Amino acid-derived \( N \)-Heterocyclic carbene palladium complexes for aqueous phase Suzuki-Miyaura couplings

**Supplementary material**

*New Journal of Chemistry*

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1) Kinetic Line Plot

2) NMR Spectra

1. \(^1\)H NMR spectrum of 1a ((1-ethanoyl-imidazol-1-ium) acetate)
2. \(^13\)C NMR spectrum of 1a ((1-ethanoyl-imidazol-1-ium) acetate)
3. \(^1\)H NMR spectrum of 1b (3-(1-propanoyl-imidazol-1-ium) propanoate)
4. \(^13\)C NMR spectrum of 1b (3-(1-propanoyl-imidazol-1-ium) propanoate)
5. \(^1\)H NMR spectrum of 1c (2-(1-((benzyl)carboxymethyl-imidazol-1-ium)-3 phenylpropanoate)
6. \(^13\)C NMR spectrum of 1c (2-(1-((benzyl)carboxymethyl-imidazol-1-ium)-3 phenylpropanoate)
7. \(^1\)H NMR spectrum of 2a (1,3-bis(2-ethoxy-2-oxoethyl)-imidazolium chloride)
8. \(^13\)C NMR spectrum of 2a (1,3-bis(2-ethoxy-2-oxoethyl)-imidazolium chloride)
9. \(^1\)H NMR spectrum of 2b (1,3-bis(2-ethoxy-2-oxopropyl)-imidazolium chloride)
10. \(^13\)C NMR spectrum of 2b (1,3-bis(2-ethoxy-2-oxopropyl)-imidazolium chloride)
11. \(^1\)H NMR spectrum of 2c (1,3-bis(2-ethoxy-2-oxo(1-((benzyl)ethyl)-imidazolium chloride)
12. \(^13\)C NMR spectrum of 2c (1,3-bis(2-ethoxy-2-oxo(1-((benzyl)ethyl)-imidazolium chloride)
13. \(^1\)H NMR spectrum of 3a (trans-chlorido-(1,3-bis(2-ethoxy-2-oxoethyl)-imidazol-2-ylidine)silver(I))
14. \(^13\)C NMR spectrum of 3a (trans-chlorido-(1,3-bis(2-ethoxy-2-oxoethyl)-imidazol-2-ylidine)silver(I))
15. $^1$H NMR spectrum of $4a$ (*trans*-dichlorido-1,3-bis(2-ethoxy-2-oxoethyl)-imidazol-2-ylidine)palladium(II))
16. $^{13}$C NMR spectrum of $4a$ (*trans*-dichlorido-1,3-bis(2-ethoxy-2-oxoethyl)-imidazol-2-ylidine)palladium(II))
17. $^1$H NMR spectrum of $4b$ (*trans*-dichlorido-1,3-bis(2-ethoxy-2-oxopropyl)-imidazol-2-ylidine)palladium(II))
18. $^{13}$C NMR spectrum of $4b$ (*trans*-dichlorido-1,3-bis(2-ethoxy-2-oxopropyl)-imidazol-2-ylidine)palladium(II))
19. $^1$H NMR spectrum of $5a$ (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxoethyl)-imidazol-2-ylidine)(pyridine)palladium(II))
20. $^{13}$C NMR spectrum of $5a$ (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxoethyl)-imidazol-2-ylidine)(pyridine)palladium(II))
21. $^1$H NMR spectrum of $5b$ (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxopropyl)-imidazol-2-ylidine)(pyridine)palladium(II))
22. $^{13}$C NMR spectrum of $5b$ (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxopropyl)-imidazol-2-ylidine)(pyridine)palladium(II))
23. $^1$H NMR spectrum of $5c$ (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxo(1-((benzyl)ethyl))-imidazol-2-ylidine)(pyridine)palladium(II))
24. $^{13}$C NMR spectrum of $5c$ (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxo(1-((benzyl)ethyl))-imidazol-2-ylidine)(pyridine)palladium(II))

3) *Single crystal X-ray structure determinations of 4a, 4b, 5a and 5b*
Graph 1 Line plot of the aqueous-phase Suzuki-Miyaura coupling of 4-bromoacetophenone with phenylboronic acid using precatalyst 5b. The pre-dissolved catalyst reached 100% yield in 50 minutes, whereas the in situ catalyst does not reach 100% yield until after 1 hour.

Reaction conditions: bromoacetophenone (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.0 mmol), 5b (1 mol%), TBAB (1.0 mmol) in pure H₂O at 60 °C. Yields determined by NMR using trimethoxybenzene as an internal standard.
1. $^1$H NMR spectrum of 1a

NMR Spectra
2. $^{13}$C NMR spectrum of 1a
3. $^1$H NMR spectrum of 1b
4. $^{13}$C NMR spectrum of 1b
5. $^1$H NMR spectrum of 1c
6. $^{13}$C NMR spectrum of 1c
7. $^1$H NMR spectrum of 2a
8. $^{13}$C NMR spectrum of 2a
9. $^1$H NMR spectrum of 2b
10. $^{13}$C NMR spectrum of 2b
11. $^1$H NMR spectrum of 2c
12. $^{13}$C NMR spectrum of 2c
13. $^1$H NMR spectrum of 3a
14. $^{13}$C NMR spectrum of 3a
15. $^1$H NMR spectrum of 4a
16. $^{13}$C NMR spectrum of 4a
17. $^1$H NMR spectrum of 4b
18. $^{13}$C NMR spectrum of 4b
19. $^1$H NMR spectrum of 5a
20. $^{13}$C NMR spectrum of 5a
21. $^1$H NMR spectrum of 5b
22. $^{13}$C NMR spectrum of 5b
23. $^{13}$C NMR spectrum of 5b
24. $^{13}$C NMR spectrum of 5c
Single crystal X-ray structure determinations of 4a, 4b, 5a and 5b

The crystals were mounted on a glass fibre. Intensity data were collected at 210 K using a STOE Imaging Plate Diffraction System IPDS-2 with graphite monochromatized MoKα radiation (λ = 0.71073 Å) at 50 kV and 40 mA. 4a: 360 frames, Δω=1°, 1 min; 4b: 180 frames, Δω=1°, 1 min; 5a: 180 frames (then decay), Δω=1°, 4 min; 5b: 360 frames, Δω=1°, 0.7 min. The data were corrected for Lorentz and polarisation effects using the program X-Area1 (Stoe, 2004). Numerical absorption corrections was applied using optimized shape.[1] The structures were solved by direct methods (SHELXS-2013/1), and refined with full-matrix least-squares on F² using the program SHELXL-2014/72b (Sheldrick, 2014). [2,3] Non-hydrogen atoms were refined with anisotropic temperature factors. In 4a, C11 is disordered over two sites with occupancies of 0.75/0.25; C22 is disordered over two sides with occupancies of 0.6788/0.3213; O12; C32 and C33 were refined as disordered over two sides (occupancies 0.5627/0.4373); O15, C43 and C44 were refined as disordered over two sides (occupancies 0.5627/0.4373); The Hirshfeld test violations (Alert_B in PLATON) are caused by vibrations of the ethyl substituents. The maximal crystal size of 5a was 1.3 mm, but it was not possible to cut the crystal into pieces without bursting. All hydrogen atoms connected to carbon atoms were calculated in their expected positions and refined as riding with C—H = 0.97 Å (CH3), 0.98 Å (CH2), 0.94 Å (Carom) and with Uiso(H) = 1.2Ueq(C) with the exception of methyl hydrogen atoms, which were refined with Uiso(H) = 1.5Ueq(C). The hydrogen atoms within the imidazole rings were located from the difference Fourier map and refined with Uiso(H) = 1.2Ueq(C). For the visualization the program DIAMOND3 (Brandenburg, 2015) was used.[4]

For further details of the refinement – see crystallographic information files (deposited cif).

CCDC-1438609 (4a), 1438610 (4b), 1438611 (5a) and 1438612 (5b) 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.
Table S1  Crystal Data, Details of Intensity Measurements, and Structure Refinement for 4a and 4b.

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<th>4b</th>
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<td>C_{26}H_{40}Cl_{2}N_{4}O_{8}Pd</td>
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<td>monoclinic</td>
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<td>C2/c (no. 15)</td>
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<tr>
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<td>10.3920(5)</td>
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<tr>
<td>b / Å</td>
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<td>12.0677(7)</td>
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<tr>
<td>c / Å</td>
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<td>98.377(3)</td>
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<td>210(2)</td>
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<td>MoKα</td>
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<tr>
<td>R(_1) / wR(_2) (all data)</td>
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<td>Goodness of fit on F(^{2})</td>
<td>1.093</td>
<td>1.052</td>
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Fig. S1 Molecular structures of 4a with the atomic numbering scheme. Hydrogen atoms were omitted for clarity.
Table S2  Selected bond lengths [Å] for 4a.

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<th>Bond</th>
<th>Length [Å]</th>
<th>Bond</th>
<th>Length [Å]</th>
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Table S3  Selected bond angles [°] for 4a.
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<th>Bond</th>
<th>Angle (°)</th>
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<td>N2—C1—N1</td>
<td>104.0 (2)</td>
<td>O13—C38—O14</td>
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<tr>
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<td>C34—Pd2—Cl3</td>
<td>91.40 (8)</td>
<td>Cl4—Pd2—Cl3</td>
<td>178.95 (3)</td>
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**Table S4** Selected torsion angles [°] for 4a.
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<th>Bond</th>
<th>Angle (deg)</th>
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<tbody>
<tr>
<td>N7—C37—C38—O14</td>
<td>163.7 (3)</td>
<td>Pd2—C34—N7—C37</td>
<td>2.8 (4)</td>
</tr>
<tr>
<td>N8—C41—C42—O15</td>
<td>39.1 (11)</td>
<td>C36—C35—N7—C34</td>
<td>1.0 (4)</td>
</tr>
<tr>
<td>N8—C41—C42—O16</td>
<td>-163.3 (4)</td>
<td>C36—C35—N7—C37</td>
<td>177.3 (3)</td>
</tr>
<tr>
<td>N2—C1—N1—C2</td>
<td>-0.1 (3)</td>
<td>C38—C37—N7—C34</td>
<td>103.6 (3)</td>
</tr>
<tr>
<td>Pd1—C1—N1—C2</td>
<td>-176.3 (2)</td>
<td>C38—C37—N7—C35</td>
<td>-72.3 (4)</td>
</tr>
<tr>
<td>N2—C1—N1—C4</td>
<td>-175.5 (3)</td>
<td>N7—C34—N8—C36</td>
<td>-0.6 (4)</td>
</tr>
<tr>
<td>Pd1—C1—N1—C4</td>
<td>8.3 (4)</td>
<td>Pd2—C34—N8—C36</td>
<td>-179.9 (2)</td>
</tr>
<tr>
<td>C3—C2—N1—C1</td>
<td>0.1 (4)</td>
<td>N7—C34—N8—C41</td>
<td>-178.8 (3)</td>
</tr>
<tr>
<td>C3—C2—N1—C4</td>
<td>175.5 (3)</td>
<td>Pd2—C34—N8—C41</td>
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<td>179.4 (3)</td>
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<td>Pd1—C1—N2—C3</td>
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<td>N1—C1—N2—C8</td>
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<td>O1—C5—O2—C6</td>
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<tr>
<td>Pd1—C1—N2—C8</td>
<td>-1.4 (4)</td>
<td>C4—C5—O2—C6</td>
<td>-177.8 (3)</td>
</tr>
<tr>
<td>C2—C3—N2—C1</td>
<td>0.0 (3)</td>
<td>C7—C6—O2—C5</td>
<td>-81.2 (5)</td>
</tr>
<tr>
<td>C2—C3—N2—C8</td>
<td>177.5 (3)</td>
<td>O3—C9—O4—C10</td>
<td>2.5 (5)</td>
</tr>
<tr>
<td>C9—C8—N2—C1</td>
<td>102.6 (3)</td>
<td>C8—C9—O4—C10</td>
<td>-176.2 (3)</td>
</tr>
<tr>
<td>C9—C8—N2—C3</td>
<td>-74.6 (4)</td>
<td>C11—C10—O4—C9</td>
<td>-87.0 (4)</td>
</tr>
<tr>
<td>N4—C12—N3—C13</td>
<td>0.2 (3)</td>
<td>O5—C16—O6—C17</td>
<td>4.4 (5)</td>
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<tr>
<td>Pd1—C12—N3—C13</td>
<td>-175.2 (2)</td>
<td>C15—C16—O6—C17</td>
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<tr>
<td>N4—C12—N3—C15</td>
<td>-174.2 (2)</td>
<td>C18—C17—O6—C16</td>
<td>-174.7 (4)</td>
</tr>
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<td>Pd1—C12—N3—C15</td>
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<td>O7—C20—O8—C21</td>
<td>-0.8 (5)</td>
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<td>C19—C20—O8—C21</td>
<td>−178.8 (3)</td>
</tr>
<tr>
<td>C14—C13—N3—C15</td>
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<td>C22—C21—O8—C20</td>
<td>−74.7 (5)</td>
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<tr>
<td>C16—C15—N3—C12</td>
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<td>O9—C27—O10—C28</td>
<td>−6.3 (6)</td>
</tr>
<tr>
<td>C16—C15—N3—C13</td>
<td>−75.4 (4)</td>
<td>C26—C27—O10—C28</td>
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<tr>
<td>N3—C12—N4—C14</td>
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<td>C29—C28—O10—C27</td>
<td>136.8 (5)</td>
</tr>
<tr>
<td>Pd1—C12—N4—C14</td>
<td>174.6 (2)</td>
<td>O11—C31—O12—C32</td>
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<tr>
<td>N3—C12—N4—C19</td>
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<td>C30—C31—O12—C32</td>
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<tr>
<td>Pd1—C12—N4—C19</td>
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<td>O13—C38—O14—C39</td>
<td>−8.5 (5)</td>
</tr>
<tr>
<td>C13—C14—N4—C12</td>
<td>0.8 (3)</td>
<td>C37—C38—O14—C39</td>
<td>171.6 (3)</td>
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<tr>
<td>C13—C14—N4—C19</td>
<td>177.9 (3)</td>
<td>C40—C39—O14—C38</td>
<td>165.7 (4)</td>
</tr>
<tr>
<td>C20—C19—N4—C12</td>
<td>108.2 (3)</td>
<td>O15—C42—O16—C43</td>
<td>−0.4 (15)</td>
</tr>
<tr>
<td>C20—C19—N4—C14</td>
<td>−68.6 (3)</td>
<td>C41—C42—O16—C43</td>
<td>−160.0 (7)</td>
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<tr>
<td>N6—C23—N5—C24</td>
<td>1.2 (3)</td>
<td>C44—C43—O16—C42</td>
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<td>Pd2—C23—N5—C24</td>
<td>−175.9 (2)</td>
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Table S5: Selected dihedral angles [°] for 4a.

| Pd/Cl$_2$/C$_2$ // N1/N2/C1-C3 | 68.60(7) | Pd/Cl$_2$/C$_2$ // N3/N4/C12-C14 | 69.12(7) |
| Pd/Cl$_2$/C$_2$ // N7/N8/C34-C36 | 62.29(9) | Pd/Cl$_2$/C$_2$ // N5/N6/C23-C25 | 69.05(7) |
**Fig. S2** Molecular structure of 4b with the atomic numbering scheme. Hydrogen atoms were omitted for clarity.

**Table S6** Selected bond lengths [Å] for 4b.

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<thead>
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<th>Bond</th>
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<td>C1—N1</td>
<td>1.352 (2)</td>
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<tr>
<td>C1—Pd1</td>
<td>2.029 (3)</td>
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<tr>
<td>C2—C2'</td>
<td>1.336 (5)</td>
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<td>C2—N1</td>
<td>1.380 (3)</td>
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<tr>
<td>C3—N1</td>
<td>1.461 (3)</td>
</tr>
<tr>
<td>C3—C4</td>
<td>1.511 (3)</td>
</tr>
<tr>
<td>C4—C5</td>
<td>1.500 (3)</td>
</tr>
<tr>
<td>C8—N2'</td>
<td>1.345 (2)</td>
</tr>
<tr>
<td>C8—Pd1</td>
<td>2.021 (3)</td>
</tr>
<tr>
<td>C9—C9'</td>
<td>1.333 (5)</td>
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<td>C9—N2</td>
<td>1.382 (3)</td>
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<td>C10—N2</td>
<td>1.460 (3)</td>
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<tr>
<td>C10—C11</td>
<td>1.511 (3)</td>
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<tr>
<td>C11—C12</td>
<td>1.488 (3)</td>
</tr>
<tr>
<td>C12—O3</td>
<td>1.158 (3)</td>
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Table S7  Selected bond angles [°] for 4b.

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<td>1.311 (3)</td>
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<td>C6—O2</td>
<td>1.458 (3)</td>
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<tr>
<td>C6—C7</td>
<td>1.492 (4)</td>
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<td>C8—N2</td>
<td>1.345 (2)</td>
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<td>C12—O4</td>
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<td>C13—C14</td>
<td>1.455 (5)</td>
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<td>C13—O4</td>
<td>1.446 (3)</td>
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<td>C6—O2</td>
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<td>C13—O4</td>
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<td>C6—C7</td>
<td>1.492 (4)</td>
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<tr>
<td>Cl1—Pd1</td>
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<td>Pd1—Cl1i</td>
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Symmetry code: ‘–x, y, -z-0.5

Table S8  Selected torsion angles [°] for 4b.

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<th>Torsion Angle</th>
<th>Torsion Angle Value (°)</th>
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</tr>
<tr>
<td>N1—C1—Pd1</td>
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</tr>
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<td>C2’—C2—N1</td>
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<td>N1—C3—C4</td>
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<td>C5—C4—C3</td>
<td>111.43 (18)</td>
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<td>O1—C5—O2</td>
<td>123.4 (2)</td>
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<tr>
<td>O1—C5—C4</td>
<td>123.8 (2)</td>
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<td>O2—C5—C4</td>
<td>112.7 (2)</td>
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<td>N2—C8—N2’</td>
<td>104.7 (2)</td>
</tr>
<tr>
<td>N2—C8—Pd1</td>
<td>127.66 (12)</td>
</tr>
<tr>
<td>N2’—C8—Pd1</td>
<td>127.66 (12)</td>
</tr>
<tr>
<td>C9’—C9—N2</td>
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</tr>
<tr>
<td>N2—C10—C11</td>
<td>110.40 (19)</td>
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<tr>
<td>C12—C11—C10</td>
<td>113.6 (2)</td>
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<tr>
<td>C3—C4—C5</td>
<td>-172.8 (2)</td>
</tr>
<tr>
<td>C3—C4—C5—O1</td>
<td>21.4 (4)</td>
</tr>
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<td>N2’—C8—N2—C9</td>
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</tr>
<tr>
<td>N2’—C8—N2—C10</td>
<td>175.5 (2)</td>
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<tr>
<td>Bond/Angle</td>
<td>Value (deg)</td>
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<td>-----------</td>
<td>-------------</td>
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<tr>
<td>N2—C10—C11—C12</td>
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<td>C10—C11—C12—O3</td>
<td>-14.2 (5)</td>
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<tr>
<td>C10—C11—C12—O4</td>
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<td>N1′—C1—N1—C2</td>
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<tr>
<td>Pd1—C1—N1—C3</td>
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<tr>
<td>C2′—C2—N1—C1</td>
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<tr>
<td>C2′—C2—N1—C3</td>
<td>-177.6 (2)</td>
</tr>
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<td>90.2 (3)</td>
</tr>
<tr>
<td>Pd1—C8—N2—C10</td>
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</tr>
<tr>
<td>C9′—C9—N2—C8</td>
<td>-0.8 (3)</td>
</tr>
<tr>
<td>C9′—C9—N2—C10</td>
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</tr>
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<td>O1—C5—O2—C6</td>
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<tr>
<td>C4—C5—O2—C6</td>
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<tr>
<td>C7—C6—O2—C5</td>
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<tr>
<td>O3—C12—O4—C13</td>
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<tr>
<td>C11—C12—O4—C13</td>
<td>177.2 (3)</td>
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<td>C14—C13—O4—C12</td>
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Table S9 Selected dihedral angles [°] for 4b.
Table S10  Crystal Data, Details of Intensity Measurements, and Structure Refinement for 5a and 5b.

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<th>5b</th>
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<td>C₁₈H₂₅Cl₂N₃O₄Pd</td>
</tr>
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<td>Molecular weight / g mol⁻¹</td>
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<td>524.71</td>
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<td>Crystal system</td>
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<td>Space group</td>
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<td>P -1 (no. 15)</td>
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<tr>
<td>b / Å</td>
<td>23.0938(8)</td>
<td>9.7104(7)</td>
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<tr>
<td>c / Å</td>
<td>9.0944(6)</td>
<td>12.2951(10)</td>
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<td>210(2)</td>
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<td>Radiation type</td>
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<td>μ / mm⁻¹</td>
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<td>Independent reflections</td>
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<td>0.0194 / 0.0525</td>
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<tr>
<td>R₁ / wR² (all data)</td>
<td>0.0327 / 0.0613</td>
<td>0.0213 / 0.0533</td>
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<tr>
<td>Goodness of fit on F²</td>
<td>1.015</td>
<td>1.059</td>
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**Fig. S3** Molecular structure of 5a with the atomic numbering scheme. Hydrogen atoms were omitted for clarity.

**Table S11** Selected bond lengths [Å] for 5a.

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<th>Bond</th>
<th>Length [Å]</th>
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<th>Length [Å]</th>
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<td>C10—O4</td>
<td>1.453 (3)</td>
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<td>C1—Pd1</td>
<td>1.969 (2)</td>
<td>C10—C11</td>
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<td>1.339 (4)</td>
<td>C12—N3</td>
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<td>C2—N1</td>
<td>1.387 (3)</td>
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<td>C3—N2</td>
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<td>1.510 (3)</td>
<td>C15—C16</td>
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### Table S12
Selected bond angles [°] for 5a.

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<th>Angle (°)</th>
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<td>1.461 (3)</td>
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<td>1.484 (4)</td>
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<td>C8—N2</td>
<td>1.450 (3)</td>
<td>Cl3—C17</td>
<td>1.734 (4)</td>
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<td>1.510 (3)</td>
<td>Cl4—C17</td>
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<tr>
<td>C9—O3</td>
<td>1.200 (3)</td>
<td>Cl5—C17</td>
<td>1.756 (4)</td>
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<table>
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<tr>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Angle (°)</th>
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<td>C1—N2—C3</td>
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</tr>
<tr>
<td>N1—C1—Pd1</td>
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<td>C1—N2—C8</td>
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</tr>
<tr>
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<td>C16—N3—C12</td>
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<td>C2—C3—N2</td>
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<td>C16—N3—Pd1</td>
<td>121.76 (17)</td>
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</tr>
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<td>N3—Pd1—Cl1</td>
<td>90.49 (6)</td>
</tr>
<tr>
<td>N3—C12—C13</td>
<td>122.3 (2)</td>
<td>Cl2—Pd1—Cl1</td>
<td>177.58 (3)</td>
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<tr>
<td>N3—C16—C15</td>
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<td>Cl3—C17—Cl5</td>
<td>110.7 (2)</td>
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Table S13 Selected torsion angles [°] for 5a.

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<td>N2—C8—C9—O3</td>
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<tr>
<td>N2—C8—C9—O4</td>
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<td>N2—C1—N1—C4</td>
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<td>Pd1—C1—N1—C4</td>
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<td>C3—C2—N1—C4</td>
<td>-174.2 (2)</td>
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<td>C5—C4—N1—C1</td>
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<td>C5—C4—N1—C2</td>
<td>79.7 (3)</td>
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<tr>
<td>N1—C1—N2—C3</td>
<td>0.2 (2)</td>
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<td>Pd1—C1—N2—C3</td>
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<td>C11—C10—O4—C9</td>
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Table S14 Selected dihedral angles [°] for 5a.

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<th>Dihedral Angle</th>
<th>Torsion Angle (°)</th>
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<td>Pd/Cl2/C2 // N1/N2/C1-C3</td>
<td>75.46(5)</td>
</tr>
<tr>
<td>Pd/Cl2/C2 // N3/C12-C16</td>
<td>47.79(7)</td>
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</table>
Fig. S4 Molecular structure of 5b with the atomic numbering scheme. Hydrogen atoms were omitted for clarity.
### Table S15  Selected bond lengths [Å] for 5b.

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<td>C11—O3</td>
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<tr>
<td>C1—N2</td>
<td>1.348 (2)</td>
<td>C11—O4</td>
<td>1.323 (3)</td>
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<tr>
<td>C1—Pd1</td>
<td>1.9578 (17)</td>
<td>C12—O4</td>
<td>1.466 (3)</td>
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<tr>
<td>C2—C3</td>
<td>1.343 (3)</td>
<td>C14—N3</td>
<td>1.330 (3)</td>
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<tr>
<td>C2—N1</td>
<td>1.387 (2)</td>
<td>C18—N3</td>
<td>1.328 (3)</td>
</tr>
<tr>
<td>C3—N2</td>
<td>1.382 (2)</td>
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<td>2.2988 (5)</td>
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<td>C4—N1</td>
<td>1.465 (2)</td>
<td>Cl2—Pd1</td>
<td>2.3167 (5)</td>
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<td>C5—C6</td>
<td>1.505 (2)</td>
<td>N3—Pd1</td>
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<td>C9—N2</td>
<td>1.465 (2)</td>
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<td>1.335 (2)</td>
<td>C10—C11</td>
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<td>C7—O2</td>
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### Table S16  Selected bond angles [°] for 5b.

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<tr>
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<td>C1—N1—C4</td>
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<tr>
<td>N2—C1—Pd1</td>
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<td>107.02 (16)</td>
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<tr>
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<td>C18—N3—Pd1</td>
<td>120.12 (15)</td>
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</table>
### Table S17: Selected torsion angles [°] for 5b.

<table>
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<th>Angle</th>
<th>Bond</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
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<td>O1—C6—C5</td>
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<td>C14—N3—Pd1</td>
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<td>177.50 (6)</td>
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<td>O3—C11—O4</td>
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<tr>
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<td>C1—Pd1—Cl2</td>
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<td>N3—C14—C15</td>
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<td>N3—Pd1—Cl2</td>
<td>91.81 (5)</td>
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<tr>
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<td>122.5 (2)</td>
<td>Cl1—Pd1—Cl2</td>
<td>176.213 (17)</td>
</tr>
</tbody>
</table>

The data above lists the selected torsion angles for the molecule 5b. Each entry shows the bond pair and its corresponding angle in degrees, followed by the uncertainties in parentheses. The table includes a variety of bonds, ranging from within the molecule to bonds involving the metal, palladium (Pd). The angles are critical for understanding the structural integrity and stability of the molecule. The data can be used for further analysis and comparison with other molecules or structures.
Table S18  Selected dihedral angles ['] for 5b.


References

1  X-Area (Stoe, 2004)
2  Sheldrick, G. M., SHELXS-2013/1, Program for the Crystal Structure Solution, University of Göttingen, Germany, 2013.
3  Sheldrick, G. M., SHELXL-2014/7, Program for the Crystal Solution Refinement, University of Göttingen, Germany, 2014.
4  Brandenburg, K., DIAMOND, Vers. 4.0.3, Crystal Impact, 2015.