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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*

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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 dicarbone 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 dicarbone 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 dicarbone platinum(II) complexes with PhICl₂, Br₂ and I₂ afforded the corresponding platinum(IV) complexes. Linkage isomerism of the Pt⁴⁺-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 dicarbone complexes are unprecedented to the best of our knowledge. A potential reason for this lack may be the synthetic challenges in metatating two carbene precursors at the C4 position. Typical procedures for the platination of NHCs at C2 include the free carbene route12–14 and transmetallation via a silver intermediate.11 Both methods are less suitable for the synthesis of C4-bound complexes, as the Ag-carbone intermediate is not stable15 and is not formed regioselectively, and the free C4-imidazolylidene is only accessible with specific angiotip 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 monocarbone 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 dicarbone 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 precursor21 (1a) or by microwave-assisted condensation of 1-hexylimidazole and CH₃Cl₂ (1b). Platination of the C4 position22 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)₆](AcOH)₂ was equally unsuccessful, and unreliable when using PtCl₆ with or without K₂CO₃ as a base.

Formation of 2 formally involves imidazolium C–H bond cleavage with concomitant release of CH₄, either directly from the platinum precursor or from a platinate such as [PtMe₂Cl₄]⁻ that may form in-situ with 1. The high yield formation of complexes 2a,b implies a strong preference for the activation of the C–H bond over C–Cl bond activation. In the absence of significant chemical differences between these two bonds, an ion pairing mechanism may be operational analogous to related palladation, thus supporting the formation of a platinate dianion that is stabilized by the diimidazolium dication. In such an ion pair, the Pt–Me bond will be in close proximity to the C–H bond and this pre-organization may thus account for the high selectivity in the first bond formation step. From such a putative monocarbene–PtMeCl₂ system, the second C–H activation may then ensue via classical cyclometalation pathways.

Complexes 2a,b are air- and moisture stable solids. They dissolve reasonably well in chlorinated solvents (CH₂Cl₂, CHCl₃) and in polar media (MeCN, DMSO). Complex 2a is moderately 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–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 carbenes compared to normal carbenes.

### 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>
</tr>
</thead>
<tbody>
<tr>
<td>Pt1–C1</td>
<td>1.946(8)</td>
<td>1.963(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(6)</td>
<td>2.362(12)</td>
</tr>
<tr>
<td>Pt1–X2</td>
<td>2.397(2)</td>
<td>2.503(7)</td>
<td>2.362(12)</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>90.09(2)</td>
<td>88.40(6)</td>
</tr>
</tbody>
</table>

* atom labelling adapted (C7 = C1a, X2 = C11a, 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 C$_2v$ symmetry on the NMR timescale. The $^{13}$C 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 $^{195}$Pt couplings to be resolved.

When recorded in DMSO-D$_2$, however, both the $^1$H NMR and the $^{13}$C NMR spectra display two sets of signals in equal ratio, pointing either to a mixture of two isomers or to a loss of the C$_2v$ molecular symmetry of the complex. The signals in each set are separated only marginally ($\Delta \delta_\mathrm{c} < 0.3$ ppm), except for the resonances of the two carbene carbon atoms ($\Delta \delta_\mathrm{c} = 7.5$ ppm) which suggest different ligands in trans positions (Table 2). Long-range $^1$H–$^{13}$C 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 $^{13}$C NMR spectrum are less pronounced (Fig. S1).

Table 2 Selected $^1$H and $^{13}$C chemical shifts for 2a, 2b, 3a in DMSO-D$_2$ and for 2a* in CDCl$_3$.

<table>
<thead>
<tr>
<th>complex</th>
<th>solvent</th>
<th>$\delta^1$(C$_\text{m-H}$)</th>
<th>$\delta^1$(C$_\text{n-H}$)</th>
<th>$\delta^1$(C$_\text{n-Pr}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>DMSO-D$_2$</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>CDCl$_3$</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-D$_2$</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-D$_2$</td>
<td>7.16, 7.11</td>
<td>121.2, 119.3</td>
<td>125.5, 121.0</td>
</tr>
</tbody>
</table>

$\delta$ in ppm.

Loss of C$_2v$ 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 chloride source such as NH$_4$Cl or Bu$_3$NCl 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.

![Scheme 2](image)

Scheme 2 Solvolysis of complexes 2 and 3 in DMSO solution.

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–CH$_3$ singlets around 2.5 ppm. Addition of 20 equiv. H$_2$O 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 CD$_2$CN. Complete solvolysis of one Pt–Cl bond was indicated by pairs of signals for C$_{\text{m-H}}$–H, the C$_{\text{n-CH$_3$}}$ and the isopropyl CH$_3$ groups in the $^1$H NMR spectrum ($\delta_\mathrm{H} = 6.98/6.96, 2.59/2.28$ and 1.45/1.42 ppm, respectively), consistent with the pattern observed for the mono-DMSO adduct of complex 2a. The chemical shift difference of the carbene nuclei in the $^{13}$C NMR spectrum is small ($\delta_\mathrm{c} = 119.1$ and 117.9, respectively), reflecting the similar trans influences of CT and MeCN (DMSO > Cl$^-$ > MeCN). No solvolysis was detected in non-coordinating solvents such as CDCl$_3$ or CD$_2$Cl$_2$. Addition of 20 equiv. DMSO to a CDCl$_3$ solution of 2a, however, gave a 3:1 mixture of 2a·DMSO and 2a. In contrast, addition of excess Bu$_3$NCl 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)Cl$_2$].

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. AgBF$_4$, in the presence of DMSO yielded complex 2a* (Scheme 3). Its $^1$H NMR spectrum in CDCl$_3$ is essentially identical to the spectrum of 2 in DMSO and features two singlets at $\delta_\mathrm{H} = 7.12$ and 7.17 ppm for the imidazolium protons (cf. Table 2) and a single resonance at $\delta_\mathrm{H} = 3.38$ ppm, attributed to a sulfur-bound DMSO ligand. The infrared spectrum of 2a* showed a vibration band at $\nu_{\text{SO}} = 1121$ cm$^{-1}$ consistent with the $\kappa$S-bonding mode of DMSO.

The structure of 2a* was further elucidated using a combination of 1D and 2D NMR spectroscopy. Specifically, long-range $^1$H–$^{13}$C correlation spectra demonstrated that the proton at $\delta_\mathrm{H} = 7.17$ ppm and the Pt-bound carbon at $\delta_\mathrm{C} = 120.0$ belong to the same heterocycle (and likewise $\delta_\mathrm{H} = 7.12$ and $\delta_\mathrm{C} = 127.5$; Scheme 3). Furthermore, a nuclear Overhauser effect (NOE) was observed between the methyl group of the DMSO and the heterocyclic proton signal at $\delta_\mathrm{H} = 7.17$ ppm, indicating that the deshielded carbene nucleus ($\delta_\mathrm{C} = 127.5$ 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 $\kappa$S-DMSO vs. Cl$^-$. However, for 2a*.

![Scheme 3](image)

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

Exchange rate constants between free DMSO and DMSO-$\kappa$S in 2a* were determined by measuring diagonal and crosspeak intensities in magnetization transfer experiments (2D EXSY).

Values for $k_1 = 0.050(\pm 2)$ s$^{-1}$ and $k_2 = 0.063(\pm 2)$ 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 pyridilidene-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 diimidazolylidenedienes 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.\(^{18a,18b}\) 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 k5-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 groups. 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.\(^{38}\)

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 C1a–H signal (\(J_{PtH} = 15.8\) 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

### Table 3

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
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<tr>
<td>5a (X = Cl)</td>
<td>1.995(4)</td>
</tr>
<tr>
<td>5a (X = Br)</td>
<td>2.003(5)</td>
</tr>
<tr>
<td>6a (X = Cl)</td>
<td>1.986(5)</td>
</tr>
<tr>
<td>6a (X = Br)</td>
<td>1.986(6)</td>
</tr>
<tr>
<td>Pt1–Cl</td>
<td>2.3169(11)</td>
</tr>
<tr>
<td>Pt1–Br</td>
<td>2.4547(6)</td>
</tr>
<tr>
<td>Pt1–X1</td>
<td>2.4290(11)</td>
</tr>
<tr>
<td>Pt1–X3</td>
<td>2.4904(12)</td>
</tr>
<tr>
<td>Pt1–X4</td>
<td>2.5391(6)</td>
</tr>
<tr>
<td>C1–Pt1–C7</td>
<td>88.05(18)</td>
</tr>
<tr>
<td>C1–Pt1–C7</td>
<td>88.2(2)</td>
</tr>
</tbody>
</table>

Fig. 2 ORTEP plots of complex 2a’ (50% probability, hydrogen atoms, and BF\(_2\) anion omitted for clarity). Selected bond lengths (Å) and angles (°): Pt1–Cl 1.988(3), Pt1–C7 2.000(4), Pt1–Cl 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).

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

Exposure of 2a to PhICl 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 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 C1a–H (DMSO–D\(_2\)). Hence, in contrast to the PtII analogues, no spontaneous ligand substitution processes with DMSO took place. Consistently, only a single set of resonances appears in the 13C NMR spectrum and indicates formal C\(_5\) symmetry of 5a,b 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).
wingtip groups, these bond length differences are attributed to the substantial trans influence of C4-bound imidazolylidene.

Bromination of 2a or addition of PhCl₂ to 3a in CH₂Cl₂ or TFE gave mixtures of several Pt⁴⁺ 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 S₄2-type pathway involving a cationic five-coordinate intermediate.⁴⁴ Consequently, the stereochemistry of the final octahedral Pt⁴⁺ product is thermodynamically controlled.

Reaction of 2b with either Br₂ or I₂ afforded single isolomers of the mixed halide platinum(IV) complexes. The NMR chemical shifts for both species are similar to those of 5b, however, the Cₛ-H resonance show a well-resolved ¹⁹⁵Pt coupling (¹⁹⁵Jₚₜ = 14.7 Hz for the Br/Cl species and 15.7 Hz for the ICl analogue).

In addition, the mixed ICl complex features an AB system for the methylene bridge (δ₁/Iₚ = 6.22 and 5.99 ppm, ²Jₚₜ = 13.6 Hz), indicative of a restricted inversion of the metallacycle. Such hindered 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.⁴⁵ 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-D₄ solution, the initially formed mixed ICl platinum(IV) complex slowly isomerized to a mixture of four Pt⁴⁺ compounds, all with lower symmetry.⁴⁶ 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.⁴⁷ No oxidative addition products were spectroscopically observed upon treatment of 2b with alkyl halides (MeI, EtBr or BnBr).

Bromination in DMSO solution

In contrast to the bromination of 3a, the reaction of Br₂ with the solvent 3a-DMSO 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 not stable and gradually isomerized to the O-bound DMSO homologue 6a-κO-DMSO (87% conversion after 27 min at RT, ¹/L₂ ~10 min). The short lifetime 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 Ru⁴⁺, Os⁵⁻ and Pt⁶⁺ chemistry. In 6a, the isomerization is probably induced by the increased hardness of platinum upon oxidation to Pt⁴⁺.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 inverse 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 Cₛ-H protons from δ₁/Iₚ = 7.29 and 7.26 ppm upfield to 7.10 and 6.98 ppm (¹⁹⁵Jₚₜ = 15.8 Hz and 10.5 Hz, respectively) for 6a-DMSO-κO.⁴⁹ 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 δ₁/Iₚ = 3.76 ppm (¹⁹⁵Jₚₜ = 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 δ₁/Iₚ = 3.87 (¹⁹⁵Jₚₜ = 15.5 Hz) and 2.80 ppm of related platinum(IV) complexes featuring S- and O-bound DMSO, respectively.⁴⁶ To the IR spectrum a strong absorbance band at 975 cm⁻¹ was assigned to ν₃O₃ of O-bound DMSO. The ν₂O₃ band of the S-bound DMSO was superimposed by the broad band of BF₄⁻ (ν₂ = 1053 cm⁻¹),⁵⁰ 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 solvolyis requires much harsher conditions in the corresponding 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-DMSO (1:5 mixture), while 50% of 6a converted to 6a-DMSO after only 0.5 h at 100 °C. This outcome demonstrates the higher electron density in the Pt⁴⁺ complexes and also the better leaving group properties of Br⁻ compared to Cl⁻. Notably, solvolysis 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, solvolysis 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 towards 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 dibenzene dichloride (PhCl₂) 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 by Varian spectrometers operating at 400 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 aluminium 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 Mattson 440 FT-IR spectrometer.

**Düimidazolium²⁺ dichloride (1a)**

3,3'-methylenebis(1-isopropyl-2-methylimidazolium) diiodide (2.77 g, 5.36 mmol) was dissolved in MeCN (10 mL) and the mixture was stirred at room temperature for 14 h with exclusion from light. The reaction mixture was stirred at room temperature by gas jet cooling. IR spectra were recorded using a Mattson 440 FT-IR spectrometer.

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

H NMR (DMSO-D₆, 400 MHz): δ 7.15, 7.06 (2 × s, 1H, Im), 6.01 (2 × s, 1H, Im), 4.60 (br, 2H, CH₂Me), 2.73 (2 × s, 6H, C–CH₃), 1.40, 1.39 (2 × d, JHH = 7.7 Hz, 6H, CH–CH₃); ¹³C{¹H} NMR (DMSO-D₆, 100 MHz): δ 141.3, 140.8 (2 × CIm), 126.6 (C carbene), 119.5, 119.4 (2 × CIm), 119.0 (C carbene), 58.6 (NCH₂), 49.3, 49.1 (2 × CH₂Me), 22.1, 22.0 (2 × C–CH₃), 9.8, 9.6 (2 × C–CH₃).

**[Pt(dicarbene)Cl(DMSO)]Br₂ (2a)**

To a solution of 2a (0.035 g, 0.666 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, Im), 6.18 (2 × s, 1H, NCH₂), 4.44, 4.44 (2 × s, 6H, C–CH₂Me), 3.38 (2 × s, 6H, CH₀(DMSO)), 2.85 (2 × s, 6H, C–CH₃), 1.50, 1.49 (2 × d, JHH = 6.5 Hz, 6H, CH–CH₃); ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 140.7, 140.3 (2 × CIm), 127.5 (C carbene), 120.7, 120.4 (2 × CIm), 120.0 (C carbene), 59.2 (NCH₂), 50.5, 50.4 (2 × CH₂Me), 44.0 (CH₂(DMSO)), 22.7, 22.7 (2 × C–CH₃), 10.5, 10.3 (2 × C–CH₃). Anal. Caled. for C₁₅H₂₀Cl₂Br₂: C 50.60, H 4.54, N 8.17. Found: C 50.62, H 4.29, N 8.28.
The reaction mixture was stirred at room temperature for 2 h.

Pt(dicarbene)Br2 (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 CH2Cl2 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]-.

1H NMR (DMSO- D6, 500 MHz): \( \delta \) 7.16, 7.12 (2 × s, 1H, H2a), 6.02 (s, 2H, H2b).

13C NMR (DMSO- D6, 100 MHz): \( \delta \) 176.8, 176.3, 139.4 (C\text{Im}), 128.4 (C\text{Me}), 55.8 (NCH3), 49.3, 49.1 (2 × CHMe), 22.1, 22.0 (2 × C–CH3), 9.8, 9.7 (2 × CH–CH3).

Pt(diimidazol-2-ylidene)Cl2 (4)

A mixture of PtCl2 (0.13 g, 0.49 mmol), NaClO (0.28 g, 4.8 mmol), NaN+OAc (0.084 g, 1.0 mmol) and 3,3’-disopropyl-1,1-methylenediimidazolium 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, CH2Cl2 (20 mL) and Et2O (80 mL) were added to give a precipitate, which was collected and washed repeatedly by adding CH2Cl2 (20 mL) followed by precipitation with Et2O (80 mL).

After drying in vacuo, complex 4 was obtained as a white powder (0.20 g, 82%), which was recrystallized from DMSO/Et2O solution with Et2O. 1H NMR (DMSO- D6, 500 MHz): \( \delta \) 7.53, 7.51 (2 × s, 2H, H2a), 6.06, 5.93 (2 × d, \( J_{HH} \) = 13.0 Hz, 2H, H2b), 2.87, 2.85, 2.83, 2.80, 2.78 (et, 4 × H, C–CH3), 2.12 (2 × s, \( J_{HH} \) = 4.4 Hz, 2H, CH2), 1.45, 1.41 (2 × d, \( J_{HH} \) = 6.7 Hz, 2H, CH2), 1.21 (2 × s, \( J_{HH} \) = 6.7 Hz, 2H, CH–CH3).

Pt(dicarbene)Cl (5a)

Iodobenzene dichloride (0.067 g, 0.24 mmol) was added to a stirring suspension of 2a (0.098 g, 0.16 mmol) in CH2Cl2 (15 mL). The reaction mixture was stirred at room temperature for 20 h. The solvent was removed under reduced pressure and the residue was washed with methanol, Et2O and dried in vacuo. Yield: 0.085 g (77%). Recrystallization from DMSO/THF gave an analytically pure sample. MS (ES+): m/z 646, [M+Cl]-.

1H NMR (DMSO- D6, 400 MHz): \( \delta \) 7.12 (s, 2H, H2a), 6.23 (s, 2H, NCH3), 4.14 (q, \( J_{HH} \) = 7.5 Hz, 4H, CH2), 2.76 (s, 6H, C–CH3), 1.78–1.59 (m, 4H, CH2), 1.38–1.22 (m, 12H, CH2), 0.87 (t, \( J_{HH} \) = 6.7 Hz, 6H, CH2), 13.8 (C\text{Im}), 9.8 (C–CH2).


Pt(dicarbene)Cl4 (5b)

Iodobenzene dichloride (0.067 g, 0.24 mmol) was added to a stirring suspension of 2a (0.098 g, 0.16 mmol) in CH2Cl2 (15 mL). The reaction mixture was stirred at room temperature for 20 h. The solvent was removed under reduced pressure and the residue was washed with methanol, Et2O and dried in vacuo. Yield: 0.085 g (77%). Recrystallization from DMSO/THF gave an analytically pure sample. MS (ES+): m/z 646, [M+Cl]-.

1H NMR (DMSO- D6, 400 MHz): \( \delta \) 7.12 (s, 2H, H2a), 6.23 (s, 2H, NCH3), 4.14 (q, \( J_{HH} \) = 7.5 Hz, 4H, CH2), 2.76 (s, 6H, C–CH3), 1.78–1.59 (m, 4H, CH2), 1.38–1.22 (m, 12H, CH2), 0.87 (t, \( J_{HH} \) = 6.7 Hz, 6H, CH2), 13.8 (C\text{Im}), 9.8 (C–CH2).


Pt(dicarbene)Br2 (6a)

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 Et2O and dried in vacuo. Yield: 0.023 g (100%). Recrystallization from DMSO/CH2Cl2/Et2O gave an analytically pure sample. X-ray-quality crystals were obtained by layering a DMSO/MeCN solution with Et2O. 1H NMR (DMSO- D6, 500 MHz): \( \delta \) 7.18 (s, \( J_{HH} \) = 15.8 Hz, 2H, H2a), 6.32 (s, 2H, NCH3), 4.69 (sept, \( J_{HH} \) = 6.6 Hz, 2H, CH2), 2.83 (s, 6H, C–CH3), 1.43 (d, \( J_{HH} \) = 6.6 Hz, 6H, C–CH3), 13.8 (C\text{Im})

NMR (DMSO- D6, 100 MHz): \( \delta \) 141.4 (C\text{Im}), 120.2 (C\text{Im}), 104.8 (C\text{Me}), 58.2 (NCH3), 49.8 (CH2Me), 22.0 (C–CH3), 9.9 (CH–CH3).

Anal. Calcd. for C33H22N2O2: C 41.05, H 5.61, N 6.41. Found: C 41.20, H 2.89, N 6.41.

Pt(dicarbene)Br3 (5d)

Bromine (0.013 g, 0.080 mmol) was added to a solution of 3a (0.010 g, 0.016 mmol) in DMSO– D6 (0.65 mL). The reaction mixture was kept at room temperature for 1 h and analyzed by NMR (Conversion 100%). 1H NMR (DMSO- D6, 500 MHz): \( \delta \) 7.10, 6.98 (2 × s, 1H, H2a), 6.25 (s, 2H, NCH3), 4.72, 4.70 (2 × s, \( J_{HH} \) = 6.7 Hz, 1H, CH2), 2.85 (s, 8H, C–CH3), 1.45, 1.42 (2 × d, \( J_{HH} \) = 6.7 Hz, 6H, CH–CH3), 13.8 (C\text{Im})

NMR (DMSO- D6, 100 MHz): \( \delta \) 143.1, 142.4 (2 × C\text{Im}), 121.1, 116.1 (2 × C\text{Im}), 106.3, 86.5 (2 × C\text{Me}), 58.5 (NCH3), 50.3, 50.2 (2 × CH2Me), 22.0 (C–CH3), 10.3, 10.7 (2 × CH–CH3).

Pt(dicarbene)Br2Cl

Bromine (0.189 g, 1.18 mmol) was added dropwise to a stirring suspension of 2b (0.080 g, 0.13 mmol) in CH2Cl2 (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%).

1 H NMR (DMSO- D₆, 400 MHz): δ 7.10 (s, 2JHH = 14.7 Hz, 2H, H₂a), 6.23 (s, 2H, NCH₃), 4.14 (q, 2JHH = 7.3 Hz, 4H, CH₂), 2.80 (s, 6H, CCH₃), 1.75–1.60 (m, 4H, CH₂), 1.35–1.15 (m, 12H, CH₃), 0.87 (t, 2JHH = 6.8 Hz, 6H, CH₃).

31C (1453 Å) used to calculate the potential solvent accessible volume (1453 Å³).

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Notes and references

† Electronic Supplementary Information (ESI) available: NMR plots, kinetic details of linkage isomerism in 6b–DMSO, and crystallographic details for complexes 2a, 2a', 3a, 4, 5a, and 6a (CCDC No. 904838–904843). See DOI: 10.1039/b000000x/


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(2).

A search in the Cambridge Crystallographic Database revealed 13 structures, containing a cationic four-coordinate Pt(II) center with mutually cis-coordinated DS-DMSO and Cl(2):


Formally, the platinated heterocyclic carbon should be labeled C5. For the sake of consistency, the nomenclature established in previous work will be used (see references cited in ref 9) and N is bearing the modular wingtip group (Me, Hex) and C4 is bound to the platinum center.


(a) Around 10% of the mixture is a symmetric compound with chemical shifts very similar to 6a (δ_C = 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 SMe_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 SMe_2 group due to the large J_{PtH} coupling constant and also because of the downfield chemical shift of the methyl group in the ^13C NMR spectrum (δ_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. Sansoress and A. D. Ryabov, J. Am. Chem. Soc., 2000, 122, 5189.

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

for ToC entry only

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.