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Synthesis of Mixed NHC/L Platinum(II) Complexes: Restricted Rotation of the NHC Group

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Summary: The use of (NHC)AgX salts as transmetallating agents for platinum can be tuned to introduce either one or two NHC ligands per platinum in high yield. Complexes with a single NHC ligand are prepared with an additional DMSO ligand, which can conveniently be replaced by other ligands such as phosphines to give mixed cis NHC/phosphine complexes. Variable-temperature NMR and DFT have been used to probe the nature of the restricted rotation of the NHC ligand about the square planar platinum center: experimentally, the barrier has been established as at least 85 kJ mol^{-1}, and the computational value has been determined to be 92 kJ mol^{-1}.

Introduction

In the past 5 years, the nitrogen-stabilized heterocyclic carbene (NHC) ligand has progressed from being an academic curiosity to its present ubiquitousness: it is now considered as a versatile ligand that is often used in preference to the more usual phosphine.[1] Electronically, the NHC ligand is usually considered to be a better σ donor, and a weaker π acceptor, than the phosphine ligand,[2] although evidence is not always clear-cut.[3,4] Synthetic procedures leading to precursor imidazolium salts have been elucidated,[5] and many routes that allow the introduction of an NHC ligand to a metal center have been developed. The reaction of imidazolium salts with silver oxide giving an NHC complex of silver, which serves as a useful transmetallating reagent, has proved particularly popular.[6−8] Other interesting methods include the utilization of an electron-reservoir complex, together with air, to generate NHCs,[9] or the use of imidazolium-2-carboxylates, which lose CO_2 to generate NHCs,[10] although, increasingly, direct reaction of the imidazolium salt with the metal has found favor.[11−14] More recently, NHC ligands have been shown not to be innocent spectators, but reactive intermediates themselves, with a number of new products being formed.[15,16]

While most studies on catalytically active systems have their emphasis on palladium-based chemistry,[17] platinum complexes are also of interest. Among other uses, platinum complexes with NHC ligands have been used for the reductive cyclization of diynes and enynes,[18] the catalytic diboration of unsaturated molecules,[19] and the tandem hydroboration-cross coupling reaction.[20] Thus, the clean, high yielding synthesis of both bis(NHC) platinum complexes and mixed (NHC)/PR_3) platinum complexes is of considerable current interest.

Results and Discussion

The direct reaction of imidazolium salts with silver oxide was used to prepare “(NHC)AgX” complexes (**1**).[21] Reaction of these salts with potassium tetrachloroplatinate in a 2:1 molar ratio in dichloromethane solvent cleanly gave the $(NHC)_2PtCl_2$ complexes (**2**) in high yield, Scheme 1. The analysis of the solution spectroscopic data did not allow us to determine the exact formulation or geometry of the new complexes as the spectra simply showed the presence of a single type of NHC, but a single-crystal X-ray structure, Figure 1, clearly showed two NHC ligands per platinum with a trans disposition of both the NHC and the chloride ligands. In fact, in this synthetic procedure, the exact proportions of silver NHC halide and potassium tetrachloroplatinate are irrelevant: the only product formed is **2**, together with unreacted material; no other byproducts can be detected.

When DMSO is used as the solvent, a different product results, Scheme 1. The new product is again formed cleanly with no byproducts observable by NMR; the only factor reducing the yield appears to be the practical problem of isolating the material from the DMSO solvent. The ^{1}H NMR spectrum of the new product clearly shows a DMSO coordinated to platinum, and the integral of this peak relative to those of an NHC ligand suggests that one NHC and one DMSO are each coordinated to the platinum. This product is formed irrespective of the relative proportions of silver NHC complex **1** and

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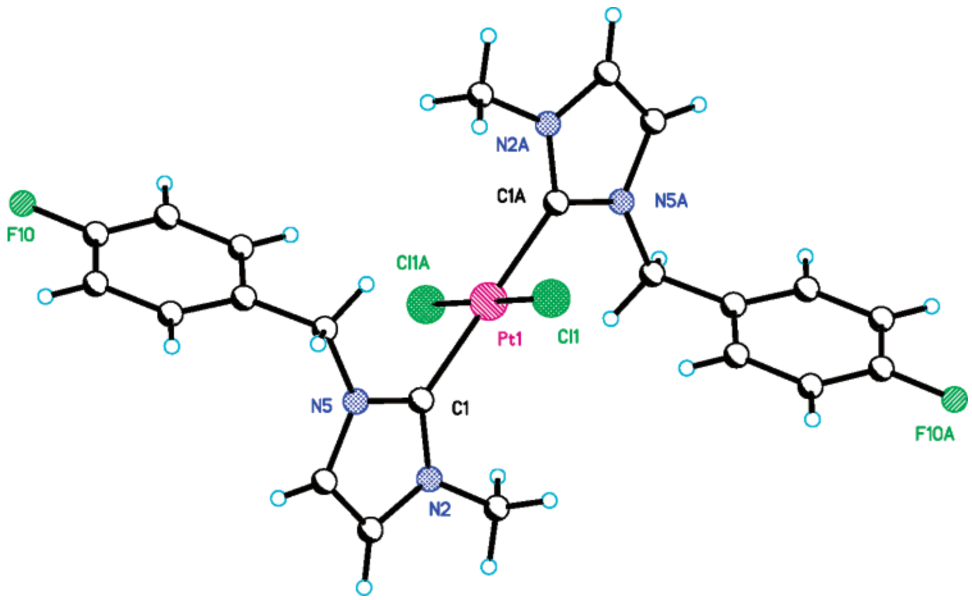
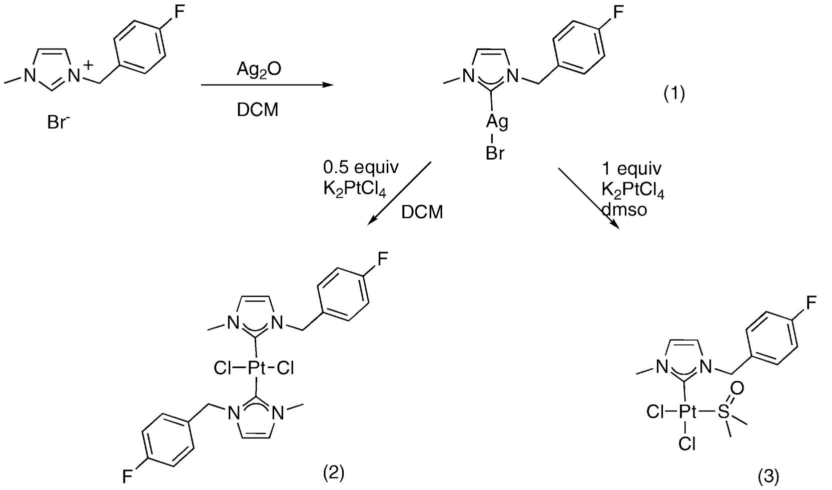


Figure 1. X-ray structure of **2**. Selected bond lengths (Å) and angles (deg): Pt1−C1 2.022(5); Pt1−Cl1 2.3439(13); C1−N2 1.345(6); C1−N5 1.347(6); C1−Pt1−C1A 180.0; C1−Pt1−Cl1 89.43(14); C1−Pt1−Cl1A 90.57(14); Cl1−Pt1−Cl1A 180.0; N2−C1−N5 105.1(4); N2−C1−Pt1 127.1(3); N5−C1−Pt1 127.7(3).

Scheme 1



platinum salt; presumably the massive excess of DMSO that is present as a solvent competes effectively with the NHC as a ligand. The value of the $^3J_{HPt}$ to the DMSO methyl groups ($^3J_{HPt}$ 22 Hz) is comparable to those we have seen before when DMSO is trans to nitrogen,[22] and substantially different from the approximately 15 Hz we would expect if the DMSO were trans to a carbon.[23,24] The magnitude of this coupling constant would therefore suggest that the DMSO and NHC ligand are cis to each other. Further evidence for this formulation comes from other features of the room-temperature ^{1}H NMR spectrum: the two benzyl protons are inequivalent (they are 0.15 ppm apart and couple with $^2J_{HH} = 16$ Hz) as are the two methyl groups on the DMSO. The only explanation for these phenomena in this complex is that the NHC and DMSO are cis to each other and that a perpendicular orientation of the NHC ring with respect to the coordination plane of the platinum results in restricted rotation of the NHC ligand about the Pt center, which then renders the two benzyl protons different, and hence the two methyl groups of the DMSO. A single-crystal X-ray structure, Figure 2, confirmed that the geometry is indeed cis (**3**), as indicated in Scheme 1, and that the NHC ligand is perpendicular to the coordination plane of the platinum.

To establish the barrier to rotation of the NHC ligand about the platinum center, a variable-temperature NMR experiment was carried out. When the temperature of an NMR sample in 1,1,2,2-tetrachloroethane was raised, neither the signals for the benzyl or for the DMSO protons coalesced, even at 140 °C. The signals for the benzyl protons (low-temperature separation of 55 Hz at 400 MHz) and those of the Me groups (low-temperature separation of 132 Hz at 400 MHz) had moved together somewhat and broadened substantially at 140 °C, but were still some way short of coalescence. Although we did not actually reach coalescence for either set of signals, a standard analysis can be used to extract a lower limit for the barrier to interconversion ($\Delta G^{\ddagger}$). If coalescence occurred at a temperature of 150 °C the barrier would be around 85 kJ mol^{-1}, whereas if coalescence occurred at 200 °C the barrier would be close to

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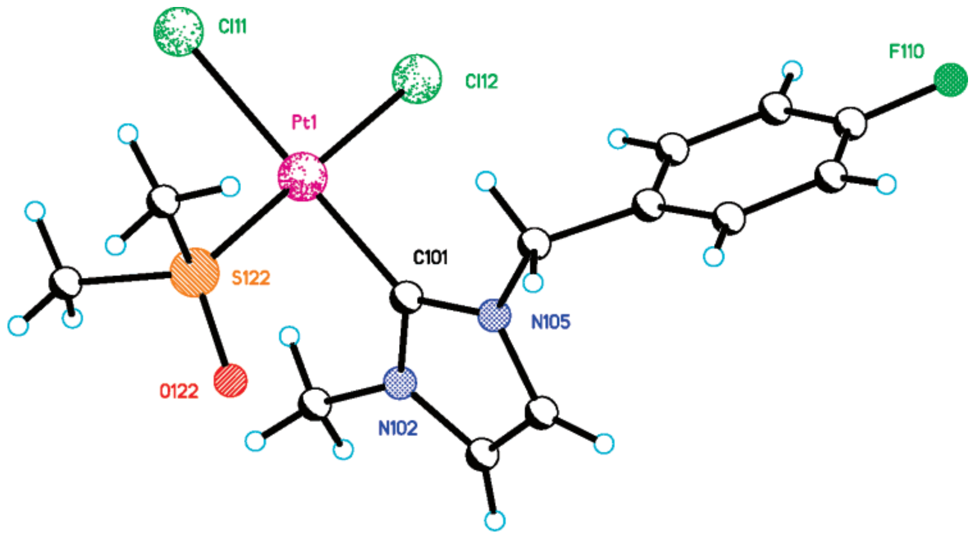

Figure 2. X-ray structure of **3**. Selected bond lengths (Å) and angles (deg): Pt1−C101 1.984(6); Pt1−S122 2.2061(17); Pt1−Cl12 2.3357(16); Pt1−Cl11 2.3765(15); C101−N102 1.346(8); C101−N105 1.348(8); S122−O122 1.465(5); C101−Pt1−S122 90.33(18); C101−Pt1−Cl12 88.86(18); S122−Pt1−Cl12 178.53(6); C101−Pt1−Cl11 178.67(19); S122−Pt1−Cl11 90.68(6); Cl12−Pt1−Cl11 90.11(6); N102−C101−N105 105.3(5); N102−C101−Pt1 125.3(4); N105−C101−Pt1 129.4(5); O122−S122−Pt1 117.1(2).

Table 1. Comparison of the X-ray and DFT Data for Complex 3

parameter	X-ray	DFT
Pt1−C101	1.984(6)	2.00
Pt1−S122	2.2061(17)	2.24
Pt1−Cl12	2.3357(16)	2.34
Pt1−Cl11	2.3765(15)	2.39
C101−N102	1.346(8)	1.36
C101−N105	1.348(8)	1.36
S122−O122	1.465(5)	1.49
C101−Pt1−S122	90.33(18)	93.5
C101−Pt1−Cl12	88.86(18)	87.0
S122−Pt1−Cl12	178.53(6)	175.9
C101−Pt1−Cl11	178.67(19)	177.3
S122−Pt1−Cl11	90.68(6)	89.2
Cl12−Pt1−Cl11	90.11(6)	90.3
N102−C101−N105	105.3(5)	105.2
N102−C101−Pt1	125.3(4)	126.1
N105−C101−Pt1	129.4(5)	128.7
O122−S122−Pt1	117.1(2)	119.6

100 kJ mol^{-1}, and if coalescence occurred at 250 °C the barrier would be closer to 110 kJ mol^{-1}.

The observed barrier to rotation could simply be related to an exchange process of the coordinated DMSO with solvent. We therefore studied the exchange of coordinated DMSO with free d_6-DMSO by ^{1}H NMR. As the coordinated DMSO is replaced on a statistical basis by the excess d_6-DMSO, the signals for the coordinated protiated DMSO disappear. The rate of this process was slow at room temperature: even with a large excess of d_6-DMSO these signals had reduced to one-half their intensity after about 4 h, with complete replacement taking more than 13 h. A further NMR experiment then confirmed that the exchange of DMSO with solvent is not the primary method of equilibration of the NMR signals of the DMSO and benzyl protons: an EXSY spectrum (0.6 s mixing time) was run of compound **3** in $CDCl_3$ in the presence of excess protiated DMSO. This spectrum clearly showed exchange between both benzyl peaks and exchange between the two peaks of the coordinated DMSO; crucially, it showed no exchange between the coordinated DMSO and the free DMSO.

Barriers to rotation of NHC ligands at rhodium centers of 35−40 kJ mol^{-1} have been reported previously,[25] where a geared motion of three NHC ligands past a carbonyl ligand was postulated. To establish that the higher barrier we see is indeed a barrier to rotation, we undertook a computational study using density functional theory (DFT) (see Computational Details). An initial geometry optimization confirmed that DFT provides an excellent description of the molecular structure (Table 1). Starting from the optimized geometry (BP86/DZP ZORA), the torsion angle around the Pt−C bond (relative to the cis Cl and one of the NHC nitrogen atoms, Figure 3) was varied from its starting value of −90° in 30° increments, leading to the energy profile shown in Figure 4.

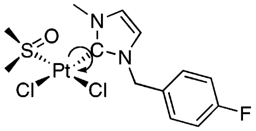

Figure 3. Starting geometry of complex **3**.

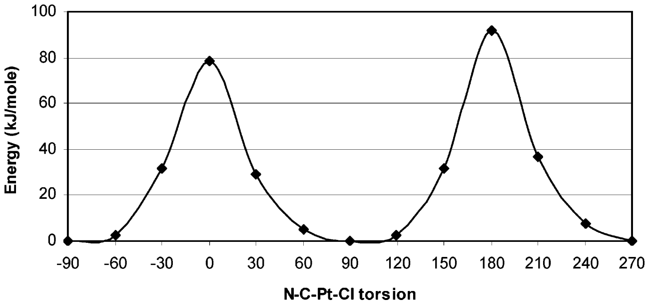

Figure 4. Energy profile of the rotation of the NHC ligand in **3**.

These calculated barriers are in excellent agreement with the experimental estimate. Figure 5 clearly shows how the DMSO is forced out of the plane of the other three donor atoms during the rotation process. In addition, the rotation is "geared" in the sense that the benzyl and methyl groups rotate around the C−N bonds as the NHC substituents pass the DMSO.

The barriers to rotation arise, in principle, from a combination of steric interactions between the DMSO and the hydrogens on the methyl and benzyl groups of the NHC ligand and electronic effects associated with changes in chemical bonding. The lower

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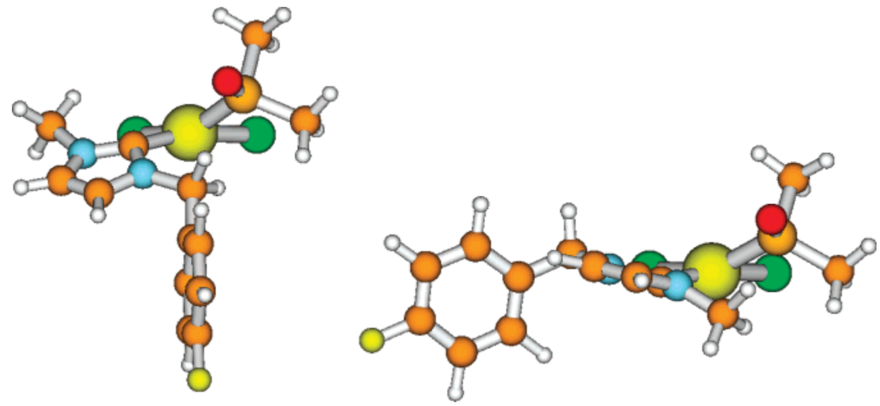


Figure 5. The DMSO ligand is forced out of plane during rotation of the NHC ligand. Part (a) shows the effect of the benzyl group, while (b) shows the effect of the methyl group.

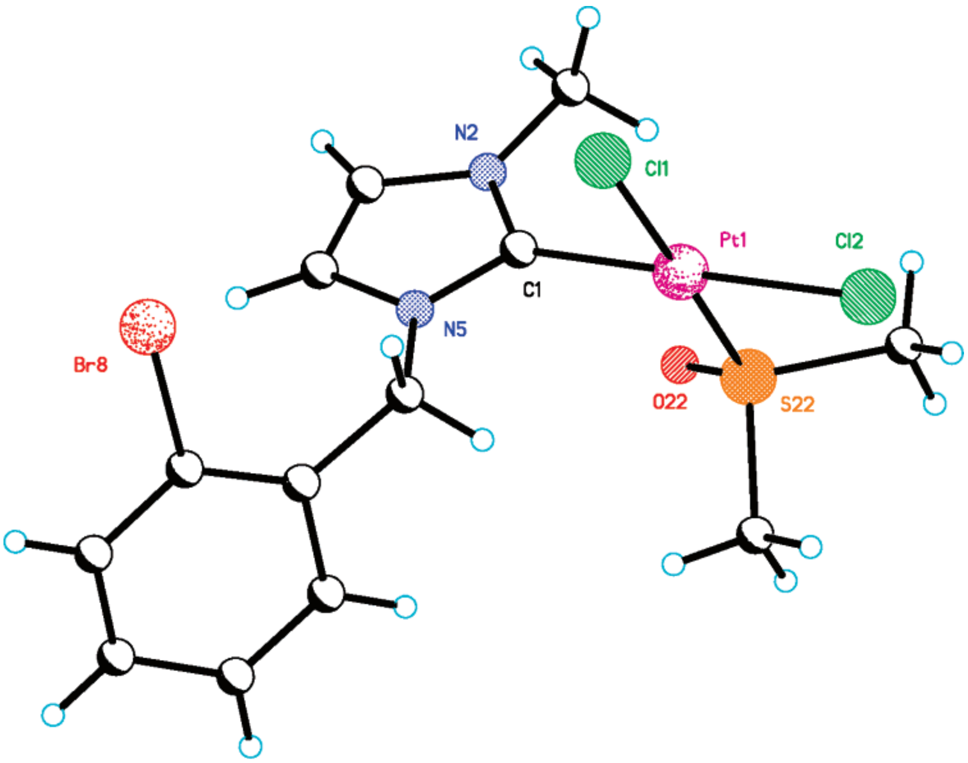
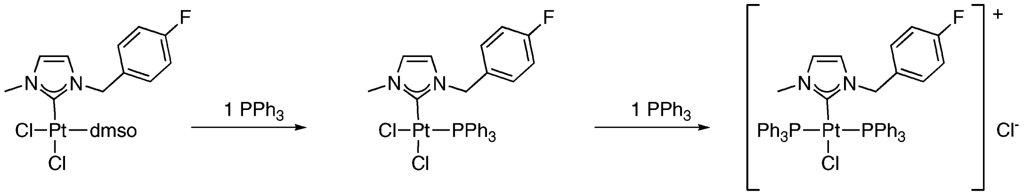


Figure 6. X-ray structure of **4**. Selected bond lengths (Å) and angles (deg): Pt1−C1 1.993(7); Pt1−S22 2.208(2); Pt1−Cl1 2.3412(17); Pt1−Cl2 2.3827(17); C1−N2 1.351(9); C1−N5 1.351(10); S22−O22 1.482(5); C1−Pt1−S22 90.9(2); C1−Pt1−Cl1 87.4(2); S22−Pt1−Cl1 178.28(7); C1−Pt1−Cl2 176.7(2); S22−Pt1−Cl2 92.21(7); Cl1−Pt1−Cl2 89.49(6); N2−C1−N5 105.3(6); N2−C1−Pt1 129.1(6); N5−C1−Pt1 125.6(5); O22−S22−C23 107.7(4); O22−S22−Pt1 117.2(3).

Scheme 2



(3) (5) (6)

barrier of 79 kJ mol^{-1} corresponds to the benzyl group approaching DMSO, while the higher barrier (92 kJ mol^{-1}) arises from the methyl group. Of course, because only the total barrier height is an observable, any explicit separation into steric and electronic components is model-dependent, and a fully quantum approach provides no mechanism for distinguishing them. Nevertheless, a rough estimate of the change in Pt−NHC bond energy can be achieved using the extended transition state facility in ADF.[26] The full molecule is separated into two fragments, NHC and $PtCl_2$(DMSO), and the interaction between these two fragments is divided into a "steric" part and an "electronic" part. The steric interaction models the (destabilizing) interaction incurred by bringing the two fragment charge densities up to their "in complex" positions but not allowing

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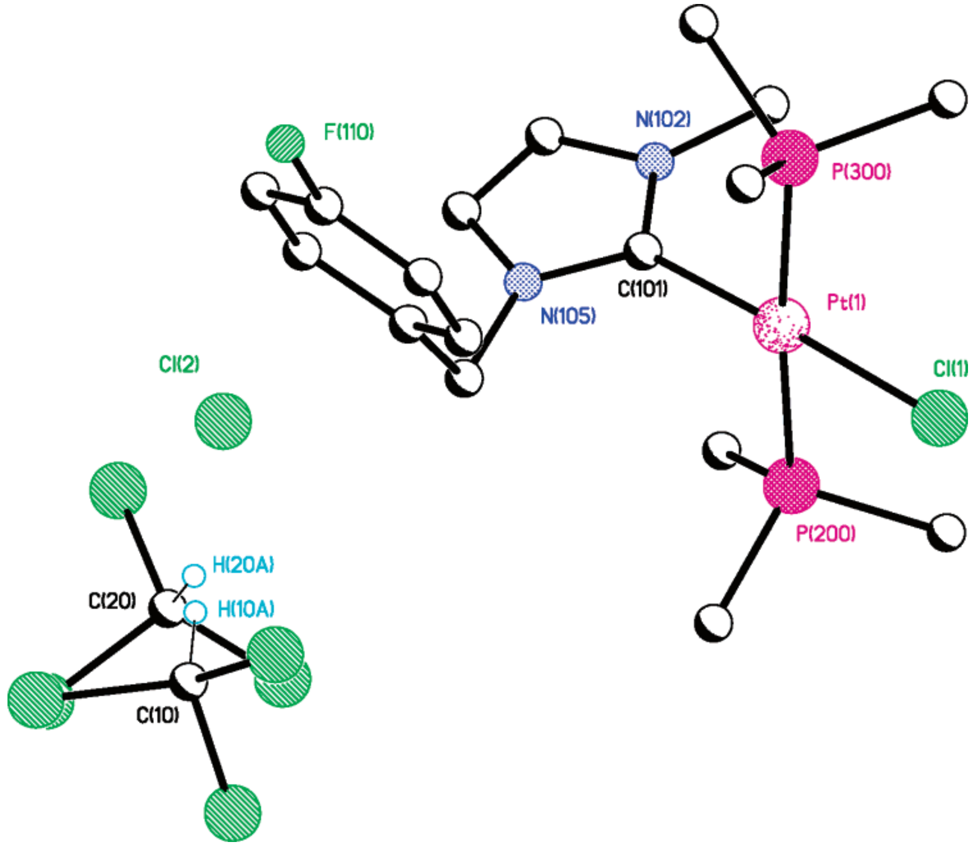
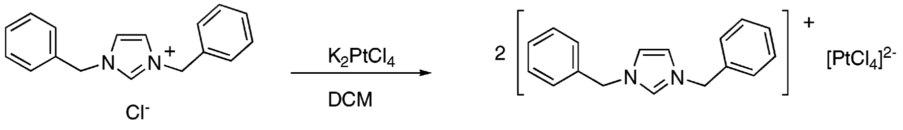


Figure 7. X-ray structure of **6**. For clarity, most of the hyrdogens and the phenyl rings of the triphenylphosphine groups are not shown. Selected bond lengths (Å) and angles (deg): Pt1−C101 2.013(7); Pt1−P200 2.329(2); Pt1−P300 2.336(2); Pt1−Cl1 2.3660(19); C101−N105 1.338(9); C101−N102 1.343(9); C10−Cl2 3.391(17); C20−Cl2 3.373(14); C101−Pt1−P200 88.6(2); C101−Pt1−P300 93.3(2); P200−Pt1−P300 174.42(8); C101−Pt1−Cl1 178.1(2); P200−Pt1−Cl1 90.73(7); P300−Pt1−Cl1 87.51(7); N105−C101−N102 106.3(6); N105−C101−Pt1 128.0(6); N102−C101−Pt1 125.7(5).

Scheme 3



(7)

the charges to mix. The electronic interaction describes the subsequent (stabilizing) relaxation of the charge density as it rearranges to its bonding configuration. The change in the latter between the ground state and the geometry at the higher barrier is an approximate measure of change in the Pt−NHC bond energy as a function of rotation and is equal to about 30 kJ mol^{-1}.

One further example of these *cis*(NHC)(DMSO)PtCl$_2$ complexes was synthesized by the same route: the 1-methyl-3-(2-bromobenzyl)NHC compound (**4**). The ^{1}H NMR spectrum showed features similar to those of the 4-fluorobenzyl compound (**3**), including inequivalent benzyl and DMSO methyl peaks, and a single-crystal X-ray structure, Figure 6, confirmed that the geometry was also cis.

The *cis*(NHC)(DMSO)PtCl$_2$ (**3**) complexes prove to be very useful in synthesising other mixed ligand complexes. For example, reaction with 1 equiv of triphenyl phosphine results in the rapid generation of a *cis*(NHC)(PPh$_3$)PtCl$_2$ complex (**5**), Scheme 2. Although we do not have an X-ray crystal structure of **5**, we are confident of the cis geometry from two pieces of spectroscopic evidence. First, the ^{31}P NMR spectrum shows a $^1J_{\mathrm{PtP}}$ of 3910 Hz, consistent with P trans to chloride, unlike the 2490 Hz we see in compound **6** where P is trans to P and similar to the values we[27] and others[28] have seen for P trans to Cl. Second, the ^{1}H NMR spectrum again shows the two benzyl protons to be inequivalent (now they are 1.46 ppm apart and couple with $^2J_{\mathrm{HH}} = 14$ Hz), and again the only explanation for this phenomenon must be a cis disposition of the PPh$_3$ and NHC, with restricted rotation about the NHC−Pt bond (again VT NMR spectra showed broadening, but not coalescence at 140 °C). It is interesting to note that the two benzyl protons have such different chemical shifts: presumably one of them is pushed up against a phenyl ring of the triphenylphosphine, and this results in its increased shielding. We can apply the same analysis of the variable-temperature NMR spectra of **5** that we did for **3** and conclude that the barrier to rotation of the NHC group about the platinum center must be more than 85 kJ mol^{-1}. We did not undertake a computational analysis of the rotation of the NHC in **5**, but simplistically we would expect it to be somewhat greater than that in **3**.

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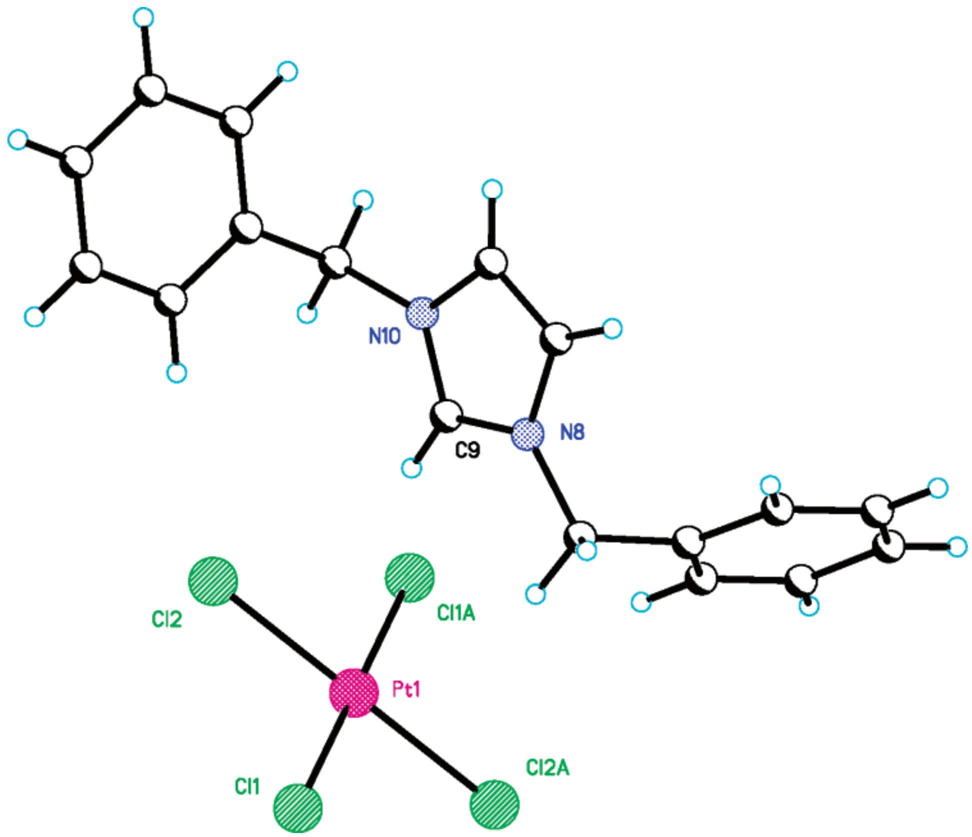

Figure 8. X-ray structure of **7**. Selected bond lengths (Å) and angles (deg): Pt1−Cl2A 2.3086(10); Pt1−Cl2 2.3086(10); Pt1−Cl1 2.3179(11); Pt1−Cl1A 2.3179(11); N8−C9 1.330(4); C9−N10 1.330(4); Cl2A−Pt1−Cl2 180.0; Cl2A−Pt1−Cl1 89.49(4); Cl2−Pt1−Cl1 90.51(4); Cl1−Pt1−Cl1A 180.0; N10−C9−N8 109.4(3).

Table 2. X-ray Data for the Complexes

	2	**3**	**4**	**6**	**7**
crystal form	yellow block	colorless block	colorless block	colorless block	yellow block
dimensions, mm	0.80 × 0.36 × 0.18	0.64 × 0.12 × 0.09	0.22 × 0.06 × 0.04	0.30 × 0.22 × 0.08	0.20 × 0.16 × 0.12
emp. formula	$C_{22}H_{22}Cl_2F_2N_4Pt$	$C_{13}H_{17}Cl_2FN_2OPtS$	$C_{13}H_{17}BrCl_2N_2OPtS$	$C_{48.25}H_{42.25}Cl_{5.75}FN_2Pt$	$C_{34}H_{34}Cl_4N_4Pt$
MW	646.43	534.34	595.25	1129.96	835.54
crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P2(1)/c$	$\bar{P}1$	$\bar{P}1$	$P2(1)/n$	$P2(1)/c$
a, Å	9.589(5)	9.8204(8)	7.8123(11)	14.3923(15)	9.690(3)
b, Å	15.738(8)	12.5661(10)	10.1259(15)	10.9389(11)	11.996(4)
c, Å	7.515(4)	20.7877(17)	11.3338(16)	32.773(3)	14.311(5)
α, deg	90	97.024(2)	91.660(3))	90	90
β, deg	94.401(11)	91.985(2)	98.459(4)	91.177(2)	92.554(8)
γ, deg	90	91.270(2)	99.046(3)	90	90
U, Å^3	1130.8(9)	2543.6(4)	874.5(2)	5158.5(9)	1661.9(10)
T, K	180(2)	180(2)	180(2)	180(2)	180(2)
Z	2	6	2	4	2
D_{calc}, Mg m^{-3}	1.899	2.093	2.260	1.455	1.670
$F(000)$	624	1524	560	2242	824
μ(Mo Kα)	6.474	8.721	10.730	3.116	4.574
θ max, deg	28.96	28.95	28.84	29.09	28.94
reflns measured	7189	32 840	11 300	55 796	20 677
unique data	2738	12 223	4210	12 860	4126
R1 [$I > 2\sigma(I)$]	0.0361	0.0396	0.0448	0.0707	0.0264
wR2	0.1020	0.0893	0.1005	0.1633	0.0635
data/rest/param	2738/0/139	12 223/0/565	4210/0/193	12 860/0/596	4126/0/196

Reaction of the *cis*(NHC)(PPh_3)$PtCl_2$ complexes with a second equivalent of triphenyl phosphine results in the rapid formation of a *trans*-chloro(NHC)bis(PPh_3)platinum(II) chloride (**6**), Scheme 2. Two triphenyl phosphine per NHC are indicated from the integrals in the proton NMR. A trans disposition of the two triphenyl phosphine groups is clearly indicated from the ^{31}P NMR, where a single resonance is observed (with a $^1J_{PtP}$ of 2490 Hz, consistent with P is trans to P). In addition, the ^{1}H NMR spectrum now shows the two benzyl protons of the NHC ligand to be equivalent, consistent with the NHC ring being perpendicular to the coordination plane of the platinum with both sides now the same (presumably there is still restricted rotation of the NHC ring, but this now has no effect on the ^{1}H NMR spectrum). Finally, a single-crystal X-ray structure, Figure 7, confirmed that the geometry was trans.

In the synthesis of the *cis*(NHC)(PPh_3)$PtCl_2$ complexes (**5**), it is important to slowly add the single equivalent of phosphine as contamination with the bis(triphenylphosphine) complex (**6**)

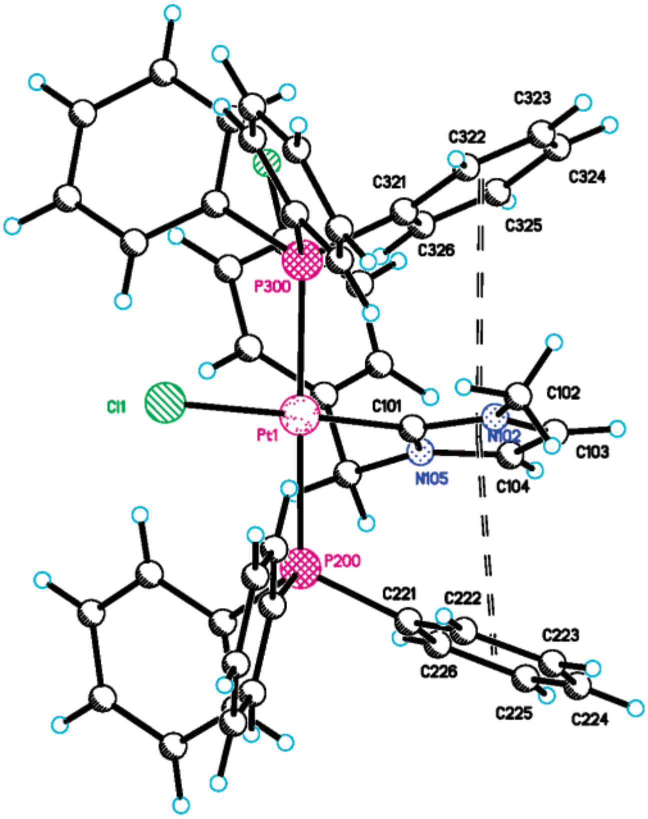

Figure 9. π-Stacking in the X-ray structure of **6**. Ring centroid to ring centroid distances: NHC to phenyl C311−C316 is 3.615 Å, and NHC to phenyl C211−C216 is 3.887 Å.

often results. Addition of more than 2 equiv of triphenyl phosphine only results in complete formation of **6** with unreacted phosphine present in solution, however. A solution mixture of complexes **3** and **6** forms complex **5** only very slowly at room temperature, and even at 60 °C the reaction requires several hours. However, it is apparent that solution mixtures of complexes **3** and **6** completely consume whichever component is present in the smaller amount, converting it all to complex **5**. Careful inspection of the NMR spectra of crude reaction mixtures, or those that come from the prolonged heating (100 °C, 4 days) of chloroform solutions of **5**, does not show any other complexes to be present other than those discussed here. In particular, there is no evidence of a trans isomer being formed. Presumably the steric relief that might accompany such an isomerization does not compensate for the loss in energy associated with placing a phosphine and NHC trans to each other.

We attempted the direct reaction of an imidazolium salt with potassium tetrachloroplatinate to see if we could form an NHC complex without the need for the silver intermediate. Although precedent for this type of reaction exists,[13] and we ourselves have used this type of reaction with palladium,[29] the only examples with platinum use added acetate as a base.[30−32] Not surprisingly then, we saw no evidence of such a reaction with the platinum even with a variety of solvents and reaction conditions; presumably the platinum salt is insufficiently basic to deprotonate the imidazolium salt. Interestingly, when we used dichloromethane as a reaction solvent, counterions were interchanged, and we were able to isolate the imidazolium tetrachloroplatinate salt (**7**) in high yield, Scheme 3. Solution NMR spectra showed a change in the chemical shifts of the imidazolium resonances, and a single-crystal X-ray structure confirmed the metathesis, Figure 8.

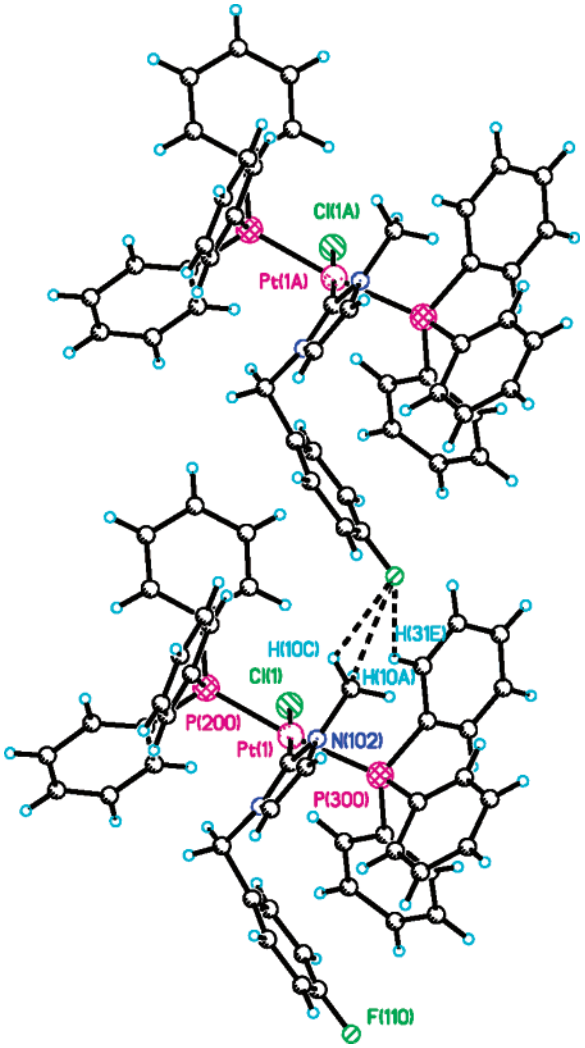

Figure 10. Intermolecular hydrogen bonding in the X-ray structure of **6**, leading to a chainlike structure.

Solid-State Structures of the Complexes. Table 2 lists the crystal data for all of the structures reported in this paper. The solid-state structure of **2** clearly shows the square planar nature of the platinum center and that the NHC rings are close to perpendicular to the coordination plane, Figure 1. While there are a number of close contacts between the Cl and F groups and hydrogens on the ligands, these do not appear to result in any major intermolecular interactions.

The asymmetric unit of **3** contains three crystallographically independent molecules (six in the unit cell). In all molecules, the metal, the two chlorides, the sulfur and oxygen of the DMSO, and the carbon of the NHC can all be considered planar. Presumably this arrangement of the DMSO, which leaves the S=O pointing toward the NHC (which is essentially perpendicular to the coordination plane), reduces any steric interactions of the methyl groups of the DMSO with the NHC. Again, there are several close contacts between the chlorides, fluorides, and the DMSO oxygen with the hydrogens on the ligands, but it is difficult to detect any over-riding effects.

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The solid-state structure of **4** shows an arrangement around the platinum center similar to that of **3**, with the S═O pointing toward the NHC, with the NHC ring close to perpendicular to the coordination plane. Again, several close intermolecular contacts exist, but nothing of particular note.

The asymmetric unit of **6** contains the platinum complex together with a chloride counterion (Cl2) and two molecules of chloroform. One molecule of chloroform was modeled as 75% occupied and one as 50% occupied and disordered by rotation about the C−H bond over two positions in the ratio 52:48 major:minor. These chloroform molecules have close H-bond contacts with the chloride counterion (C−H···Cl distances of 3.373(14) and 3.391(17) Å), and there is a π-stacking between the NHC ring and phenyl groups of either PPh_3 above and below. The rings are not exactly parallel (NHC to phenyl C311−C316 angle 26.68° and NHC to phenyl C211−C216 angle 22.38°), but ring centroid to ring centroids are in the right range: NHC to phenyl C311−C316, 3.615 Å and NHC to phenyl C211−C216, 3.887 Å, Figure 9. There is also an intermolecular interaction leading to a chainlike structure joining the molecules: H-bonding exists between the methyl on the carbene and the phenyls of one of the triphenyl phosphines with the fluorine of an adjacent molecule, Figure 10.

The asymmetric unit of **7** contains one difluorobenzyl imidazolium and one-half a $PtCl_4$, with the angle between the mean plane of the imidazolium and the mean plane of the $PtCl_4$ being 86.50(9)°. There are many close contacts between the chlorides and the imidazolium, but again it is difficult to identify any over-riding effects.

Conclusions

Silver NHC salts can be used to cleanly introduce either one or two NHC ligands to a platinum center. When only one NHC ligand has been introduced, the platinum center has a readily replaceable DMSO as an additional ligand cis to the NHC. In these cis DMSO/NHC complexes, the restricted rotation of the NHC ligand is evident from the effect it has on the ^1H NMR spectrum, and we were able to establish a lower limit of 85 kJ mol^{-1} for this barrier from VT NMR measurements. DFT studies on this restricted rotation suggest a value of 92 kJ mol^{-1} for this barrier, in excellent agreement with the measured value.

Experimental Section

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 400 or 500 in $CDCl_3$ and are referenced to external TMS, 85% H_3PO_4, and $CFCl_3$, as appropriate, assignments being made with the use of decoupling, NOE, and COSY pulse sequences. Elemental analyses were performed by Warwick Analytical Services. Potassium tetrachloroplatinate and silver(I) oxide were used as supplied from Strem. Symmetrical bis(benzyl)imidazolium chloride was synthesized via a literature route,[33] and the unsymmetrical 1-methyl-3-(4-fluoro)benzylimidazolium and 1-methyl-3-(2-bromo)benzylimidazolium salts were prepared via the reaction of methyl imidazole with 4-fluoro-2-(bromomethyl)benzene and 1-bromo-2-(bromomethyl)benzene, respectively. Silver NHC salts were then prepared via the reaction of imidazolium salt with silver oxide in DCM.[6,7,21]

***trans*-Dichloro-bis(1-methyl-3-(4-fluorobenzyl)imidazol-2-ylidine)platinum(II) (2).** (1-Methyl-3-(4-fluorobenzyl)imidazol-2-ylidine)silver bromide (132 mg, 3.48×10^{-4} mol) and potassium tetrachloroplatinate (72 mg, 1.74×10^{-4} mol) were dissolved/suspended in dichloromethane (5 mL), and the mixture was stirred under ambient conditions for 24 h. The resulting solution was filtered, concentrated in vacuo, and precipitation was induced by addition of diethyl ether (1 mL). The product was collected by filtration and recrystallized from dichloromethane/diethyl ether. Yield: 87 mg (78%, 1.36×10^{-4} mol).

$\delta_H(CDCl_3)$: 7.45 (m, 4H); 7.0 (t, $^3J_{HH}$ 8 Hz, $^3J_{HF}$ 8 Hz); 6.75 (d, 2H, $^3J_{HH}$ 2 Hz, NHC ring); 6.6 (d, 2H, $^3J_{HH}$ 2 Hz, NHC ring); 5.75 (s, 4H, benzyl); 4.05 (s, 6H, Me). $\delta_C(CDCl_3)$: 167.5 (carbene); 162.6 ($^1J_{CF}$ 247 Hz); 132.5; 130.3 (d, $^3J_{CF}$ 8 Hz); 122.2 (NHC ring); 119.8 (NHC ring); 115.6 (d, $^2J_{CF}$ 22 Hz); 52.8 (benzyl); 37.2 (Me). $\delta_F(CDCl_3)$: −114.1. MS (LSIMS): *m/z* 646 (M^+). Microanalysis: found (expected) C 40.6 (40.9); H 3.3 (3.4); N 8.3 (8.7).

***cis*-Dichloro-(1-methyl-3-(4-fluorobenzyl)imidazol-2-ylidine)-(DMSO)platinum(II) (3).** Potassium tetrachloroplatinate (98 mg, 2.35×10^{-4} mol) and (1-methyl-3-(4-fluorobenzyl) imidazol-2-ylidine)silver bromide (89 mg, 2.35×10^{-4} mol) were suspended in DMSO (5 mL) and heated, in the dark, with stirring at 60 °C for 15 h. Upon cooling, the mixture was flooded with water (25 mL) and extracted with dichloromethane (2 × 10 mL). The organic washings were combined, washed with water (2 × 5 mL), and dried over $MgSO_4$. Precipitation was induced by addition of diethyl ether (5 mL). The product was collected by filtration. Yield: 82 mg (66%, 1.55×10^{-4} mol).

$\delta_H(CDCl_3)$: 7.3 (dd, 2H, $^3J_{HH}$ 9 Hz, $^4J_{HF}$ 5 Hz); 7.0 (t, 2H, $^3J_{HH}$ 9 Hz, $^3J_{HF}$ 9 Hz); 6.9 (d, 1H, $^3J_{HH}$ 2 Hz, NHC ring); 6.75 (d, 1H, $^3J_{HH}$ 2 Hz, NHC ring); 5.65 (d, 1H, $^2J_{HH}$ 15 Hz, benzyl); 5.5 (d, 1H, $^2J_{HH}$ 15 Hz, benzyl); 3.95 (s, 3H, Me); 3.45 (s, 3H, $^3J_{HPt}$ 22 Hz, DMSO); 3.1 (s, 3H, $^3J_{HPt}$ 22 Hz, DMSO). $\delta_C(CDCl_3)$: 162.7 (d, $^1J_{CF}$ 248 Hz); 144.5 (carbene); 131.2; 130.0 (d, $^3J_{CF}$ 8 Hz); 122.7 (NHC ring); 121.0 (NHC ring); 116.0 (d, $^2J_{CF}$ 21.5 Hz); 53.5 (benzyl); 46.2 (DMSO); 45.6 (DMSO); 38.0 (Me). $\delta_F(CDCl_3)$: −113.6. MS (LSIMS): *m/z* 499 ($M^+ - Cl$); 421 ($M^+ - Cl -$ DMSO). Microanalysis: found (expected) C 28.8 (29.2); H 3.1 (3.2); N 4.8 (5.2).

***cis*-Dichloro-(1-methyl-3-(2-bromobenzyl)imidazol-2-ylidine)-(DMSO)platinum(II) (4).** (1-Methyl-3-(2-bromobenzyl)imidazol-2-ylidine)silver bromide (95 mg, 2.16×10^{-4} mol) and potassium tetrachloroplatinate (90 mg, 2.16×10^{-4} mol) were suspended in DMSO (5 mL) and heated, in the dark, with stirring at 60 °C for 15 h. Upon cooling, the mixture was flooded with water (25 mL) and extracted with dichloromethane (2 × 10 mL). The organic washings were combined, washed with water (2 × 5 mL), and dried over $MgSO_4$. Precipitation was induced by addition of diethyl ether (5 mL). The product was collected by filtration. Yield: 79 mg (62%, 1.34×10^{-4} mol).

$\delta_H(CDCl_3)$: 7.6 (d, 1H, $^3J_{HH}$ 8 Hz); 7.25 (m, 2H); 7.15 (td, 1H, $^3J_{HH}$ 8 Hz, $^4J_{HH}$ 3 Hz); 6.9 (d, 1H, $^3J_{HH}$ 2 Hz, NHC ring); 6.8 (d, 1H, $^3J_{HH}$ 2 Hz, NHC ring); 5.8 (d, 1H, $^2J_{HH}$ 16 Hz, benzyl); 5.45 (d, 1H, $^2J_{HH}$ 16 Hz, benzyl); 3.95 (s, 3H, Me); 3.5 (s, 3H, $^3J_{HPt}$ 21 Hz, DMSO Me); 3.15 (s, 3H, $^3J_{HPt}$ 21 Hz, DMSO Me). δ_C-$(CDCl_3)$: 144.8 (carbene); 134.6; 133.2; 130.6; 130.2; 128.1; 123.5; 122.6 (NHC ring); 121.4 (NHC ring); 54.1 (benzyl); 46.2 (DMSO); 45.7 (DMSO); 38.1 (Me). MS (LSIMS): *m/z* 595 (M^+).

***cis*-Dichloro-(PPh_3)(1-methyl-3-(4-fluorobenzyl)imidazol-2-ylidine)platinum(II) (5).** Triphenylphosphine (27 mg, 1.03×10^{-4} mol) dissolved in chloroform (1 mL) was slowly added to a solution of *cis*(1-methyl-3-(4-fluorobenzyl)imidazol-2-ylidine)(DMSO)platinumdichloride (55 mg, 1.03×10^{-4} mol) in chloroform (5 mL). The mixture was stirred (5 min) and then washed with water (2 × 5 mL) before being dried ($MgSO_4$). The solvent was removed, and the solid was collected. Yield: 67 mg (91%, 9.37×10^{-4} mol).

$\delta_H(CDCl_3)$: 7.48 (m, 6H); 7.37 (t, 3H); 7.30 (m, 8H, PPh_3 + benzene ring); 6.83 (t, 2H, $^3J_{HH}$ 9 Hz, $^3J_{HF}$ 9 Hz); 6.48 (d, 1H, $^3J_{HH}$ 2 Hz, NHC ring); 6.29 (d, 1H, $^3J_{HH}$ 2 Hz, NHC ring); 5.76 (d, 1H, $^2J_{HH}$ 14 Hz, benzyl); 4.30 (d, 1H, $^2J_{HH}$ 14 Hz, benzyl); 3.50 (s, 3H, Me). δ_P: 8.87 ($^1J_{PPt}$ 3910 Hz). $\delta_F(CDCl_3)$: −112.8. MS (LSIMS): *m/z* 718 (M^+); 682 ($M^+ - Cl^-$); 647 ($M^+ -$ (Cl^- &

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PPh_3)); 384 ($M^+ - (PPh_3$ & 2Cl). Microanalysis: found (expected) C 48.2 (48.5); H 3.6 (3.7); N 4.1 (3.9).

***trans*-Chloro(bis(PPh_3))(1-methyl-3-(4-fluorobenzyl)imidazol-2-ylidine)platinum(II) Chloride (6).** Triphenylphosphine (116 mg, 4.42×10^{-4} mol) was added to a solution of *cis*(1-methyl-3-(4-fluorobenzyl)imidazol-2-ylidine)(DMSO)platinumdichloride (118 mg, 2.21×10^{-4} mol) in dichloromethane (10 mL). The mixture was stirred (15 min) and then washed with water (2×10 mL) before being dried ($MgSO_4$). The solvent was removed, and the solid was collected. Yield: 184 mg (85%, 3.76×10^{-4} mol). Crystals suitable for X-ray analysis were grown from chloroform/diethyl ether.

$\delta_H(CDCl_3)$: 7.5 (t, 6H, $^3J_{HH}$ 7 Hz); 7.35 (m, 24H); 6.90 (d, 1H, $^3J_{HH}$ 2 Hz, NHC ring); 6.8 (m, 3H, NHC ring + benzene ring); 6.6 (t, 2H, $^3J_{HH}$ 9 Hz, $^3J_{HF}$ 9 Hz); 4.6 (s, 2H, benzyl); 3.1 (s, 3H, Me). $\delta_C(CDCl_3)$: 162.5 (d, $^1J_{CF}$ 249 Hz); 145.8 (t, $^2J_{PC}$ 10 Hz, carbene); 133.6; 131.6; 131.2 (d, $^3J_{CF}$ 8.5 Hz); 128.9; 124.4 (NHC ring); 121.9 (NHC ring); 115.7 (d, $^2J_{CF}$ 22 Hz); 53.3 (benzyl); 37.4 (Me). δ_P-($CDCl_3$): 18.7 ($^1J_{PPt}$ 2490 Hz). δ_F: −112.0. MS (LSIMS): *m*/*z* 944 ($M^+ - Cl^-$); 647 ($M^+ - (2Cl^-$ & PPh_3)); 383 ($M^+ - (2PPh_3$ & $2Cl^-$)). Microanalysis: found (expected, $CHCl_3$) C 52.4 (52.4); H 4.1 (3.85); N 2.2 (2.55).

Bis(1-3-dibenzyl-imidazolium)tetrachloroplatinate(II) (7). Bis-(1-3-dibenzyl-imidazolium)chloride (110 mg, 3.86×10^{-4} mol) and potassium tetrachloroplatinate (80 mg, 1.93×10^{-4} mol) were stirred together in dichloromethane (10 mL) for 15 h. The mixture was filtered, and the solvent was evaporated to give a pale yellow solid. Yield: 153 mg (95%, 1.83×10^{-4} mol). Crystals suitable for X-ray analysis were grown from dichloromethane/diethyl ether.

$\delta_H(d_6\text{-DMSO})$: 9.61 (t, 1H, $^4J_{HH}$ 2 Hz, imidazolium); 7.84 (2, 2H, $^4J_{HH}$ 2 Hz, imidazolium); 7.42 (m, 10H, benzene); 5.48 (s, 4H, benzyl). Microanalysis: found (expected) C 48.5 (48.9); H 4.1 (4.1); N 6.6 (6.7).

Computational Details. All calculations employed the Amsterdam Density Functional program version 2006.[34] Geometry optimizations were carried out in the gas phase using the BP86 functional,[35,36] DZP basis sets on all atoms and small frozen cores.[37] Scalar relativisitic corrections were applied within the ZORA formalism.[38−41] Default SCF and geometry convergence criteria were used except for the torsion angle criterion, which was relaxed from 0.5° to 2°.

Supporting Information Available: Crystallographic data on compounds **2**, **3**, **4**, **6**, and **7**, and DFT-optimized structure of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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