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<td><strong>Publication date</strong></td>
<td>2013-03-28</td>
</tr>
<tr>
<td><strong>Publication information</strong></td>
<td>Dalton Transactions, 42 (12): 4197-4207</td>
</tr>
<tr>
<td><strong>Publisher</strong></td>
<td>Royal Society of Chemistry</td>
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<tr>
<td><strong>Item record/more information</strong></td>
<td><a href="http://hdl.handle.net/10197/6832">http://hdl.handle.net/10197/6832</a></td>
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<tr>
<td><strong>Publisher's version (DOI)</strong></td>
<td>10.1039/c2dt32423g</td>
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Platinum(II) and platinum(IV) complexes stabilized by abnormal/mesoionic C4-bound dicarbenes †

Vsevolod Khlebnikov, Marion Heckenroth, Helge Müller-Bunz and Martin Albrecht*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Platinum(II) complexes comprising abnormal diimidazolylidene ligands were synthesized from cis-PtMe₂(DMSO)₂ using microwave-assisted double C–H bond activation. NMR analysis revealed an unusual solvolysis process, induced by coordinating solvents such as DMSO and MeCN, which has not been observed in related normal dicarbene complexes. NMR and IR spectroscopy and crystallographic analysis of the mono-substituted DMSO complex indicate a sulfur–bonding of the DMSO ligand to the platinum(II) center. Analysis of the DMSO exchange kinetics provided for the first time a quantitative measure of the trans effect of abnormal carbene ligands. The kinetic exchange rate in these bidentate abnormal dicarbene complexes is 0.050(±2) s⁻¹ and thus similar to analogous platinum(II) complexes containing phenylpyridine, yet significantly slower than that induced by pyridylidene pyridine. Reaction of the dicarbene platinum(II) complexes with PhICl₂, Br₂ and I₂ afforded the corresponding platinum(IV) complexes. Linkage isomerism of the PtIV-bound DMSO was observed when the bromination reaction was performed in DMSO solution. Moreover, solvolysis was less pronounced in the platinum(IV) complexes than in the corresponding platinum(II) analogues.

Introduction

Oxidative addition and its reverse counterpart, reductive elimination, are fundamental reactions in organometallic chemistry. They play an important role as basic steps in many catalytic cycles and synthetic transformations.¹ For example, platinum(IV) species are considered as the key intermediates in alkane C–H bond activation and functionalization.² Hence, stabilization of high oxidation states will provide useful insights for understanding the reactivity of such intermediates. A suitable approach consists of using strong Lewis base ligands such as N-heterocyclic carbenes (NHCs)³ for accessing high-valent metal centers.⁴ During the past decade NHCs have become widespread in high performance catalytic systems, e.g. for C–C coupling,⁵ olefin metathesis⁶ and hydroformylation.⁷ Recently, so-called abnormal or mesoionic carbenes⁸ have been investigated as a subclass of NHC ligands which bind the metal through the imidazole C4 or C5 site.⁹ These abnormal carbenes have demonstrated stronger σ-donor properties than their C2-bound congeners, thus facilitating the oxidative addition to the bound metal center.¹⁰ While Arduengo-type NHC platinum complexes have been known,¹¹,¹² C4-bound analogues are very rare¹³ and chelating dicarbenes complexes are unprecedented to the best of our knowledge. A potential reason for this lack may be the synthetic challenges in metalating two carbene precursors at the C4 position. Typical procedures for the platination of NHCs at C2 include the free carbene route¹²–¹⁴ and transmetalation via a silver intermediate.¹¹ Both methods are less suitable for the synthesis of C4-bound complexes, as the Ag-carbene intermediate is not stable¹⁵ and is not formed regioselectively, and the free C4-imidazolylidene is only accessible with specific wingtip substitution patterns.¹⁶ Oxidative addition has been demonstrated to yield C4-bound imidazolylidene complexes¹³,¹⁶ and has been applied for the preparation of C2-bound monocarbene platinum complexes,¹⁷ though this methodology is obviously inappropriate for installing two carbene ligands. Therefore, C(4)-H bond activation would be most attractive¹⁸ as it avoids laborious ligand functionalization and has precedents in abnormal dicarbene complexation.¹⁹ Here we report on the successful coordination of C4-bound dicarbenes to platinum and on our efforts to exploit the ligand-induced high electron density at the platinum center to access stable platinum(IV) complexes.²⁰

Results and discussion

Synthesis of the platinum(II) complexes

The desired diimidazolium ligand precursors 1 feature a methyl substituent at the C2 position in order to inhibit normal bonding of the imidazolylidene and to facilitate C4/C5 coordination (Scheme 1). The diimidazolium salts were prepared either by ion exchange from the known iodide precursor (1a) or by microwave-assisted condensation of 1-hexylimidazole and CH₂Cl₂ (1b). Platination of the C4 position in 1 was accomplished via microwave-assisted direct C–H bond activation using cis-PtMe₂(DMSO)₂ as metal precursor. Optimization of the...
reaction conditions gave 2a almost quantitatively (40 min, 100 °C) and complex 2b in 62% yield (15 min, 140 °C). MeCN was the solvent of choice and reactions in CH₂Cl₂, acetone or 1,2-dichloroethane gave lower yields under reflux conditions or after microwave irradiation. Metallation of 1 with [Pt₂(OAc)₃](AcOH) was equally unsuccessful, and unreliable when using PtCl₂ with or without K₂CO₃ as a base.

Previously published analogues. Complexes now in pseudo

larger for characterised by the N between the carbene heterocycles and the platinum square plane, metallacycle which adopts a boat slightly distorted square complexes. Was prepared according to procedures published for similar stable towards weak acids (HOAc) and decomposes gradually over 24 h in the presence of stronger acids (H₂SO₄). It was transformed to the corresponding dibromide 3a upon refluxing a MeCN solution in the presence of excess KBr. Single crystals suitable for X-ray diffraction analysis were obtained for complexes 2a, 3a, and for comparative reasons also for a normal dicarbene platinum analogue 4 (Scheme 1), which was prepared according to procedures published for similar complexes. The complexes all feature a platinum centered in a slightly distorted square-planar environment (Fig. 1). Chelation of the dicarbene ligand entails formation of a six-membered metallacycle which adopts a boat-like conformation. The torsion between the carbene heterocycles and the platinum square plane, characterized by the N–Pt–C dihedral angle, is 24° for 2a, larger for 3a (33°) presumably due to the different ionic radii of Cl⁻ and Br⁻, and even larger for 4 (42°) because of the bulky iPr substituents now in pseudo-ortho position to platinum.

The Pt–C bond lengths are slightly shorter in the chloride complex 2a than in the bromide analogue 3a, possibly due to the marginally larger trans influence of bromide vs. chloride. The carbene binding mode has no significant influence on the Pt–C bond lengths as they are comparable in 2–4 and similar to previously published analogues. The Pt–X bonds in 2a and 3a are slightly longer than those in C2-bound analogues despite the absence of the steric bulk adjacent to the carbene, inherent to 4 and related C2-bound NHC complexes. Hence, this elongation further illustrates the higher trans influence of abnormal carbene compared to normal carbenes.

Fig. 1 ORTEP plots of complexes a) 2a, b) 3a, and c) 4 (50% probability; hydrogen atoms and co-crystallised solvent molecules omitted for clarity).

### Table 1 Selected bond lengths (Å) and angles (°) in complexes 2a, 3a, and 4.

<table>
<thead>
<tr>
<th></th>
<th>2a (X = Cl)</th>
<th>3a (X = Br)</th>
<th>4 (X = Cl)</th>
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<tbody>
<tr>
<td>Pt1–C1</td>
<td>1.946(8)</td>
<td>1.965(7)</td>
<td>1.963(5)</td>
</tr>
<tr>
<td>Pt1–C7</td>
<td>1.949(8)</td>
<td>1.980(7)</td>
<td>1.963(5)</td>
</tr>
<tr>
<td>Pt1–X1</td>
<td>2.376(2)</td>
<td>2.503(9)</td>
<td>2.362(8)</td>
</tr>
<tr>
<td>Pt1–X2</td>
<td>2.397(2)</td>
<td>2.503(7)</td>
<td>2.362(8)</td>
</tr>
<tr>
<td>C1–C2</td>
<td>1.349(12)</td>
<td>1.357(9)</td>
<td>1.337(8)</td>
</tr>
<tr>
<td>C6–C7</td>
<td>1.397(11)</td>
<td>1.354(9)</td>
<td>1.337(8)</td>
</tr>
<tr>
<td>C1–Pt1–C7</td>
<td>89.1(3)</td>
<td>87.7(3)</td>
<td>84.7(3)</td>
</tr>
<tr>
<td>X1–Pt1–X2</td>
<td>90.49(7)</td>
<td>90.99(2)</td>
<td>88.40(6)</td>
</tr>
</tbody>
</table>

* atom labelling adapted (C7 = C1a, X2 = Cl1a, C1–C2 = C2–C3, C6–C7 = C2a–C3a).

**NMR spectroscopy**

Successful platination of the imidazolium precursor was supported by the disappearance of the signal attributed to the C4-bound imidazolium protons in the 1H NMR spectra. The two C5-bound protons of complexes 2a,b and the bridging methylene group appear as single resonances (δH = 7.04 ppm and 6.3 ppm, respectively, for 2a in CDCl₃), indicating a flexible boat-type
conformation and an average C₂ν symmetry on the NMR timescale. The ¹³C NMR spectrum of 2a displays a signal at 121.1 ppm, which was unambiguously attributed to the Pt-bound carbene carbons using 2D NMR spectroscopy, though the signal was too weak for the ¹⁹F Pt couplings to be resolved.

When recorded in DMSO-δ₆, however, both the ¹H NMR and the ¹³C NMR spectra display two sets of signals in equal ratio, pointing either to a mixture of two isomers or to a loss of the C₂ν molecular symmetry of the complex. The signals in each set are separated only marginally (Δδc < 0.3 ppm), except for the resonances of the two carbene carbon atoms (Δδc = 7.5 ppm) which suggest different ligands in trans positions (Table 2). Long-range ¹H–¹³C correlation spectroscopy revealed a coupling of each imidazolylidene proton with a different set of quaternary ring carbons and a three-bond correlation between the bridging methylene group and all four quaternary carbons, clearly indicating the presence of a single isomer rather than a mixture of two molecules. Qualitatively identical results were obtained with the dibromide complex 3, though the chemical shift differences in the ¹³C NMR spectrum are less pronounced (Fig. S1).

<table>
<thead>
<tr>
<th>complex</th>
<th>solvent</th>
<th>δ(C=C–H)</th>
<th>δ(C=C–H)</th>
<th>δ(C=C–Pt)</th>
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<tr>
<td>2a</td>
<td>DMSO-δ₆</td>
<td>7.15, 7.06</td>
<td>119.5, 119.4</td>
<td>126.6, 119.0</td>
</tr>
<tr>
<td>2a’</td>
<td>CDCl₃</td>
<td>7.17, 7.12</td>
<td>120.7, 120.4</td>
<td>127.5, 120.0</td>
</tr>
<tr>
<td>2b</td>
<td>DMSO-δ₆</td>
<td>7.02, 7.08</td>
<td>123.9, 123.7</td>
<td>126.0, 118.5</td>
</tr>
<tr>
<td>3a</td>
<td>DMSO-δ₆</td>
<td>7.16, 7.11</td>
<td>121.2, 119.3</td>
<td>125.5, 121.0</td>
</tr>
</tbody>
</table>

δ in ppm.

Loss of C₂ν symmetry in complexes 2 and 3 may be rationalized by the substitution of one of the halide ligands with a strongly coordinating molecule of DMSO, leading to the selective formation of the ionic mono-solvento complexes 2-DMSO and 3-DMSO, respectively (Scheme 2). Addition of 10 equiv. of a chloro source such as NH₄Cl or Bu₃NCl to DMSO solutions of 2 did not change the spectra and revealed that the DMSO adduct is the predominant species in solution. Similar DMSO solvolysis processes leading to mono-substituted species, were reported previously for several platinum(II) diamino dichloride complexes, though they have not been noted in homologous complexes containing normal C₂-bound diimidazolylidene ligands. Facile halide dissociation in complexes 2 and 3 thus demonstrates the strong donor ability of these C4-bound carbene ligands.

In contrast to the complete solvolysis in DMSO solution, only about 10% of mono-solvento species was observed in MeCN solutions of 2 and 3 (Fig. S2), as deduced from the integration of the C–CH₃ singlets around 2.5 ppm. Addition of 20 equiv. H₂O increased the fraction of solvento complex to ca. 35%, probably due to the change in the polarity of the solution. A similar effect was observed when adding HCl to a solution of 2a in CD₂CN. Complete solvolysis of one Pt–Cl bond was indicated by pairs of signals for C=C–H, the C=C–CH₃ and the isopropyl CH₃ groups in the ¹H NMR spectrum (δH = 6.98/6.96, 2.59/2.28 and 1.45/1.42 ppm, respectively), consistent with the pattern observed for the a mono-DMSO adduct of complex 2a. The chemical shift difference of the carbene nuclei in the ¹³C NMR spectrum is small (δC = 119.1 and 117.9, respectively), reflecting the similar trans influences of Cl and MeCN (DMSO > Cl ≥ MeCN). No solvolysis was detected in non-coordinating solvents such as CDCl₃ or CD₂Cl₂. Addition of 20 equiv. DMSO to a CDCl₃ solution of 2a, however, gave a 3:1 mixture of 2a-DMSO and 2a. In contrast, addition of excess Bu₃NCl prior to DMSO addition stabilized 2a and reduced the ratio between 2a-DMSO and 2a to 1:6. Similar inhibition of the chloride displacement by DMSO was reported for [Pt(en)Cl₂].

Synthesis of the locked DMSO complex 2a’

A separate experiment was performed in order to independently confirm the structure of the mono-solvento complex 2-DMSO. Abstraction of one of the halides in 2a using 1 equiv. AgBF₄ in the presence of DMSO yielded complex 2a’ (Scheme 3). Its ¹H NMR spectrum in CDCl₃ is essentially identical to the spectrum of 2 in DMSO and features two singlets at δH 7.12 and 7.17 ppm for the imidazolium protons (cf Table 2) and a single resonance at δH 3.38 ppm, attributed to a sulfon-bonded DMSO ligand. The infrared spectrum of 2a’ showed a vibration band at ννₛ = 1121 cm⁻¹ consistent with the κS-bonding mode of DMSO. The structure of 2a’ was further elucidated using a combination of 1D and 2D NMR spectroscopy. Specifically, long-range ¹H–¹³C correlation spectra demonstrated that the proton at δH 7.17 ppm and the Pt-bound carbon at δC 120.0 belong to the same heterocycle (and likewise δH 7.12 and δC 127.5; Scheme 3). Furthermore, a nuclear Overhauser effect (NOE) was observed between the methyl group of the DMSO and the heterocyclic proton signal at δH 7.17 ppm, indicating that the deshielded carbene nucleus (δC 127.5 ppm) is coordinated trans to DMSO. The 7.5 ppm downfield shift of the carbene resonance can thus be attributed to the greater trans influence of κS-DMSO vs. Cl⁻.

Scheme 3: Synthesis of 2a’ and characteristic NMR chemical shifts.

Exchange rate constants between free DMSO and DMSO-κS in 2a’ were determined by measuring diagonal and crosspeak intensities in magnetization transfer experiments (2D EXSY). Values for k₁ = 0.050±0.02 s⁻¹ and k₂ = 0.063±0.02 s⁻¹ (mixing times 600 – 1200 ms) were deduced. These exchange rates are similar to those in a related phenylpyridine platinum(II) complex, yet they are about two orders of magnitude smaller than those
reported for the pyridylidene-pyridine analogue of \(2\), suggesting a weaker trans effect of the C4-bound dicarbene ligand.\(^{35}\) While this apparently weaker trans labilizing ability of the abnormal dicarbene may be counterintuitive, it is interesting to note that the DMSO coordination is spontaneous when the diimidazolylidines are bound via the C4 carbon (cf \(2\) DMSO), while complex \(4\) and related homologues that are bound via C2 do not show any DMSO bonding.\(^{18,36}\) Hence the combination of the C4-bonding mode of the NHC ligand and the soft, electron rich platinum(II) metal center with high affinity for sulfur bonding, is critical for stabilizing the monocationic complexes \(2\) DMSO and \(3\) DMSO.

The bonding situation in complex \(2a’\) was unambiguously confirmed by a single crystal X-ray diffraction. The molecular structure (Fig. 2) is in agreement with the conclusions from solution analyses, featuring a \(\kappa^3\)-bound DMSO molecule. The environment around the sulfur atom is distorted tetrahedral with angles ranging from 102 to 108°, which is in good agreement with previously reported values.\(^{31}\) The Pt–S bond distance in \(2a’\) is 2.2928(11) Å and hence significantly longer than the average value of 2.213 Å for related structures.\(^{37}\) Similarly, the Pt–Cl bond distance in \(2a’\) (2.3634(9) Å) is markedly longer than the average 2.294 Å. The elongation of both the Pt–Cl and the Pt–S bond strongly reflects the exceptional donor ability of C4-bound carbene. Moreover, short contacts between the chloride and the methyl groups of DMSO were identified. The distances C17–H–Cl and C16–H–Cl are 2.801 and 2.756 Å, respectively, and may point to weak intramolecular hydrogen bonding interactions in the solid state.\(^{38}\)

**Oxidative addition to the platinum(II) complexes 2 and 3**

Exposure of \(2a\) to PhICl\(_2\) in 2,2,2-trifluoroethanol (TFE) induced oxidative chlorine addition and gave the platinum(IV) complex \(5a\) (Scheme 4).\(^{39}\) Reactions performed in CD\(_2\)Cl\(_2\) gave a mixture of at least two compounds, whereas the use of chlorine gas lead to a complex product mixture. In contrast, reaction of \(2b\) with PhICl\(_2\) proceeded smoothly in CH\(_2\)Cl\(_2\) and yielded the platinum(IV) complex \(5b\). The NMR spectra of \(5a\) and \(5b\) were similar and showed a single resonance at 7.09 ppm for C\(_{18}\)–H (DMSO-D\(_4\)). Hence, in contrast to the Pt\(^{II}\) analogues, no spontaneous ligand substitution processes with DMSO took place. Consistently, only a single set of resonances appears in the \(^{13}\)C NMR spectrum and indicates formal \(\kappa^3\) symmetry of \(5a, 5b\) in solution. Most diagnostically, platinum oxidation induces a 15.0 ppm upfield shift of the metal-bound carbene resonances (\(\delta\(C = 105.1\) and 104.5 for \(5a\) and \(5b\), respectively).

**Addition of bromine to 3a** gave the platinum(IV) complex \(6a\) as a single product in quantitative yield both in CH\(_2\)Cl\(_2\) and in TFE. The NMR chemical shifts and multiplicities are similar to those of the tetrachloride complex \(5a\) apart from the fact that in \(6a\), the \(^{195}\)Pt satellites are well resolved for the C\(_{18}\)–H signal (\(\delta_J = 15.8\) Hz).

Single crystals suitable for X-ray diffraction analysis were obtained for complexes \(5a\) and \(6a\). The platinum center is slightly distorted octahedral in both complexes (Fig. 3). Similar to \(2a\) and \(3a\), the dihedral angles between the chelating heterocycles and the platinum xy plane are around 25°. The change in oxidation state induced an elongation of distinct bonds (Table 3). In \(5a\), the Pt–C bonds (by 0.04 Å) and one of the Pt–Cl bonds are significantly longer than in the platinum(II) precursor \(2a\). In \(6a\), the Pt–Br bonds trans to the carbene are stretched by 0.04 Å compared to \(3a\). In both complexes \(5a\) and \(6a\), the mutually trans Pt–X bonds are almost 0.1 Å shorter than the Pt–X bonds trans to the carbene. In the absence of significant steric effects of the

![Fig. 2 ORTEP plots of complex 2a’ (50% probability, hydrogen atoms, and BF\(_2\) ion omitted for clarity). Selected bond lengths (Å) and angles (°): Pt1–C1 1.988(3), Pt1–C7 2.006(4), Pt1–S1 2.2928(11), Pt1–C11 2.3634(9), C1–C2 1.347(6), C6–C7 1.362(5), S1–O1 1.469(3), C1–Pt1–C7 88.15(15), N2–C1–Pt1–C7 29.0(3), N3–C7–Pt1–C1 27.1(3).](image)

![Scheme 4 Synthesis of platinum(IV) complexes 5 and 6.](image)

![Fig. 3 ORTEP plots of a) complex 5a and b) complex 6a (50% probability, hydrogen atoms and co-crystallized solvent molecules omitted for clarity).](image)

**Table 3 Selected bond lengths (Å) and angles (°) for 5a and 6a.**

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<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
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<tbody>
<tr>
<td>Pt1–C1</td>
<td>1.995(4)</td>
<td>2.003(5)</td>
</tr>
<tr>
<td>Pt1–C7</td>
<td>1.986(5)</td>
<td>1.986(6)</td>
</tr>
<tr>
<td>Pt1–X1</td>
<td>2.3169(11)</td>
<td>2.4547(6)</td>
</tr>
<tr>
<td>Pt1–X2</td>
<td>2.3290(11)</td>
<td>2.4692(6)</td>
</tr>
<tr>
<td>Pt1–X3</td>
<td>2.4094(12)</td>
<td>2.5410(6)</td>
</tr>
<tr>
<td>Pt1–X4</td>
<td>2.4057(12)</td>
<td>2.5391(6)</td>
</tr>
<tr>
<td>C1–Pt1–C7</td>
<td>88.05(18)</td>
<td>88.2(2)</td>
</tr>
</tbody>
</table>
wingtip groups, these bond length differences are attributed to the 
substantial trans influence of C4-bound imidazolylidenes.

Bromination of 2a or addition of PhCl2 to 3a in CH2Cl2 or TFE 
gave mixtures of several PtIV isomers. The composition of 
these mixtures was similar in both setups (Fig. S3), indicating a 
thermodynamic control of the oxidative addition. Such a 
conclusion corroborates an S₄Ne-type pathway involving a cationic 
five-coordinate intermediate. Consequently, the stereochemistry 
of the final octahedral PtIV product is thermodynamically controlled.

Reaction of 2b with either Br2 or I2 afforded single isomers of 
the mixed halide platinum(IV) complexes. The NMR chemical 
shifts for both species are similar to those of 5b, however, the 
C₋H resonance show a well-resolved ¹³⁵Pt coupling (¹JPtH = 
14.7 Hz for the BrCl species and 15.7 Hz for the ICl analogue).

In addition, the mixed ICl complex features an AB system for 
the methylene bridge (δH1 6.22 and 5.99 ppm, ²JIII = 13.6 Hz), 
indicative of a restricted inversion of the metallacycle. Such 
hybrid inversion was also observed in complex 4 and related 
platinum(II) and palladium(II) complexes with C₂-bound NHCs 
due presumably to steric constrains between the wingtip groups 
and the halide ligand.¹⁰⁻¹¹ Consequently, the large iodide 
ligands are assumed to be trans to the dicarbene ligand and thus 
impose significant repulsion in a putative planar transition state 
of metallacycle inversion. Upon standing in DMSO-D₂ solution, 
the initially formed mixed ICl platinum(IV) complex slowly 
isoomerized to a mixture of four PtIV compounds, all with lower 
symmetry. Complicated product mixtures from oxidative 
addition of iodine are not uncommon because of the 
complex redox chemistry of iodine and its ability to bind to the platinum 
center as well as to the Pt-bound iodide.¹² No oxidative addition 
products were spectroscopically observed upon treatment of 2b 
with alkyl halides (Mel, EtBr or BnBr).

Bromination in DMSO solution

In contrast to the bromination of 3a, the reaction of Br₂ with the 
DMSO adduct proceeded via a two-step process (Scheme 5). 
Initial oxidative addition yielded the platinum(IV) complex 
₆a·κS-DMSO almost instantaneously. This kinetic product was 
stable and gradually isomerized to the O-bound DMSO homologue 
₆a·κO-DMSO (87% conversion after 27 min at RT, 
₄₁/₂ ~10 min). The short life-time of this intermediate prevented 
the acquisition of pertinent ¹³C NMR data. Linkage isomerism 
due to the ambidentate nature of the DMSO ligand was also 
observed upon addition of Br₂ to 2b·DMSO and has ample 
precedents in Ru,³⁴ Os,³⁵ and Pt⁶ chemistry. In 6a, the 
isomerization is probably induced by the increased hardness of 
platinum upon oxidation to PtIV.⁴⁷ In addition, steric congestion 
around the octahedral platinum(IV) center is more pronounced 
than in the square-planar platinum(II) precursor and may thus 
promote coordination of the least substituted donor site.

The carbene carbon trans to DMSO appeared at an unusually 
low frequency (δC 86.5 ppm) in the ¹³C NMR spectrum of ₆a·κO-
DMSO, while the nucleus trans to bromide resolved at δC 106.3 
ppm. This 20 ppm shift to higher field is due to the downfield 
shift observed in the S-bound complex 3a·DMSO, thus strongly 
supporting a change in the DMSO binding mode. According to 
these chemical shifts the trans influence decreases in the order 
κS-DMSO > Cl, Br > κO-DMSO. The same trend was recently 
reported for isoelectronic rhodium(III) complexes.⁴⁸

Isomerization was indicated by shift of the two inequivalent 
C₋H protons from δH 7.29 and 7.26 ppm upfield to δH 7.10 and 
6.98 ppm (¹JPtH = 15.8 Hz and 10.5 Hz, respectively) for 
₆a·κO-DMSO. Time-dependent monitoring of the ratio of these 
signals indicated the expected first-order kinetics for the 
isomerization process (Fig. S4). Treatment of a mixture of S- 
and O-bound 6a·DMSO with 1 equiv using AgBF₄ induced the 
substitution of the non-coordinating bromide anion to BF₄⁻ and 
enabled spectroscopic analyses in CD₂Cl₂. Accordingly, ₆a·κS-
DMSO displayed a singlet at δH 3.76 ppm (¹JPtH = 8 Hz) for the 
 methyl groups of DMSO, while isomerization to the O-bound 
species imparted an upfield shift to 2.92 ppm. These values are 
similar to δH 3.87 (¹JPtH = 15.5 Hz) and 2.80 ppm of related 
platinum(IV) complexes featuring S- and O-bound DMSO, 
respectively.⁴⁶,⁵⁰ In the IR spectrum a strong absorbance band 
at 975 cm⁻¹ was assigned to ν₅BF₂ of O-bound DMSO. The ν₅BF₂ 
band of the S-bound DMSO was superimposed by the broad band of BF₄⁻ 
(v₅ = 1053 cm⁻¹), which prevented unequivocal identification.

While the platinum(II) complexes 2 and 3 spontaneously 
transform to 2·DMSO and 3·DMSO within seconds and at RT, 
analogous solvolysis requires much harsher conditions in the 
platinum(IV) systems 5 and 6. Heating a DMSO 
solution of complex 5a for 1 h at 100 °C produced less than 20% of 
₅a·κO-DMSO (1:5 mixture), while 50% of 6a converted to 
₆a·κO-DMSO after only 0.5 h at 100 °C. This outcome demonstrates 
the higher electron density in the PtIV complexes and also the 
better leaving group properties of Br⁻ compared to Cl⁻. Notably, 
soyolysis in the octahedral platinum(IV) complexes 5 and 6 
produced exclusively the thermodynamically more favored O-
bound DMSO isomer and no traces of the sulfur-bound isomer 
were detected. In line with the electronic considerations, 
soyolysis in platinum(IV) species is reversible and the neutral 
complex 6a was obtained upon stirring 6a·DMSO in the presence of 50 equiv. KBr (DMSO solution, RT).

Conclusions

A double C–H bond activation strategy was applied to prepare 
C₄-bound dicarbene platinum complexes. The high electron 
density at the platinum center in these complexes, imparted to a 
significant extent by the strong donor properties of the mesoionic 
imidazol-4-ylidene ligand sites, has a marked influence on the 
reactivity. Thus, exchange of a metal-bound halide ligand for a 
neutral solvent molecule readily took place in DMSO and in the
presence of other polar solvents (H2O, MeCN). Furthermore, oxidative addition processes were smooth and afforded stable platinum(IV) complexes. These reactivity patterns may be relevant for developing novel catalyst precursors for bond activation processes that require oxidative substrate addition, such as in the Shilov system. Current work is directed toward an expansion of the scope for oxidative addition to a broader range of substrates and towards exploiting the platinum(IV) complexes for chemoselective reductive transfer processes.

### Experimental section

#### General comments

The N-alkylated imidazoles, 3,3'-methylenebis(1-isopropyl-2-methylimidazolium) diiodide, cis-PtMe2(DMSO)2, and toluene-dichloride (PhI)(Cl) were prepared according to literature procedures. All other reagents were purchased from commercial sources and used without further purification. 1H and 13C{1H} NMR spectra were recorded at room temperature on Varian spectrometers operating at 400 or 500 MHz unless stated otherwise. Chemical shifts (δ) are given in ppm and referenced to SiMe₄, coupling constants (J) are given in Hz. Signal assignments are based on homo- and heteronuclear (multiple-bond) correlation spectroscopy. Microanalyses were performed with an Exeter Analytical Instrument CE-440. High resolution mass spectrometry was carried out with a Micromass/Waters Corp. USA liquid chromatography Time-Of-Flight spectrometer equipped with an electrospray source. All microwave irradiation experiments were carried out in Biotage Initiator 2.5 single-mode microwave apparatus, operating at 2.45 GHz with continuous irradiation power from 0 to 400 W. The reactions were carried out in glass vials equipped with a magnetic stirring bar and sealed with an aluminum septum cap. After the irradiation period, the reaction vessel was cooled rapidly (<120 s) to ambient temperature by gas jet cooling. IR spectra were recorded using a Vertex 70 (Bruker) FT-IR spectrometer equipped with a Globar Infrared source, a mercury cadmium telluride detector and a Diffuse Reflectance Infrared Fourier Transform Spectroscopy accessory.

#### Dümiezaloid[4v] dichloride (1a)

3,3'-methylenebis(1-isopropyl-2-methylimidazolium) diiodide (2.77 g, 5.36 mmol) was dissolved in MeOH (20 mL) and filtered over a Dowex ion-exchange resin (1 × 4 chloride form, 100-200 mesh). After removal of the solvent in vacuo, 2b was obtained as an off-white solid. Yield: 1.34 g (75%). 1H NMR (DMSO–D₆, 400 MHz): δ 7.96, 7.93 (2 × d, JHH = 2.3 Hz, 2H-H), 6.55 (s, 2H, NCH₂N), 4.72 (sept, JHH = 6.6 Hz, 2H, CMCH₂), 2.80 (s, 6H, CH₂-C), 1.44 (d, JHH = 6.6 Hz, 12H, CH₂–CH₂); 13C{1H} NMR (DMSO–D₆, 100 MHz): δ 145.3, 122.1, 118.6 (3 × C₈H₄), 56.4 (NCH₂N), 50.5 (CMCH₂), 22.0 (CH₂–CH₂), 10.4 (C–CH₂); Exact Mass Calcd for C₁₅H₁₅N₂Cl²: 297.1846. Found: 297.1859.

#### Dümiezaloid[4k] dichloride (1b)

A solution of 1-hexyl-2-methylimidazole (3.63 g, 21.8 mmol) in CH₂Cl₂ (8 mL) was irradiated under microwave irradiation for 1 h at 150 °C. Addition of excess Et₃O produced an off-white precipitate, which was filtered, washed with Et₃O, and dried in vacuo (3.66 g, 80%). 1H NMR (DMSO–D₆, 500 MHz): δ 8.15, 7.87 (2 × d, JHH = 2.1 Hz, 2H, H₈), 6.84 (s, 2H, NCH₂N), 4.14 (t, JHH = 7.5 Hz, 4H, NCH₂), 2.82 (s, 6H, CH₂–CH₃), 1.76–1.66 (m, 4H, CH₂), 1.35–1.23 (m, 12H, CH₂), 0.86 (s, JHH = 6.4 Hz, 6H, CH₃(CH₂)); 13C{1H} NMR (DSMO–D₆, 125 MHz): δ 140.6 (C₁₅H₁₅N₂Cl²: 416.2784. Found: 416.2393.

**Pt(dicarbene)Cl₂ (2a)**

Compound 2a (0.100 g, 0.33 mmol) and cis-PtMe₂(DMSO)₂ (0.114 g, 0.33 mmol) were dissolved in MeCN (10 mL). The mixture was then irradiated for 40 min at 100 °C. The solvent was removed under reduced pressure. The resulting off-white solid was dissolved in small amount of CH₂Cl₂ and precipitated with an excess of Et₃O. The solid was then dried in vacuo. Yield: 0.155 g (98%). MS (ES+): m/z 491, [M+Cl]². 1H NMR (CDCl₃, 400 MHz): δ 7.04 (s, 2H, H₈), 6.30 (s, 2H, NCH₂N), 4.35 (sept, JHH = 6.6 Hz, 2H, CMCH₂), 2.86 (s, 6H, C–CH₃), 1.41 (d, JHH = 6.6 Hz, 12H, CH₂–CH₂); 13C{1H} NMR (CDCl₃, 100 MHz): δ 138.7 (C₁₅H₁₅N₂Cl²: 112.1 (C₆H₅C₆H₅), 117.9 (C₁₅H₁₅N₂Cl²: 60.0 (NCH₂N), 48.9 (CH₂–CH₂), 22.7 (C–CH₃), 11.3 (C–CH₃). Anal. Calcd. for C₁₅H₁₅N₂Pt (526.37) × 0.25 CH₂Cl₂: C 31.44, H 4.29, N 9.17. Found: C 31.95, H 4.33, N 9.34.

**Spectroscopic data for [Pt(dicarbene)Cl(DMSO)]Cl (2a-DMSO)**

1H NMR (DMSO–D₆, 400 MHz): δ 7.15, 7.06 (2 × s, 1H, H₈), 6.01 (s, 2H, NCH₂N), 4.60 (br, 2H, CMCH₂), 2.73 (s, 6H, C–CH₃), 1.40, 1.39 (2 × d, JHH = 7.7 Hz, 6H, CH₂–CH₂); 13C{1H} NMR (DMSO–D₆, 100 MHz): δ 141.3, 140.8 (2 × C₁₅H₁₅N₂Cl²: 126.6 (C₆H₅C₆H₅), 119.5, 119.4 (2 × C₁₅H₁₅N₂Cl²: 119.0 (C₆H₅C₆H₅), 58.6 (NCH₂N), 49.3, 49.1 (2 × CH₂–CH₂), 22.1, 22.0 (2 × C–CH₂), 9.8, 9.6 (2 × C–CH₂).

**Pt(dicarbene)Cl(DMSO)][BF₄] (2a')**

To a solution of 2a (0.035 g, 0.066 mmol) in CH₂Cl₂ (2 mL) was added DMSO (0.039 g, 0.50 mmol) followed by AgBF₄ (0.013 g, 0.066 mmol). The reaction mixture was stirred at room temperature for 14 h with exclusion from light. The mixture was filtered over Celite and all volatiles were removed under reduced pressure (0.039 g, 89%). Recrystallization from CH₂Cl₂/Et₂O gave an analytically pure sample. 1H NMR (CDCl₃, 400 MHz): δ 7.17, 7.12 (2 × s, 1H, H₈), 6.18 (s, 2H, NCH₂N), 4.44, 4.44 (2 × sept, JHH = 6.5 Hz, 1H, CH₂–CH₂), 3.38 (s, 6H, CH₃(CH₂)), 2.85 (s, 6H, C–CH₃), 1.50, 1.49 (2 × d, JHH = 6.5 Hz, 6H, CH₂–CH₂); 13C{1H} NMR (CDCl₃, 100 MHz): δ 140.7, 140.3 (2 × C₁₅H₁₅N₂Cl²: 127.5 (C₆H₅C₆H₅), 120.7, 120.4 (2 × C₁₅H₁₅N₂Cl²: 120.0 (C₆H₅C₆H₅), 59.2 (NCH₂N), 50.5, 50.4 (2 × CH₂–CH₂), 44.0 (CH₃(DMSO)), 22.7, 22.7 (2 × C–CH₂), 10.5, 10.3 (2 × C–CH₂). Anal. Calcd. for C₁₉H₁₉BF₄N₂OCl²: 655.85 × 0.25 CH₂Cl₂: C 30.60, H 4.54, N 8.17. Found: C 30.62, H 4.49, N 8.28.

**Pt(dicarbene)Cl₂ (2b)**

Compound 1b (0.21 g, 0.5 mmol) and cis-PtMe₂(DMSO)₂ (0.19 g, 0.5 mmol) were dissolved in MeCN (10 mL) and the mixture was microwave irradiated for 15 min at 140 °C. The resulting off-white solid was filtered off washed with Et₃O and dried in vacuo. Yield: 0.166 g (54%). Recrystallization from DMSO/THF gave an analytically pure sample. MS (ES+): m/z 575, [M+Cl]². 1H
NMR (DMSO–D$_6$, 400 MHz): $\delta$ 7.08, 7.02 (2 × s, 1H, H$_{im}$), 5.97 (s, 2H, NCH$_3$N), 4.03 (q, $J_{HiHi} = 6.6$ Hz, 4H, NCH$_2$), 2.70 (s, 6H, C$_6$H$_{4}$-CH$_3$), 1.69–1.59 (m, 4H, CH$_2$), 1.38–1.18 (m, 12H, CH$_2$), 0.86 (t, $J_{CH} = 6.6$ Hz, 6H, CH$_3$-tethyl), $^{13}$C(H) NMR (DMSO–D$_6$, 100 MHz): $\delta$ 141.9, 141.6 (2 × C$_{in}$), 126.0 (C$_{Carbene}$), 123.9, 123.7 (2 × C$_{in}$), 118.5 (C$_{Carbene}$), 58.8 (NCH$_3$N), 46.9 (NCH$_2$), 30.7, 30.7, 29.5, 29.5, 25.4, 21.9, 21.9 (8 × CH$_2$), 13.9, 13.9 (2 × CH$_3$-tethyl), 9.7, 9.7 (2 × C$_{Me}$-CH$_3$); Anal. Calcd. for C$_2$H$_5$Cl$_4$N$_2$: C 41.3, H 5.94, N 9.18. Found: C 41.5, H 5.88, N 8.88.

Pt(dicarbene)$^6$Br$_2$ (3a)

KBr (1.20 g, 5.0 mmol) was added to a solution of 2a (0.14 g, 0.27 mmol) in MeCN (15 mL) and the suspension was refluxed for 12 h. Reaction mixture was filtered and volatiles were removed under reduced pressure. The solid was dissolved in CH$_2$Cl$_2$ and filtered through a celite plug. After removal of the solvent, the resulting light brown solid was dried in vacuo. Yield: 0.148 g (90%). MS (ES+): $m/z$ 535, [M-Br]$^-$. $^1$H NMR (DMSO–D$_6$, 500 MHz): $\delta$ 7.16, 7.12 (2 × s, 1H, H$_{im}$), 6.02 (s, 2H, NCH$_3$N), 4.60, 4.58 (2 × $J_{CH} = 6.5$ Hz, 1H, CHMe$_3$), 2.72 (s, 6H, C–CH$_3$), 1.39, 1.37 (2 × $J_{HiHi} = 6.5$ Hz, 6H, CH–CH$_2$); $^{13}$C(H) NMR (DMSO–D$_6$, 100 MHz): $\delta$ 141.3, 140.7 (2 × C$_{in}$), 125.5 (C$_{Carbene}$), 121.2 (C$_{in}$), 121.0 (C$_{im}$), 119.3 (C$_{im}$), 58.6 (NCH$_3$N), 49.3, 49.1 (2 × CHMe$_3$), 22.1, 22.0 (2 × C–CH$_3$), 9.8, 9.7 (2 × CH–CH$_3$); Anal. Calcd. for C$_2$H$_5$Br$_2$PtCl$_4$: 615.2 (C$_{Carbene}$) × 0.5 CH$_2$Cl$_2$: 28.30, H 3.83, N 8.52. Found: C 28.23, H 3.53, N 8.39.

Pt(diimidazol-2-yldiene)Cl$_2$ (4)

A mixture of PtCl$_2$ (0.13 g, 0.49 mmol), NaCl (0.28 g, 4.8 mmol), NaOAc (0.084 g, 1.0 mmol) and 3,3′-dipropyl-1,1-methylene-diimidazolium chloride (0.15 g, 0.49 mmol) was stirred in DMSO (5 mL) at 50 °C for 2 h and subsequently at 120 °C for 3 h. After cooling to room temperature, CH$_2$Cl$_2$ (20 mL) and Et$_2$O (80 mL) were added to give a precipitate, which was collected and washed repeatedly by adding CH$_2$Cl$_2$ (20 mL) followed by precipitation with Et$_2$O (80 mL). After drying in vacuo, complex 4 was obtained as a white powder (0.20 g, 82%), which was recrystallized from DMSO/Et$_2$O (1:1). $^1$H NMR (DMSO–D$_6$, 400 MHz): $\delta$ 7.53, 7.51 (2 × s, 2H, H$_{im}$), 6.06, 5.93 (2 × $J_{HiHi} = 13.0$ Hz, 2H, NCH$_3$N), 5.55 (sept, $J_{HiHi} = 6.7$ Hz, 2H, CHMe$_2$), 1.43, 1.21 (2 × $J_{HiHi} = 6.7$ Hz, 6H, CH–CH$_2$), $^{13}$C(H) NMR (DMSO–D$_6$, 100 MHz): $\delta$ 143.2 (C$_{Carbene}$), 121.1, 117.5 (2 × C$_{in}$), 61.8 (NCH$_3$N), 50.8 (CHMe$_2$), 23.4, 21.8 (2 × CH–CH$_3$).

Pt(dicarbene)$^{11}$Cl$_2$ (5a)

Iodobenzene dichloride (0.061 g, 0.22 mmol) was added to a stirring suspension of 2b (0.105 g, 0.20 mmol) in TFE (10 mL). The reaction mixture was stirred at room temperature for 2 h followed by filtration through a celite plug. The solvent volume was reduced to 2 mL and the solid was precipitated by adding an excess of Et$_2$O. The solid was centrifuged and washed 2 × with Et$_2$O (50 mL). The resulting light yellow solid was dried in vacuo. Yield: 0.114 g (95%). Recrystallization from DMSO/CH$_2$Cl$_2$/Et$_2$O gave an analytically pure sample. X-ray-quality crystals were obtained by layering a DMSO/MeCN solution with Et$_2$O. $^1$H NMR (DMSO–D$_6$, 500 MHz): $\delta$ 7.18 (s, $J_{HiHi} = 15.8$ Hz, 2H, H$_{im}$); 6.32 (s, 2H, NCH$_3$N), 4.69 (sept, $J_{HiHi} = 6.6$ Hz, 2H, CHMe$_2$), 2.83 (s, 6H, C–CH$_3$), 1.43 (d, $J_{HiHi} = 6.6$ Hz, 6H, CH–CH$_3$); $^{13}$C(H) NMR (DMSO–D$_6$, 100 MHz): $\delta$ 141.4 (C$_{in}$), 120.2 (C$_{in}$), 104.8 (C$_{Carbene}$), 58.2 (NCH$_3$N), 49.8 (CHMe$_2$), 22.0 (C–CH$_3$), 9.9 (CH–CH$_3$); Anal. Calcd. for C$_2$H$_5$Br$_2$PtCl$_4$: 775.08 × 0.5 CH$_2$Cl$_2$: C 22.35, H 3.05, N 6.51. Found: C 22.01, H 2.89, N 6.41.

Pt(dicarbene)$^{11}$Br$_3$(DMSO)Br (6a–X–O–DMSO)

Bromine (0.034 g, 0.21 mmol) was added dropwise to a stirring suspension of compound 3a (0.019 g, 0.031 mmol) in TFE (3 mL). The reaction mixture was stirred at room temperature for 75 min. The volatiles were removed under reduced pressure and the residue was washed with Et$_2$O and dried in vacuo. Yield: 0.023 g (100%). Recrystallization from DMSO/CH$_2$Cl$_2$/Et$_2$O gave an analytically pure sample. X-ray-quality crystals were obtained by layering a DMSO/MeCN solution with Et$_2$O. $^1$H NMR (DMSO–D$_6$, 500 MHz): $\delta$ 7.10, 6.98 (2 × s, 1H, H$_{im}$), 6.25 (2s, 2H, NCH$_3$N), 4.72, 4.70 (2 × $J_{HiHi} = 6.7$ Hz, 1H, CHMe$_2$), 2.85 (s, 6H, C–CH$_3$), 1.45, 1.42 (2 × $J_{HiHi} = 6.7$ Hz, 6H, CH–CH$_3$); $^{13}$C(H) NMR (DMSO–D$_6$, 100 MHz): $\delta$ 143.1, 142.4 (2 × C$_{in}$), 121.1, 116.1 (2 × C$_{in}$), 106.3, 86.5 (2 × C$_{Carbene}$), 58.5 (NCH$_3$N), 50.3, 50.2 (2 × CHMe$_2$), 22.0 (C–CH$_3$), 10.3, 10.7 (2 × CH–CH$_3$).

Pt(dicarbene)$^{11}$Br$_2$Cl$_2$

Bromine (0.189 g, 1.18 mmol) was added dropwise to a stirring suspension of 2b (0.080 g, 0.13 mmol) in CH$_2$Cl$_2$ (5 mL). The reaction mixture was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure and the residue
was washed with Et₂O and dried in vacuo. Yield: 0.10 g (100%).

1H NMR (DMSO-D₆, 400 MHz): δ 7.10 (s, J₊HH = 14.7 Hz, 2H, H₅), 6.23 (s, 2H, NCH₃(N)), 4.14 (q, J₃J-H₂ = 7.3 Hz, 4H, CH₂(NCH₃)), 2.80 (s, 6H, CCH₃), 1.75–1.60 (m, 4H, CH₂), 1.35–1.15 (m, 12H, CH₂), 0.87 (t, J₅J-CH₃ = 6.8 Hz, 6H, CH₃); 13C{(¹H)} NMR (DMSO-D₆, 100 MHz): δ 141.8 (C₂NCH₃), 123.4 (C²CH₂, Jpc = 34 Hz), 102.3 (Ccarbene, Jpc = 947 Hz), 58.5 (NCH₃(N)), 47.3 (NCH₃), 30.6, 29.5, 25.3, 21.9 (4 × CH₂), 13.8 (CH₃tessyl), 9.7 (C₈=C₉-CH₃).

P{(dicarben)e}₂Cl₂

33.5, 25.3, 21.9 (4 × CH₂), 13.8 (CH₃tessyl), 9.7 (C₈=C₉-CH₃).

Crystal structure determination

Crystal data for 2a and 4 were collected using a Stoe Mark II Imaging Plate Diffractometer System (Stoe & Cie, 2002) equipped with graphite monochromator. Semi-empirical absorption correction was applied using MULscanABS as implemented in PLATON. Crystal data for 2a, 3a, 5a, and 6a were collected using an Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector. Crystals were measured with Mo-Kα (0.71073 Å). At least an complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical absorption correction based on the shape of the crystal was performed for all these crystals. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F² for all data using SHELXL-97. Their isotropic thermal displacement parameters were fixed to 1.2 times (1.5 times for methyl groups) the equivalent one of the parent atom. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms.

Complex 2a co-crystallized with pronouncedy disordered DMSO molecules. Therefore, the SQUEEZE option in PLATON was used to calculate the potential solvent accessible volume (1453 Å³ calculated containing about 223 electrons). Six DMSO molecules (6 × 42 electrons) per unit cell were included in all further calculations. The co-crystallized molecule of DMSO in the unit cell of 4 is also disordered. Further crystallographic details are compiled in Tables S1-2. CCDC numbers 904838 (6a), 904839 (5a), 904840 (3a), 904841 (2a), 904842 (2a) and 904843 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment

We thank A. Neels for the crystallographic analysis of complexes 2a and 4 and Y. Ortin for NMR spectroscopy assistance. This work was supported financially by the Swiss National Science Foundation and University College Dublin.

Notes and references


Addition of HCl (5 equiv.) to 2a yielded a 3:2 mixture of 2a’ and the platinum(IV) complex 4a, implying oxidative addition of HCl or transient formation of Cl− (see below for details).


(a) Around 10% of the mixture is a symmetric compound with chemical shifts very similar to 6a ($\delta_H = 7.20$ and 6.35 ppm). Performing the bromination of 3a in pure DMSO on a larger scale (0.040 g, 0.065 mmol) gave a residue with a characteristic SM$_2$ odor. NMR spectroscopic analysis revealed a 3:1 mixture of a symmetric compound and a new platinum(IV) complex with a signal at 2.80 ppm ($J_{PtH} = 18.8$ Hz). The resonance was attributed to a Pt-bound SM$_2$ group due to the large $J_{PtH}$ coupling constant and also because of the downfield chemical shift of the methyl group in the $^{13}$C NMR spectrum ($\delta_C = 22.6$ ppm). In addition, no resonances in support of $O$-bound DMSO were observed. Deoxygenation of DMSO may have occurred during purification, e.g. upon distillation of the DMSO at 100 °C under high vacuum. For a related reactivity pattern, see sec: (b) L. Alexandrova, O. G. D’Yachenko, G. M. Kazankov, V. A. Polyakov, P. V. Samuleev, E. Sansores and A. D. Ryabov, J. Am. Chem. Soc., 2000, 122, 5189.

The smaller $J_{PtH}$ value in 5a compared to published values may be attributed to the higher trans influence of C4-bound imidazolylidene vs. pyridine.


C4-bound imidazolylidene-type dicarbene ligands bound to platinum(II) centers induce solvolysis of the metal-bound halide and facile oxidative addition to yield stable platinum(IV) complexes.