Electronic Supporting Information

Platinum(II) and platinum(IV) complexes stabilized by C4-bound dicarbenes

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Figure S1. Aromatic region of \(^{1}H-^{13}C\) HMBC spectrum of 3 DMSO in DMSO-D_6.
Figure S2. Region of $^1$H NMR spectra of 2a recorded in a range of solvents depicting the difference in chemical shifts and multiplicity of the signals of imidazolium and methylene protons.

Figure S3. Region of $^1$H NMR spectra recorded in DMSO-$D_6$ for mixtures obtained from addition of Br$_2$ to 2a and PhICl$_2$ to 3a.
Figure S4. Time-dependent consumption of the initial product from 2b·DMSO and Br₂ in DMSO, 6b·κS-DMSO, during the isomerization to the O-bound isomer; the inset shows a first order fit.
<table>
<thead>
<tr>
<th></th>
<th>2a</th>
<th>2a'</th>
<th>3a</th>
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<td>904841</td>
<td>904840</td>
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<td>Crystal size /mm(^{\text{-1}})</td>
<td>0.40 × 0.15 × 0.10</td>
<td>0.11 × 0.07 × 0.04</td>
<td>0.16 × 0.15 × 0.10</td>
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<td>Empirical formula</td>
<td>C(<em>{15})H(</em>{24})Cl(_2)N(_4)Pt × 1.5 C(_2)H(_6)OS</td>
<td>C(<em>{17})H(</em>{30})BN(_4)OF(_4)SCl(_2)Pt</td>
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<td>Fw</td>
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<td>815.94</td>
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<td>T /K</td>
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<td>100(2)</td>
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<td>Monoclinic</td>
<td>Orthorhombic</td>
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<td>P2(_1)/c (#14)</td>
<td>Pbca (#61)</td>
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<td>γ /°</td>
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<td>4</td>
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<td>Analytical</td>
<td>Semi-empirical</td>
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<td>−1.301, 0.998</td>
<td>−0.453, 1.223</td>
<td>−0.683, 1.246</td>
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\(^{a}\) R\(_1\) = Σ||F\(_{\text{O}}\)||−||F\(_{\text{C}}\)||/Σ||F\(_{\text{C}}\||; \ wR\(_2\) = \left( Σ(w(F\(_{\text{O}}^2}−F\(_{\text{C}}^2)^2)/Σ(w(F\(_{\text{O}}^2)^{1/2}\right)
Table S2. Crystallographic data for complexes 4, 5a, and 6a.

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<td>0.28 × 0.18 × 0.17</td>
<td>0.26 × 0.18 × 0.17</td>
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<tr>
<td>Empirical formula</td>
<td>C$<em>{13}$H$</em>{20}$Cl$_2$N$_4$Pt × C$_2$H$_6$OS</td>
<td>C$<em>{15}$H$</em>{24}$N$_4$Cl$_4$Pt × C$_2$H$_6$OS × C$_2$H$_3$N</td>
<td>C$<em>{15}$H$</em>{24}$N$_4$Br$_4$Pt × C$_2$H$_3$N</td>
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<td>Crystal system</td>
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<td>Monoclinic</td>
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<td>a /Å</td>
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<td>b /Å</td>
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<td>R$_{int}$</td>
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<td>Transmission range</td>
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<td>No. parameters, restraints</td>
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<td>R$_1$, wR$_2$, I &gt; 2σ(I) $^a$</td>
<td>0.0326, 0.0706</td>
<td>0.0252, 0.0593</td>
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<td>R$_1$, wR$_2$, all data</td>
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<td>0.0270, 0.0604</td>
<td>0.0338, 0.0838</td>
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<tr>
<td>Largest diff. hole, peak /e Å$^{-3}$</td>
<td>–1.307, 3.261</td>
<td>–0.820, 1.021</td>
<td>–1.112, 1.453</td>
</tr>
</tbody>
</table>

$^a$ R$_1$ = Σ|F$_O$|–|F$_C$|/Σ|F$_O$|; wR$_2$ = [Σw(F$_O^2$−F$_C^2$)/Σ(w(F$_O^2$))]$^{1/2}$