtained from **2c** (89.3 mg, 0.141 mmol) as a white, spectroscopically pure solid (84.8 mg, 92%). Ratio of diastereoisomers (*SP*-4−3/*SP*-4−4): 32:68 (D_2O), 48:52 (dmso-d_6). Very broad resonances were observed in the ^{1}H NMR spectrum of **3c** in D_2O at room temperature; only selected resonances are given. ^{1}H NMR (300 MHz, D_2O): δ [*SP*-4−3] 3.05 (s br, 3H, Me_2SO), 2.87 (s br, 3H, Me_2SO), 0.42 (br, 3H, PtMe); [*SP*-4−4] 3.09 (s br, 3H,

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Me_2SO), 2.99 (s br, 3H, Me_2SO), 0.28 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 84.0, 3H, PtMe). ^{1}H NMR (500 MHz, dmso-d_6): δ [*SP*-4−3] 7.62 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 7.30 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 7.02 (s, 1H, Ar), 7.01 (s, 1H, Ar), 4.46 (m, 1H, NCH_2), 4.28 (m, 1H, NCH_2), 2.44 (m, 2H, CH_2S), 2.294 (s, 3H, Ar *p*-Me), 2.24 (m, 2H, $CH_2CH_2CH_2$), 2.10 (s, 3H, Ar-*o*-Me), 1.97 (s, 3H, Ar-*o*-Me), 0.28 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 61.2, 3H, PtMe); [*SP*-4−4] 7.64 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 7.30 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 6.99 (s, 1H, Ar), 6.98 (s, 1H, Ar), 4.76 (m, 1H, NCH_2), 4.21 (m, 1H, NCH_2), 2.44 (m, 2H, CH_2S), 2.29 (s, 3H, Ar-*p*-Me), 2.24 (m, 2H, $CH_2CH_2CH_2$), 2.18 (s, 3H, Ar-*o*-Me), 1.96 (s, 3H, Ar-*o*-Me), 0.14 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 81.0, 3H, PtMe). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ [*SP*-4−3] 152.5 (s, Imz-C^2), 137.6 (s, Ar-C^4), 135.3 (s, Ar-C^2), 135.1 (s, Ar-C^2), 134.6 (s, Ar-C^1), 128.4 (s, Ar-C^3), 128.3 (s, Ar-C^3), 122.9 (s, Imz-C^4), 120.7 (s, Imz-C^5), 48.7 (s, NCH_2), 48.0 (s, CH_2S), 25.7 (s, $CH_2CH_2CH_2$), 20.1 (s, Ar-*p*-Me), 18.2 (s, Ar-*o*-Me), 17.8 (s, Ar-*o*-Me), −11.5 (s, PtMe); [*SP*-4−4] 162.0 (s, Imz-C^2), 137.5 (s, Ar-C^4), 135.1 (s, Ar-C^2), 135.0 (s, Ar-C^2), 134.0 (s, Ar-C^1), 128.4 (s, Ar-C^3), 127.9 (s, Ar-C^3), 122.7 (s, Imz-C^4), 121.3 (s, Imz-C^5), 49.1 (s, NCH_2), 47.9 (s, CH_2S), 26.1 (s, $CH_2CH_2CH_2$), 20.2 (s, Ar-*p*-Me), 17.7 (s, Ar-*o*-Me), 17.3 (s, Ar-*o*-Me), −19.8 (s, PtMe). ^{195}Pt NMR (64 MHz, dmso-d_6): δ [*SP*-4−3] −3929; [*SP*-4−4] −4098. ESI-MS (negative ion, MeOH): *m*/*z* 630.0781 $[M - Na]^-$ (calcd 630.0832) 0.9%; 552.0718 $[M - Na - dmso]^-$ (calcd 552.0693) 100%; 536.0402 $[M - Na - dmso - CH_4]^-$ (calcd 536.0380) 54%.

Chlorido[1-(2,6-diisopropylphenyl)-3-(3-sodium sulfonatopropyl)imidazol-2-ylidene](dimethyl sulfoxide)-methylplatinum(II) ***(3d)***. Compound **3d** was obtained from **2d** (95.3 mg, 0.141 mmol) as a white, spectroscopically pure solid (92.3 mg, 94%). Ratio of diastereoisomers (*SP*-4−3/*SP*-4−4): 30:70 (D_2O), 43:57 (dmso-d_6). Very broad resonances were observed in the ^{1}H NMR spectrum of **3d** in D_2O at room temperature; only selected resonances are given. ^{1}H NMR (300 MHz, D_2O): δ [*SP*-4−3] 3.01 (s, 3H, Me_2SO), 2.84 (s, 3H, Me_2SO); [*SP*-4−4] 3.07 (s, 6H, Me_2SO), 2.95 (s, 6H, Me_2SO). ^{1}H NMR (500 MHz, dmso-d_6): δ [*SP*-4−3] 7.64 (d, $^3J_{HH}$ = 1.5, 1H, Imz), 7.47 (d, $^3J_{HH}$ = 3.0, 1H, Imz), 7.43 (m, 1H, Ar-H^4), 7.31 (d, $^3J_{HH}$ = 8.5, 1H, Ar-H^3), 7.307 (d, $^3J_{HH}$ = 8.5, 1H, Ar-H^3), 4.57 (m, 1H, NCH_2), 4.31 (m, 1H, NCH_2), 3.02 (m, 1H, $CHMe_2$), 2.36 (m, 1H, $CHMe_2$), 2.24 (m, 2H, CH_2S), 2.239 (m, 2H, $CH_2CH_2CH_2$), 1.29 (d, $^3J_{HH}$ = 6.5, 3H, $CHMe_2$), 1.21 (d, $^3J_{HH}$ = 6.5, 3H, $CHMe_2$), 1.04 (d, $^3J_{HH}$ = 7.0, 3H, $CHMe_2$), 0.91 (d, $^3J_{HH}$ = 6.5, 3H, $CHMe_2$), 0.25 (s, 3H, PtMe); [*SP*-4−4] 7.65 (d, $^3J_{HH}$ = 1.5, 1H, Imz), 7.44 (d, $^3J_{HH}$ = 1.5, 1H, Imz), 7.45 (m, 1H, Ar-H^4), 7.29 (d, $^3J_{HH}$ = 8.0, 1H, Ar-H^3), 7.27 (d, $^3J_{HH}$ = 7.5, 1H, Ar-H^3), 4.84 (m, 1H, NCH_2); 4.20 (m, 1H, NCH_2), 3.15 (m, 1H, $CHMe_2$), 2.46 (m, 2H, CH_2S), 2.27 (m, 1H, $CHMe_2$), 2.24 (m, 2H, $CH_2CH_2CH_2$), 1.25 (d, $^3J_{HH}$ = 6.5, 3H, $CHMe_2$), 1.19 (d, $^3J_{HH}$ = 7.0, 3H, $CHMe_2$), 1.11 (d, $^3J_{HH}$ = 7.0, 3H, $CHMe_2$), 0.89 (d, $^3J_{HH}$ = 7.0, 3H, $CHMe_2$), 0.10 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 78.0, 3H, PtMe). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ [*SP*-4−3] 145.7 (s, Ar-C^2), 145.6 (s, Ar-C^2), 135.4 (s, Ar-C^1), 129.21 (s, Ar-C^4), 124.41 (s, Imz-C^5), 123.24 (s, Ar-C^3), 123.0 (s, Ar-C^3), 120.9 (s, Imz-C^4), 48.0 (s, CH_2S), 47.1 (s, NCH_2), 27.6 (s, $CHMe_2$ isochronous for both isomers), 27.1 (s, $CHMe_2$), 26.3 (s, $CH_2CH_2CH_2$ isochronous for both isomers), 25.9 (s, $CHMe_2$), 25.5 (s, $CHMe_2$), 22.1 (s, $CHMe_2$), 21.8 (s, $CHMe_2$), −11.4 (s, PtMe), Imz-C^2 not observed; [*SP*-4−4] 162.7 (s, Imz-C^2), 146.0 (s, Ar-C^2), 144.8 (s, Ar-C^2), 134.5 (s, Ar-C^1), 129.17 (s, Ar-C^4), 124.36 (s, Imz-C^5), 123.17 (s, Ar-C^3), 122.9 (s, Ar-C^3), 120.8 (s, Imz-C^4), 48.9 (s, NCH_2), 47.9 (s, CH_2S), 27.6 (s, $CHMe_2$ isochronous for both isomers), 26.9 (s, $CHMe_2$), 26.3 (s, $CH_2CH_2CH_2$ isochronous for both isomers), 25.8 (s, $CHMe_2$), 25.2 (s, $CHMe_2$), 22.3 (s, $CHMe_2$), 22.0 (s, $CHMe_2$), −19.4 (s, PtMe). ^{195}Pt NMR (64 MHz, dmso-d_6): δ [*SP*-4−3] −3927; [*SP*-4−4] −4106. ESI-MS (negative ion, MeOH): *m*/*z* 672.1316 $[M - Na]^-$ (calcd 672.1302) 3.2%; 594.1179 $[M - Na - dmso]^-$ (calcd 594.1162) 100%; 578.0869 $[M - Na - dmso - CH_4]^-$ (calcd 578.0849) 4.4%.

$[PtCl_2(dmso)(NHC{\cdot}Na)]$ (4). A titrated aqueous solution of HCl (0.942 M, 150 μL, 0.141 mmol) was added dropwise to a solution of **2** (0.071 mmol) in water (2 mL). The mixture was stirred at room temperature until methane evolution ceased (ca. 5−10 min). The solvent was then removed under high vacuum at 50 °C, and the solid thus obtained dried for 6 h at 70 °C and 4 mbar of pressure. Complexes **4a**−**d** were characterized by comparison with their previously reported NMR data.[28]

$[PtMe(OH_2)(dmso)(NHC)]$ (5). A 50% aqueous solution of HBF_4 (19 μL, 0.151 mmol) was added dropwise to a solution of **2** (0.151 mmol) in water (2 mL). The mixture was stirred at room temperature until methane evolution ceased (ca. 5−10 min). The solvent was then removed under high vacuum at 50 °C, and the solid thus obtained dried for 6 h at 70 °C and 4 mbar of pressure. Solid samples of **5** thus obtained are contaminated with $NaBF_4$.

Sodium Aqua[1,3-bis(3-sulfonatopropyl)imidazol-2-ylidene](dimethyl sulfoxide)methylplatinate(II) ***(5a)***. Complex **5a** was obtained from **2a** (99.6 mg, 0.151 mmol) as a white solid (0.109 g). ESI-MS (positive ion, H_2O): *m*/*z* 644.0043 $[M + Na - H_2O]^+$ (calcd 644.0105) 100%; 618.0969 $[M - Na + 2H]^+$ (calcd 618.0572) 40%; 584.0052 $[M + Na - dmso]^+$ (calcd 584.0071) 45%; 565.9926 $[M + Na - H_2O - dmso]^+$ (calcd 565.9966) 83%; 549.9574 $[M + Na - H_2O - dmso - CH_4]^+$ (calcd 549.9653) 8.9%; 544.0088 $[M + H - H_2O - dmso]^+$ (calcd 544.0146) 10%; 527.9805 $[M + H - H_2O - dmso - CH_4]^+$ (calcd 527.9833) 4.3%. ESI-MS (negative ion, H_2O): *m*/*z* 598.0026 $[M - Na - H_2O]^-$ (calcd 598.0321) 4.5%; 519.9917 $[M - Na - H_2O - dmso]^-$ (calcd 520.0181) 2.3%; 503.9597 $[M - Na - H_2O - dmso - CH_4]^-$ (calcd 503.9868) 100%. ESI-MS (positive ion, H_2O/DMSO): *m*/*z* 722.02 $[M + Na - H_2O + dmso]^+$ (calcd 722.02) 11%; 644.01 $[M + Na - H_2O]^+$ (calcd 644.01) 100%.

Aqua(dimethyl sulfoxide)methyl[1-methyl-3-(3-sulfonatopropyl)-imidazol-2-ylidene]platinum(II) ***(5b)***. Complex **5b** was obtained from **2b** (0.080 g, 0.151 mmol) as a white solid (0.092 g). ESI-MS (positive ion, H_2O): *m*/*z* 514.0268 $[M + Na - H_2O]^+$ (calcd 514.0404) 69%; 492.0506 $[M + H - H_2O]^+$ (calcd 492.0585) 83%; 436.0188 $[M + Na - H_2O - dmso]^+$ (calcd 436.0265) 25%; 419.9847 $[M + Na - H_2O - dmso - CH_4]^+$ (calcd 419.9952) 83%; 414.0386 $[M + H - H_2O - dmso]^+$ (calcd 414.0446) 9.6%; 398.0074 $[M + H - H_2O - dmso - CH_4]^+$ (calcd 398.0133) 100%.

Aqua(dimethyl sulfoxide)methyl[1-(3-sulfonatopropyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]platinum(II) ***(5c)***. Complex **5c** was obtained from **2c** (95.7 mg, 0.151 mmol) as a pale brown solid (0.105 g). ESI-MS (positive ion, H_2O): *m*/*z* 618.0936 $[M + Na - H_2O]^+$ (calcd 618.1030) 100%; 596.1119 $[M + H - H_2O]^+$ (calcd 596.1211) 35%; 540.0808 $[M + Na - H_2O - dmso]^+$ (calcd 540.0891) 4.9%; 524.0496 $[M + Na - H_2O - dmso - CH_4]^+$ (calcd 524.0578) 16%; 518.0957 $[M + H - H_2O - dmso]^+$ (calcd 518.1072) 1.4%; 502.0639 $[M + H - H_2O - dmso - CH_4]^+$ (calcd 502.0759) 5.5%.

Aqua[1-(2,6-diisopropylphenyl)-3-(3-sulfonatopropyl)imidazol-2-ylidene](dimethyl sulfoxide)methylplatinum(II) ***(5d)***. Complex **5d** was obtained from **2d** (0.102 g, 0.151 mmol) as a pale brown solid (0.105 g). ESI-MS (positive ion, H_2O): *m*/*z* 678.1622 $[M + Na]^+$ (calcd 678.1606) 1.0%; 660.1463 $[M + Na - H_2O]^+$ (calcd 660.1500) 100%; 638.1628 $[M + H - H_2O]^+$ (calcd 638.1680) 31%; 582.1331 $[M + Na - H_2O - dmso]^+$ (calcd 582.1361) 11%; 566.1012 $[M + Na - H_2O - dmso - CH_4]^+$ (calcd 566.1048) 3.4%; 560.1491 $[M + H - H_2O - dmso]^+$ (calcd 560.1541) 6.5%; 544.1241 $[M + H - H_2O - dmso - CH_4]^+$ (calcd 544.1228) 1.0%.

$[PtMe(dmso\text{-}d_6)_2(NHC)]$ (6). These complexes were obtained by dissolution of **5** in dmso-d_6.

Complex ***6a***. ^{1}H NMR (300 MHz, dmso-d_6): δ 7.48 (s, 2H, Imz), 4.32 (t, $^3J_{HH}$ = 7.0, 4H, NCH_2), 2.53 (m, 4H, CH_2S), 2.12 (m, 4H, $CH_2CH_2CH_2$), 0.29 (s with ^{195}Pt satellites, $^1J(^1H-^{195}Pt)$ = 65.3, PtMe). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ 156.2 (s, Imz-C^2), 121.7 (s, Imz-$C^{4,5}$), 48.8 (s, NCH_2), 47.6 (s, CH_2S), 26.0 (s, $CH_2CH_2CH_2$), −11.9 (s, PtMe). ^{195}Pt NMR (64 MHz, dmso-d_6): δ −4196.

Complex ***6b***. ^{1}H NMR (300 MHz, dmso-d_6): δ 7.51 (s, 1H, Imz), 7.45 (s, 1H, Imz), 4.34 (m, 2H, NCH_2), 3.78 (s, NMe), 2.52 (m, 2H, CH_2S), 2.11 (m, 2H, $CH_2CH_2CH_2$), 0.34 (s with ^{195}Pt satellites, $^1J(^1H-^{195}Pt)$ = 69.3, PtMe). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ 156.0 (s, Imz-C^2), 123.0 and 121.7 (2 × s, Imz-$C^{4,5}$), 48.6 (s, NCH_2), 47.5 (s, CH_2S), 36.8 (s, NMe), 26.0 (s, $CH_2CH_2CH_2$), −12.4 (s, PtMe). ^{195}Pt NMR (64 MHz, dmso-d_6): δ −4192.

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Complex ***6c***. ^{1}H NMR (300 MHz, dmso-d_6): δ 7.73 (s, 1H, Imz), 7.52 (s, 1H, Imz), 7.05 (s, 2H, Ar), 4.56 (m, 1H, NCH_2), 4.42 (m, 1H, NCH_2), 2.54 (m, 2H, CH_2S), 2.31 (s, 3H, Ar-*p*-Me), 2.20 (m, 2H, $CH_2CH_2CH_2$), 2.10 (s, 3H, Ar-*o*-Me), 2.01 (s, 3H, Ar-*o*-Me), 0.28 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 63.3, 3H, PtMe). ^{2}H NMR (77 MHz, dmso-d_6): δ 3.30 (br s, 3D, $(CD_3)_2SO$), 2.99 (br s, 3D, two $(CD_3)_2SO$ overlapping), 2.92 (br s, 3D, $(CD_3)_2SO$). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ 157.3 (s, Imz-C^2), 138.4 (s, Ar-C^4), 135.3 (s, Ar-C^2), 134.5 (s, Ar-C^2), 134.0 (s, Ar-C^1), 128.82 (s, Ar-C^3), 128.77 (s, Ar-C^3), 124.7 (s, Imz-C^4), 121.8 (s, Imz-C^5), 49.2 (s, NCH_2), 47.4 (s, CH_2S), 42.1 (s, Me_2SO), 26.3 (s, $CH_2CH_2CH_2$), 20.3 (s, Ar-*p*-Me), 18.1 (s, Ar-*o*-Me), 18.0 (s, Ar-*o*-Me), −10.1 (s, PtMe). ^{195}Pt NMR (64 MHz, dmso-d_6): δ −4174.

Complex ***6d***. ^{1}H NMR (300 MHz, dmso-d_6): δ 7.80 (s, 1H, Imz), 7.66 (s, 1H, Imz), 7.41 (t, $^3J_{HH}$ = 7.3, 1H, Ar-H^4), 7.39 (m, 2H, Ar-$H^{3,5}$), 4.65 (m, 1H, NCH_2), 4.49 (m, 1H, NCH_2), 2.76 (m, 1H, C*H*Me), 2.60 (m, 2H, CH_2S), 2.26 (m, 1H, C*H*Me), 2.19 (m, 2H, $CH_2CH_2CH_2$), 1.27 (d, $^3J_{HH}$ = 5.9, 3H, CH*Me*), 0.99 (d, $^3J_{HH}$ = 6.0, 3H, CH*Me*), 0.25 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 64.2, 3H, PtMe). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ 157.8 (s, Imz-C^2), 145.6 (s, Ar-C^2), 145.5 (s, Ar-C^2), 133.7 (s, Ar-C^1), 130.0 (s, Ar-C^4), 126.1 (s, Imz-C^5), 123.6 (s, Ar-C^3), 121.3 (s, Imz-C^4), 49.3 (s, NCH_2), 47.1 (s, CH_2S), 27.7 (s, CHMe_2), 27.4 (s, CHMe_2), 26.6 (s, $CH_2CH_2CH_2$), 26.2 (s, CHMe_2), 25.7 (s, CHMe_2), 22.2 (s, CHMe_2), 21.8 (s, CHMe_2), −10.1 (s, PtMe). ^{195}Pt NMR (64 MHz, dmso-d_6): δ −4173.

$[Pt(OH_2)_2(dmso)(NHC)][BF_4]$ (7). A 50% aqueous solution of HBF_4 (67 μL, 0.53 mmol) was added dropwise to a solution of **2** (0.177 mmol) in water (2 mL). The mixture was stirred at room temperature until methane evolution ceased (ca. 5−10 min). The solvent was then removed under high vacuum at 50 °C, and the solid thus obtained dried for 6 h at 70 °C and 4 mbar of pressure. Solid samples of **7** thus obtained are contaminated with $NaBF_4$.

*cis-Diaqua[1,3-bis(3-sulfonatopropyl)imidazol-2-ylidene](dimethyl sulfoxide)platinum(II) (**7a**).* Complex **7a** was obtained from **2a** (116.8 mg, 0.177 mmol) as a white solid (0.119 g). ^{1}H NMR (300 MHz, D_2O): δ 7.32 (s, 2H, Imz), 4.57 (m, 2H, NCH_2), 4.45 (m, 2H, NCH_2), 3.45 (s, 6H, Me_2SO), 2.94 (t, $^3J_{HH}$ = 7.2, 4H, CH_2S), 2.28 (m, 4H, $CH_2CH_2CH_2$). ESI-MS (positive ion, H_2O): *m*/*z* 605.9920 $[M + Na - 2H_2O]^+$ (calcd 605.9973) 100%.

*cis-Diaqua(dimethyl sulfoxide)[1-methyl-3-(3-sulfonatopropyl)-imidazol-2-ylidene]platinum(II) tetrafluoroborate (**7b**).* Complex **7b** was obtained from **2b** (93.7 mg, 0.177 mmol) as a pale yellow solid (0.100 g). ^{1}H NMR (300 MHz, D_2O): δ 7.29 (d, $^3J_{HH}$ = 2.1, 1H, Imz), 7.23 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 4.62 (m, 1H, NCH_2), 4.36 (m, 1H, NCH_2), 3.97 (s, 3H, NMe), 3.42 (s, 3H, Me_2SO), 3.41 (s, 3H, Me_2SO), 2.92 (m, 2H, CH_2S), 2.29 (m, 2H, $CH_2CH_2CH_2$). ESI-MS (positive ion, H_2O): *m*/*z* 476.0275 $[M - BF_4 - 2H_2O]^+$ (calcd 476.0272) 100%.

*cis-Diaqua(dimethyl sulfoxide)[1-(3-sulfonatopropyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]platinum(II) tetrafluoroborate (**7c**).* Complex **7c** was obtained from **2c** (112.2 mg, 0.177 mmol) as a yellow solid (0.121 g). ^{1}H NMR (300 MHz, D_2O): δ 7.47 (d, $^3J_{HH}$ = 1.2, 1H, Imz), 7.32 (d, $^3J_{HH}$ = 1.5, 1H, Imz), 7.19 (s, 1H, Ar), 7.06 (s, 1H, Ar), 4.91 (m, 1H, NCH_2), 4.29 (m, 1H, NCH_2), 3.32 (s, 3H, Me_2SO), 2.92 (m, 2H, CH_2S), 2.55 (s, 3H, Me_2SO), 2.38 (m, 2H, $CH_2CH_2CH_2$), 2.25 (s, 3H, Ar-*p*-Me), 2.17 (s, 3H, Ar-*o*-Me), 1.86 (s, 3H, Ar-*o*-Me). ESI-MS (positive ion, H_2O): *m*/*z* 598.1071 $[M - BF_4 - H_2O]^+$ (calcd 598.1004) 20%, 580.0887 $[M - BF_4 - 2H_2O]^+$ (calcd 580.0898) 100%.

*cis-Diaqua[1-(2,6-diisopropylphenyl)-3-(3-sulfonatopropyl)-imidazol-2-ylidene](dimethyl sulfoxide)platinum(II) (**7d**).* Complex **7d** was obtained from **2d** (119.6 mg, 0.177 mmol) as a yellow solid (0.125 g). ^{1}H NMR (300 MHz, D_2O): δ 7.46 (t, $^3J_{HH}$ = 7.8, 1H, Ar-H^4), 7.29 (s, 1H, Imz overlapped), 7.29 (m, 2H, Ar-$H^{3,5}$ overlapped), 7.10 (d, $^3J_{HH}$ = 2.1, 1H, Imz), 4.53 (m, 1H, NCH_2), 4.33 (m, 1H, NCH_2), 3.00 (s, 3H, Me_2SO), 2.88 (m, 2H, CH_2S), 2.58 (s, 3H, Me_2SO), 2.35 (m, 2H, C*H*Me), 2.27 (m, 2H, $CH_2CH_2CH_2$), 1.17 (m, 6H, CH*Me*), 0.92 (m, 6H, CH*Me*). ESI-MS (positive ion, H_2O): *m*/*z* 622.1389 $[M - BF_4 - 2H_2O]^+$ (calcd 622.1367) 100%.

K[*cis*-$PtMe_2$(CN)(NHC·Na)] (8). Formation of these complexes was monitored by ^{1}H NMR spectroscopy. Potassium cyanide (2.3 mg, 0.035 mmol) was added to an NMR tube fitted with a J. Young valve containing a solution of the corresponding complex **2** (0.035 mmol) in D_2O (0.7 mL).

Complex ***8a***. ^{1}H NMR (300 MHz, D_2O): δ 7.05 (s, 2H, Imz), 4.21 (t, $^3J_{HH}$ = 6.6, 4H, NCH_2), 2.81 (m, 4H, CH_2S), 2.16 (m, 4H, $CH_2CH_2CH_2$), 0.03 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 62.4, 3H, PtMe *trans* to NHC), −0.23 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 69.4, 3H, PtMe *cis* to NHC).

Complex ***8b***. ^{1}H NMR (300 MHz, D_2O): δ 7.01 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 6.95 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 4.19 (t, $^3J_{HH}$ = 7.0, 2H, NCH_2), 3.59 (s, 3H, NMe), 2.80 (m, 2H, CH_2S), 2.16 (m, 2H, $CH_2CH_2CH_2$), 0.04 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 63.8, 3H, PtMe *trans* to NHC), −0.21 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 68.8, 3H, PtMe *cis* to NHC).

Complex ***8c***. ^{1}H NMR (300 MHz, D_2O): δ 7.26 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 6.96 (s, 2H, Ar), 6.82 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 4.36 (t, $^3J_{HH}$ = 6.7, 2H, NCH_2), 2.90 (t, $^3J_{HH}$ = 7.9, 2H, CH_2S), 2.26 (m, 2H, $CH_2CH_2CH_2$), 2.23 (s, 3H, Ar-*p*-Me), 1.99 (s, 3H, Ar-*o*-Me); −0.15 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 63.6, 3H, PtMe *trans* to NHC), −0.30 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 69.7, 3H, PtMe *cis* to NHC).

K[*cis*-PtMe$(CN)_2$(NHC·Na)] (9). Potassium cyanide (26.0 mg, 0.400 mmol) was added to a solution of the corresponding complex **2** (0.200 mmol) in water (3 mL). The mixture was stirred for 3 h at room temperature. The solvent was removed under vacuum, and the solid thus obtained was dried for 5 h at 80 °C and 4 mbar of pressure. No further purification was attempted.

Complex ***9a***. This complex was obtained from **2a** (0.132 g, 0.200 mmol) as a white solid (0.124 g). IR (cm^{-1}): ν (C≡N) 2118 (s), 2102 (s). ^{1}H NMR (300 MHz, D_2O): δ 7.13 (s, 2H, Imz), 4.18 (t, $^3J_{HH}$ = 6.8, 4H, NCH_2), 2.81 (m, 4H, CH_2S), 2.19 (m, 4H, $CH_2CH_2CH_2$), −0.02 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 67.1, 3H, PtMe). $^{13}C\{^1H\}$ NMR (75 MHz, D_2O): δ 168.5 (s, Imz-C^2), 145.2 (s, CN *cis* to NHC), 141.8 (s, CN *trans* to NHC), 121.4 (s with ^{195}Pt satellites, $^3J(^{13}C-^{195}Pt)$ = 30.9, Imz-$C^{4,5}$), 48.7 (s, NCH_2), 48.4 (s, CH_2S), 25.6 (s, $CH_2CH_2CH_2$), −18.2 (s with ^{195}Pt satellites, $^1J(^{13}C-^{195}Pt)$ = 508.6, PtMe). ESI-MS (negative ion, MeOH): *m*/*z* 633.9463 $[M - Na]^-$ (calcd 633.9777) 31%; 617.9711 $[M - Na - CH_4]^-$ (calcd 617.9464) 17%; 595.9322 $[M - 2Na + H - CH_4]^-$ (calcd 595.9645) 24%; 557.9776 $[M - 2Na + 2H - K - CH_4]^-$ (calcd 558.0086) 91%; 530.9663 $[M - 2Na + H - KCN - CH_4]^-$ (calcd 530.9977) 27%; 503.9581 $[M - 2Na - KCN - CN - CH_4]^-$ (calcd 503.9874) 100%.

Complex ***9b***. This complex was obtained from **2b** (0.106 g, 0.200 mmol) as a pale yellow solid (0.102 g). IR (cm^{-1}): ν (C≡N) 2119 (s), 2101 (s). ^{1}H NMR (300 MHz, D_2O): δ 7.08 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 7.02 (d, $^3J_{HH}$ = 1.8, 1H, Imz), 4.16 (m, 2H, NCH_2), 3.60 (s, 3H, NMe), 2.80 (m, 2H, CH_2S), 2.16 (m, 2H, $CH_2CH_2CH_2$), −0.02 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 67.1, 3H, PtMe). $^{13}C\{^1H\}$ NMR (75 MHz, D_2O): δ 168.1 (s, Imz-C^2), 145.1 (s, CN *cis* to NHC), 141.9 (s, CN *trans* to NHC), 122.7 (s with ^{195}Pt satellites, $^3J(^{13}C-^{195}Pt)$ = 31.4, Imz-C^5), 120.8 (s with ^{195}Pt satellites, $^3J(^{13}C-^{195}Pt)$ = 31.8, Imz-C^4), 48.5 (s, NCH_2), 48.4 (s, CH_2S), 37.1 (s, NMe), 25.7 (s, $CH_2CH_2CH_2$), −18.6 (s, PtMe). ESI-MS (negative ion, MeOH): *m*/*z* 488.0342 $[M - K]^-$ (calcd 488.0338) 100%; 504.0078 $[M - Na]^-$ (calcd 504.0077) 93%; 439.0417 $[M - Na - KCN]^-$ (calcd 439.0409) 9.0%; 450.0200 $[M - Na - K + H - CH_4]^-$ (calcd 450.0205) 21%; 423.0087 $[M - Na - KCN - CH_4]^-$ (calcd 423.0096) 41%.

Complex ***9c***. This complex was obtained from **2c** (0.127 g, 0.200 mmol) as a yellow solid (0.120 g). IR (cm^{-1}): ν (C≡C) 2117 (s), 2102 (s). ^{1}H NMR (300 MHz, D_2O): δ 7.33 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 6.99 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 6.97 (s br, 2H, Ar), 4.31 (m, 2H, NCH_2), 2.84 (m, 2H, CH_2S), 2.26 (m, 2H, $CH_2CH_2CH_2$), 2.22 (s, 3H, Ar-*p*-Me), 2.00 (s, 3H, Ar-*o*-Me), 1.93 (s, 3H, Ar-*o*-Me), −0.13 (s with ^{195}Pt satellites, $^2J(^1H-^{195}Pt)$ = 67.1, 3H, PtMe). $^{13}C\{^1H\}$ NMR (75 MHz, D_2O): δ 169.4 (s, Imz-C^2), 145.5 (s, CN *cis* to NHC), 141.2 (s, CN *trans* to NHC), 139.4 (s, Ar-C^4), 136.0 (s, Ar-C^1), 135.6 (s, Ar-C^2), 135.5 (s, Ar-C^2), 129.0 (s, Ar-C^3), 128.9 (s, Ar-C^3), 123.4 (s with

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^{195}Pt satellites, $^{3}J(^{13}C-^{195}Pt)$ = 27.0, Imz-C^4), 121.4 (s with ^{195}Pt satellites, $^{3}J(^{13}C-^{195}Pt)$ = 28.5, Imz-C^5), 48.4 (s, NCH_2), 48.0 (s, CH_2S), 25.3 (s, $CH_2CH_2CH_2$), 20.1 (s, Ar-*p*-Me), 17.6 (s, Ar-*o*-Me), 17.2 (s, Ar-*o*-Me), −18.0 (s, PtMe). ESI-MS (negative ion, MeOH): *m*/*z* 608.0708 $[M - Na]^-$ (calcd 608.0703) 17%; 592.0954 $[M - K]^-$ (calcd 592.0964) 27%; 554.0818 $[M - Na - K + H - CH_4]^-$ (calcd 554.0831) 100%; 543.1042 $[M - Na - KCN]^-$ (calcd 543.1035) 7.6%; 527.0723 $[M - Na - KCN - CH_4]^-$ (calcd 527.0727) 41%.

[PtMe$_2$(CNCH$_2$COOK)(NHC·Na)] (10). Potassium 2-isocyanoacetate (85% purity, 0.0217 g, 0.150 mmol) was added to a solution of the corresponding complex **2** (0.150 mmol) in water (5 mL), and the mixture stirred for 2 h at room temperature. The solvent was then removed under vacuum, and the solid thus obtained dried for 5 h at 80 °C and 4 mbar of pressure.

*cis-[1,3-Bis(3-sodium sulfonatopropyl)imidazol-2-ylidene]-dimethyl(potassium-2-isocyanidoacetate)platinum(II) (**10a**).* This complex was obtained from **2a** (98.9 mg, 0.150 mmol) as a white solid (0.103 g, 97%). IR (cm^{-1}): ν (C≡N) 2167 (m). ^{1}H NMR (300 MHz, D_2O): δ 7.10 (s, 2H, Imz), 4.19 (t, $^{3}J_{HH}$ = 6.7, 4H, NCH_2), 2.78 (m, 4H, CH_2S), 2.14 (m, 4H, $CH_2CH_2CH_2$), 0.16 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 64.4, 3H, PtMe *trans* to NHC); −0.06 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 69.4, 3H, PtMe *cis* to NHC). $^{13}C\{^1H\}$ NMR (75 MHz, D_2O): δ 180.8 (s with ^{195}Pt satellites, $^{1}J(^{13}C-^{195}Pt)$ = 811.5, Imz-C^2), 171.3 (s, COOK), 142.8 (s, PtCNR), 121.0 (s with ^{195}Pt satellites, $^{3}J(^{13}C-^{195}Pt)$ = 20.1, Imz-C^{4,5}), 48.4 (s, CH_2S), 48.2 (s, $CNCH_2COOK$), 48.0 (s, NCH_2), 25.7 (s, $CH_2CH_2CH_2$), −6.1 (s, with ^{195}Pt satellites, $^{1}J(^{13}C-^{195}Pt)$ = 591.8, PtMe *cis* to NHC), −11.7 (s, with ^{195}Pt satellites, $^{1}J(^{13}C-^{195}Pt)$ = 498.8, PtMe *trans* to NHC). ESI-MS (negative ion, H_2O): *m*/*z* 621.0477 $[M - 2Na - K + 2H]^-$ (calcd 621.0658) 3.8%, 627.0263 $[M - Na - K + H - CH_4]^-$ (calcd 627.0164) 7.0%, 605.0263 $[M - 2Na - K + 2H - CH_4]^-$ (calcd 605.0345) 19%, 558.0356 $[M - Na - CNCH_2COOK]^-$ (calcd 558.0314) 3.5%, 536.0474 $[M - 2Na + H - CNCH_2COOK]^-$ (calcd 536.0494) 2.3%, 503.9894 $[M - 2Na + H - CNCH_2COOK - 2CH_4]^-$ (calcd 503.9868) 20%, 267.5213 $[M - 2Na - CNCH_2COOK]^{2-}$ (calcd 267.5210) 100%.

*cis-Dimethyl[1-methyl-3-(3-sodium sulfonatopropyl)imidazol-2-ylidene](potassium-2-isocyanidoacetate)platinum(II) (**10b**).* This complex was obtained from **2b** (79.4 mg, 0.150 mmol) as a pale yellow solid (84.5 mg, 98%). IR (cm^{-1}): ν (C≡N) 2168 (s). ^{1}H NMR (300 MHz, D_2O): δ 7.06 (d, $^{3}J_{HH}$ = 1.5, 1H, Imz), 7.00 (d, $^{3}J_{HH}$ = 1.5, 1H, Imz), 4.17 (t, $^{3}J_{HH}$ = 6.6, 2H, NCH_2), 3.99 (d, $^{3}J_{HH}$ = 5.7, 1H, $CNCH_2CO_2K$), 3.97 (d, $^{3}J_{HH}$ = 5.7, 1H, $CNCH_2CO_2K$), 3.60 (s, 3H, NMe), 2.79 (t, $^{3}J_{HH}$ = 6.9, 2H, CH_2S), 2.14 (q, $^{3}J_{HH}$ = 6.9, 2H, $CH_2CH_2CH_2$), 0.17 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 64.3, 3H, PtMe *trans* to NHC), −0.03 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 70.6, 3H, PtMe *cis* to NHC). $^{13}C\{^1H\}$ NMR (75 MHz, D_2O): δ 180.5 (s with ^{195}Pt satellites, $^{1}J(^{13}C-^{195}Pt)$ = 810.5, Imz-C^2), 171.3 (s, COOK), 142.7 (s, PtCNR), 122.5 (s with ^{195}Pt satellites, $^{3}J(^{13}C-^{195}Pt)$ = 20.5, Imz-C^5), 120.3 (s with ^{195}Pt satellites, $^{3}J(^{13}C-^{195}Pt)$ = 20.0, Imz-C^4), 48.4 (s, CH_2S), 48.3 (s, $CNCH_2COOK$), 48.1 (s, NCH_2), 36.9 (s, NMe), 25.8 (s, $CH_2CH_2CH_2$), −6.5 (s, with ^{195}Pt satellites, $^{1}J(^{13}C-^{195}Pt)$ = 591.1, PtMe *cis* to NHC), −11.5 (s, with ^{195}Pt satellites, $^{1}J(^{13}C-^{195}Pt)$ = 496.4, PtMe *trans* to NHC). ESI-MS (negative ion, MeOH): *m*/*z* 551.0324 $[M - Na]^-$ (calcd 551.0336) 3.6%, 535.0596 $[M - K]^-$ (calcd 535.0596) 12%, 513.0770 $[M - Na - K + H]^-$ (calcd 513.0777) 100%, 497.0479 $[M - Na - K + H - CH_4]^-$ (calcd 497.0464) 2.7%, 428.0610 $[M - Na - CNCH_2COOK]^-$ (calcd 428.0613) 28%, 412.0286 $[M - Na - CNCH_2COOK - CH_4]^-$ (calcd 412.0300) 7.8%, 395.9987 $[M - Na - CNCH_2COOK - 2CH_4]^-$ (calcd 395.9987) 3.5%.

*cis-Dimethyl(potassium-2-isocyanidoacetate)[1-(3-sodium sulfonatopropyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]platinum-(II) (**10c**).* This complex was obtained from **2c** (95.1 mg, 0.150 mmol) as a yellow solid (97.7 mg, 96%). IR (cm^{-1}): ν (C≡N) 2172 (m). ^{1}H NMR (300 MHz, D_2O): δ 7.31 (d, $^{3}J_{HH}$ = 1.8, 1H, Imz), 6.96 (s, 2H, Ar), 6.94 (d, $^{3}J_{HH}$ = 1.8, 1H, Imz), 4.28 (t, $^{3}J_{HH}$ = 6.9, 2H, NCH_2), 3.92 (d, $^{3}J_{HH}$ = 5.9, 1H, $CNCH_2CO_2K$), 3.90 (d, $^{3}J_{HH}$ = 5.9, 1H, $CNCH_2CO_2K$), 2.82 (m, 2H, CH_2S), 2.21 (m, 2H, $CH_2CH_2CH_2$), 2.21 (s, 3H, Ar-*p*-Me), 1.90 (s, 6H, Ar-*o*-Me), −0.05 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 64.6, 3H, PtMe *trans* to NHC), −0.08 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 70.9, 3H, PtMe *cis* to NHC). ^{1}H NMR (300 MHz, dmso-d_6): δ 7.49 (d, $^{3}J_{HH}$ = 1.8, 1H, Imz), 7.08 (d, $^{3}J_{HH}$ = 1.8, 1H, Imz), 6.92 (s, 2H, Ar), 4.29 (m, 2H, NCH_2), 3.61 (s, 2H, $CNCH_2CO_2K$), 2.45 (m, 2H, CH_2S), 2.26 (s, 3H, Ar-*p*-Me), 2.11 (m, 2H, $CH_2CH_2CH_2$), 1.94 (s, 6H, Ar-*o*-Me), −0.13 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 64.8, 3H, PtMe *trans* to NHC), −0.24 (s with ^{195}Pt satellites, $^{2}J(^{1}H-^{195}Pt)$ = 69.0, 3H, PtMe *cis* to NHC). $^{13}C\{^1H\}$ NMR (75 MHz, D_2O): δ 181.7 (s with ^{195}Pt satellites, $^{1}J(^{13}C-^{195}Pt)$ = 791.6, Imz-C^2), 170.6 (s, COOK), 142.9 (s, PtCNR), 139.2 (s, Ar-C^4), 136.2 (s, Ar-C^1), 135.7 (s, Ar-C^2), 128.5 (s, Ar-C^3), 122.4 (s with ^{195}Pt satellites, $^{3}J(^{13}C-^{195}Pt)$ = 21.9, Imz-C^4), 120.7 (s with ^{195}Pt satellites, $^{3}J(^{13}C-^{195}Pt)$ = 17.8, Imz-C^5), 48.1 (s, CH_2S), 47.9 (s, $CNCH_2COOK$), 47.8 (s, NCH_2), 25.5 (s, $CH_2CH_2CH_2$), 20.1 (s, Ar-*p*-Me), 17.1 (s, Ar-*o*-Me), −5.3 (s with ^{195}Pt satellites, $^{1}J(^{13}C-^{195}Pt)$ = 595.8, PtMe *cis* to NHC), −11.8 (s with ^{195}Pt satellites, $^{1}J(^{13}C-^{195}Pt)$ = 496.9, PtMe *trans* to NHC). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ 182.2 (s, Imz-C^2), 164.5 (s, COOK), 140.8 (s, PtCNR), 136.6 (s, Ar-C^4), 136.3 (s, Ar-C^1), 134.5 (s, Ar-C^2), 127.9 (s, Ar-C^3), 121.3 (s, Imz-C^4), 120.1 (s, Imz-C^5), 47.9 (s, CH_2S), 47.6 (s, $CNCH_2COOK$), 47.0 (s, NCH_2), 25.9 (s, $CH_2CH_2CH_2$), 20.2 (s, Ar-*p*-Me), 17.2 (s, Ar-*o*-Me), −4.9 (s, PtMe *cis* to NHC), −9.0 (s, PtMe *trans* to NHC). ESI-MS (negative ion, MeOH): *m*/*z* 617.1402 $[M - Na - K + H]^-$ (calcd 617.1403) 68%, 557.1177 $[M - Na - K + H - CO_2 - CH_4]^-$ (calcd 557.1192) 100%, 541.0859 $[M - Na - K + H - CO_2 - 2CH_4]^-$ (calcd 541.0879) 64%, 516.0909 $[M - Na - CNCH_2COOK - CH_4]^-$ (calcd 516.0926) 97%, 500.0604 $[M - Na - CNCH_2COOK - 2CH_4]^-$ (calcd 500.0613) 33%.

X-ray Crystallographic Studies. Suitable single crystals were obtained by slow diffusion of acetone into an aqueous solution of **2a** or of diethyl ether into a methanol solution of **3a** or **9a**. A summary of crystal data and data collection and refinement parameters for the structural analyses is given in Table S1 (Supporting Information). Crystals of **2a** were fitted on a MiTeGen micromount (**2a**) and mounted at room temperature (296 K) in a Bruker Kappa Apex II diffractometer (**2a**). Crystals of **3a** and **9a** were glued to a glass fiber using an inert polyfluorinated oil and mounted in the low-temperature N_2 stream (200 K) of a Bruker-Nonius Kappa-CCD diffractometer equipped with an area detector and an Oxford Cryostream 700 unit.

Intensities were collected using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data were measured with exposure times of 10 s per frame for **2a** (5 sets; 1075 frames; phi/omega scans; 0.5° scan-width), 9 s per frame for **3a** (9 sets; 471 frames; phi/omega scans; 1.8° scan-width), and 63 s per frame for **9a** (5 sets; 811 frames; phi/omega scans; 0.9° scan-width). Raw data were corrected for Lorenz and polarization effects. The structures were solved by direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares on F^2 (SHELXL-97).[49] Anisotropic thermal parameters were used in the last cycles of refinement for the non-hydrogen atoms, with the exception of **3a**, for which a disorder was found and the sulfur S(7B) and Na(2) were refined isotropically. In compound **9a**, some disordered water was observed and some remaining electronic density due to another disordered solvent molecule was squeezed with Platon.[50] Absorption correction procedures were carried out using the multiscan SADABS (**2a**)[51] or SORTAV programs (semiempirical from equivalent, **3a** and **9a**).[52] Hydrogen atoms were included in the last cycle of refinement from geometrical calculations and refined using a riding model. All calculations were performed using the SHELXTL software package (**2a**) or the WINGX system (**3a** and **9a**).[53]

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra of selected complexes, crystallographic data, and CIF files for compounds **2a**, *SP*-4−3-**3a**, and **9a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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