Supporting Information

The Solid-state Hierarchy and Iodination Potential of

$[\text{bis}(3\text{-acetaminopyridine})\text{iodine(I)}]\text{PF}_6$

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Synthesis

General Considerations

All reagents and solvents were obtained from commercial suppliers and used without further purification. For structural NMR assignments, $^1$H NMR, $^{13}$C NMR, and $^1$H-$^{15}$N NMR correlation spectra were recorded on a Bruker Avance III 500 MHz spectrometer at 25°C in CD$_3$CN or CD$_2$Cl$_2$. Chemical shifts are reported on the δ scale in ppm using the residual solvent signal as internal standard (CH$_3$CN in CD$_3$CN: δ$_H$ 1.94, δ$_C$ 1.32/118.26; CH$_2$Cl$_2$ in CD$_2$Cl$_2$: δ$_H$ 5.32, δ$_C$ 53.84), or for $^1$H-$^{15}$N NMR spectroscopy, to an external CD$_3$NO$_2$ standard. For the $^1$H NMR spectroscopy, each resonance was assigned according to the following conventions: chemical shift (δ) measured in ppm, observed multiplicity, observed coupling constant (J Hz), and number of hydrogens. Multiplicities are denoted as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). For the $^1$H-$^{15}$N HMBC spectroscopy, spectral windows of 8 ppm ($^1$H) and 300 ppm ($^{15}$N) were used, with 1024 points in the direct dimension and 512 increments used in the indirect dimension, with subsequent peak shape analysis being performed to give the reported $^{15}$N NMR resonances.

The single crystal X-ray data for 2-2(MeCN), 3_1, 3_2, and 4 were collected at 120 K using an Agilent SuperNova dual wavelength diffractometer with an Atlas detector using mirror-monochromated Cu-Kα (λ = 1.54184 Å) radiation. The program CrysAlisPro was used for the data collection and reduction on the SuperNova diffractometers. All structures were solved by intrinsic phasing (SHELXT) and refined by full-matrix least squares on $F^2$ using Olex2, utilising the SHELXL module. Anisotropic displacement parameters were assigned to non-H atoms and isotropic displacement parameters for all H atoms were constrained to multiples of the equivalent displacement parameters of their parent atoms with $U_{iso}(H) = 1.2 U_{eq}$ (aromatic) or $U_{iso}(H) = 1.5 U_{eq}$ (alkyl) of their respective parent atoms. The X-ray single crystal data and CCDC numbers of all new structures are included below.

The following abbreviations are used: DCM = dichloromethane, MeCN = acetonitrile, TBME = 1-butylmethylether.
Preparation and Characterisation Details

3-acetaminopyridine (1): Ligand 1 was synthesised as previously reported in the literature.\(^5\) \(^1\)H NMR (500 MHz, CD\(_3\)CN) \(\delta\) 8.65 (d, \(J = 2.2\) Hz, 1H), 8.45 (s, br, 1H), 8.26 (dd, \(J = 4.5, 1.0\) Hz, 1H), 8.02 (d, \(J = 8.2\) Hz, 1H), 7.27 (dd, \(J = 8.2, 4.7\) Hz, 1H), 2.08 (s, 3H); \(^{13}\)C NMR (126 MHz, CD\(_3\)CN) \(\delta\) 170.0, 145.4, 141.9, 136.7, 127.1, 124.4, 24.14; \(^{15}\)N NMR (\(^{1}\)H-\(^{15}\)N HMBC, CD\(_3\)CN) \(\delta\) -63.7 (pyridinic), -254.4 (amido).

\([\text{Ag(3-acetaminopyridine)}_2]\text{PF}_6\) (2): A solution (DCM or MeCN; 3.5 mL) of 1 (10.9 mg, 0.08 mmol) was added to an MeCN (0.5 mL) solution of AgPF\(_6\) (10.1 mg, 0.04 mmol), and stirred for 15 minutes to give a colourless solution. All volatiles removed under reduced pressure to leave a white solid. Yield is quantitative. \(^1\)H NMR (500 MHz, CD\(_3\)CN) \(\delta\) 8.78 (d, \(J = 2.1\) Hz, 2H), 8.59 (s, br, 2H), 8.23 (dd, \(J = 4.8, 1.2\) Hz, 2H), 8.02 (d, \(J = 8.3\) Hz, 2H), 7.37 (dd, \(J = 8.3, 4.9\) Hz, 2H), 2.09 (s, 6H); \(^{13}\)C NMR (126 MHz, CD\(_3\)CN) \(\delta\) 170.2, 146.0, 142.5, 137.4, 128.1, 125.2, 24.1; \(^{15}\)N NMR (\(^{1}\)H-\(^{15}\)N HMBC, CD\(_3\)CN) \(\delta\) -85.8 (pyridinic), -254.2 (amido). Crystals suitable for single crystal X-ray diffraction were obtained from a DCM:MeCN (7:1) solution of 2 vapour diffused with pentane. Crystal data for 2: CCDC2193903, \([\text{C}_{18}\text{H}_{22}\text{AgN}_{6}\text{O}_{2}]\text{PF}_6\), \(M = 607.25\), colourless block, \(0.10 \times 0.26 \times 0.38 \text{ mm}^3\), triclinic, space group \(P-1\) (No. 2), \(a = 7.2685(3)\) Å, \(b = 12.4304(6)\) Å, \(c = 14.1913(6)\) Å, \(\alpha = 108.995(4)^\circ\), \(\beta = 101.944(4)^\circ\), \(\gamma = 92.083(4)^\circ\), \(V = 1178.64(10)\) Å\(^3\), \(Z = 2\), \(D_{\text{calc}} = 1.711\) g cm\(^{-3}\), \(F(000) = 608\), \(\mu = 8.20\) mm\(^{-1}\), \(T = 120.0(1)\) K, \(\theta_{\text{max}} = 76.5^\circ\), 4755 total reflections, 4505 with \(I_o > 2\sigma(I_o)\), \(R_{\text{int}} = 0.027\), 4755 data, 317 parameters, no restraints, \(GooF = 1.03\), \(0.54 < d\Delta p < 0.55\) eÅ\(^{-3}\), \(R[F^2 > 2\sigma(F^2)] = 0.028\), \(wR(F^2) = 0.078\).

Figure S1: The X-ray crystal structure of \([\text{Ag(3-acetaminopyridine)}_2]\text{PF}_6\)·2MeCN (PF\(_6\) anion omitted for clarity). Colour key: light grey = silver, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.
[\{(3-acetaminopyridine)\}_2]PF_6 (3): Elemental iodine (10.2 mg, 0.04 mmol) was added as a solid to a solution (either 7:1 DCM:MeCN or neat MeCN; 4 mL) of 2 (21.0 mg, 0.04 mmol) to give a pale orange solution and yellow precipitate (AgI) once all the I\(_2\) had dissolved (~5 minutes). The yellow precipitate was removed by filtration. Yield is quantitative. The pure complex can be isolated by precipitation with petroleum ether, with a minor loss of yield, to give a white solid. \(^1\)H NMR (500 MHz, CD\(_3\)CN) \(\delta\) 9.30 (s, 2H), 8.91 (s.br, 2H), 8.45 (d, \(J = 5.2\) Hz, 2H), 8.12 (dd, \(J = 8.5, 0.7\) Hz, 2H), 7.51 (dd, \(J = 8.3, 5.5\) Hz, 2H), 2.13 (s, 6H); \(^13\)C NMR (126 MHz, CD\(_3\)CN) \(\delta\) 170.6, 144.9, 141.0, 140.1, 131.9, 128.7, 24.1; \(^15\)N NMR (\(^1\)H-\(^15\)N HMBC, CD\(_3\)CN) \(\delta\) -174.5 (pyridinic), -253.5 (amido).

Two crystallographic polymorphs were identified for 3.

Crystals suitable for single crystal X-ray diffraction were obtained from a DCM:MeCN (7:1) solution of 3 vapour diffused with pentane at -20°C. Crystal data for 3_1: CCDC2193904, [C\(_{14}\)H\(_{16}\)IN\(_4\)O\(_2\)]PF\(_6\), M = 544.18, colourless plate, 0.03 \(\times\) 0.31 \(\times\) 0.38 mm\(^3\), triclinic, space group P-1 (No. 2), a = 8.1008(4) Å, b = 10.1196(7) Å, c = 12.4667(6) Å, \(\alpha = 98.710(5)^\circ\), \(\beta = 92.055(4)^\circ\), \(\gamma = 105.936(5)^\circ\), \(V = 968.14(10)\) Å\(^3\), \(Z = 2\), \(D_{calc} = 1.867\) gcm\(^{-3}\), \(F000 = 532\), \(\mu = 14.49\) mm\(^{-1}\), \(T = 200.0(1)\) K (crystals found to catastrophically shatter at temperatures below 200 K), \(\theta_{max} = 76.8^\circ\), 3914 total reflections, 3523 with \(I_o > 2\sigma(I_o)\), \(R_{int} = 0.055\), 3914 data, 289 parameters, 126 restraints, \(\text{Goof} = 1.03\), 2.33 < \(d\Delta\rho < -1.45\) eÅ\(^{-3}\), \(R[F^2 > 2\sigma(F^2)] = 0.061\), \(wR(F^2) = 0.174\).

Figure S2: The X-ray crystal structure of 3_1 (PF\(_6\) anion omitted for clarity). Colour key: purple = iodine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

S4
Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of an MeCN solution of 3.

Crystal data for 3_2: CCDC2193905, [C_{14}H_{16}IN_4O_2]PF_6, M = 544.18, colourless plate, 0.01 × 0.16 × 0.17 mm^3, triclinic, space group P-1 (No. 2), a = 9.9264(3) Å, b = 13.3351(4) Å, c = 14.6878(5) Å, α = 103.504(3)°, β = 99.401(2)°, γ = 90.172(2)°, V = 1863.36(10) Å³, Z = 4, D_{calc} = 1.940 gcm⁻³, F000 = 1064, μ = 15.06 mm⁻¹, T = 120.0(1) K, θ_{max} = 76.6°, 7610 total reflections, 6527 with |I_o| > 2σ(I_o), R_{int} = 0.054, 7610 data, 509 parameters, no restraints, GooF = 1.08, 6.17 < dΔρ < -1.35 eÅ⁻³, R[F^2 > 2σ(F^2)] = 0.056, wR(F^2) = 0.151.
[3-acetamido-1-(1-iodo-2-methylpropan-2-yl)pyridin-1-ium]PF₆ (4): A solution (either 7:1 DCM:MeCN or neat MeCN; 4 mL) of 3 (21.8 mg, 0.04 mmol) was vapour diffused with TBME (16 mL) over 48 hours to give the product as colourless crystals, which were decanted and dried to give a colourless crystalline solid. Yield = 12.0 mg (0.026 mmol, 65%). ¹H NMR (500 MHz, CD₃CN) δ 9.48 (s, 1H), 9.15 (s.br, 1H), 8.53 (d, J = 6.2 Hz, 1H), 8.36 (dd, J = 8.5, 1.1 Hz, 1H), 7.97 (dd, J = 8.2, 6.6 Hz, 1H), 3.82 (s, 2H), 2.19 (s, 3H), 1.94 (s, 6H; overlapping with CH₃CN at 1.94 ppm); ¹³C NMR (126 MHz, CD₃CN) δ 171.1, 140.6, 136.9, 135.2, 132.7, 129.1, 71.8, 27.2, 24.2, 17.1; ¹⁵N NMR (¹H-¹⁵N HMBC, CD₃CN) δ -154.5 (pyridinic), -252.9 (amido).

NMR analyses also performed in CD₂Cl₂ due to the overlap of the residual CH₃CN and water peaks with some of the alkyl resonances when performed in CD₃CN. ¹H NMR (500 MHz, CD₂Cl₂) δ 9.32 (s, 1H), 8.96 (dd, J = 8.6, 1.1 Hz, 1H), 8.92 (s, 1H), 8.27 (d, J = 6.2 Hz, 1H), 7.95 (dd, J = 8.4, 6.4 Hz, 1H), 3.76 (s, 2H), 2.29 (s, 3H), 2.02 (s, 6H); ¹³C NMR (126 MHz, CD₂Cl₂) δ 171.1, 141.2, 135.4, 134.3, 131.9, 128.5, 71.4, 27.7, 27.1, 24.4, 15.8; ¹⁵N NMR (¹H-¹⁵N HMBC, CD₂Cl₂) δ -154.6 (pyridinic), -254.0 (amido).

Crystals suitable for single crystal X-ray diffraction were obtained from a DCM:MeCN (7:1) solution of 3 vapour diffused with TBME. Crystal data for 4: CCDC2193906, [C₁₁H₁₆IN₂O]PF₆, M = 464.13, colourless needle, 0.05 × 0.08 × 0.24 mm³, monoclinic, space group P2₁/c, a = 10.4701(1) Å, b = 14.7904(1) Å, c = 10.5256(1) Å, β = 100.659(1)°, V = 1601.84(2) Å³, Z = 4, Dcalc = 1.925 gcm⁻³, F₀₀₀ = 904, µ = 17.28 mm⁻¹, T = 120.0(1) K, θmax = 76.2°, 3333 total reflections, 3248 with I > 2σ(I), Rint = 0.021, 3333 data, 202 parameters, no restraints, GooF = 1.04, 1.19 < dΔρ < -0.66 eÅ⁻³, R[F²] > 2σ(F²)] = 0.023, wR(F²) = 0.058.

Figure S5: The unit cell packing of 3₁.
Figure S6: The X-ray crystal structure of 4.
Colour key: purple = iodine, orange = phosphorus, lime green = fluorine, red = oxygen, blue = nitrogen, dark grey = carbon, white = hydrogen.

Comparison Table of $^{15}$N NMR Chemical Shifts

Table S1: Comparison of the pyridinic and amido $^{15}$N NMR chemical shifts (in CD$_3$CN) of complexes 1-4 (in ppm).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Pyridinic nitrogen ($\delta_N$)</th>
<th>Amido nitrogen ($\delta_N$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-63.7</td>
<td>-254.4</td>
</tr>
<tr>
<td>2</td>
<td>-85.8</td>
<td>-254.2</td>
</tr>
<tr>
<td>3</td>
<td>-174.5</td>
<td>-253.5</td>
</tr>
<tr>
<td>4</td>
<td>-154.5</td>
<td>-252.9</td>
</tr>
</tbody>
</table>
Reaction of Complex 3 with tBuOMe

Figure S7: A proposed mechanism to explain the observation of complex 4 as the major product upon reaction of complex 3 with tBuOMe, which relies upon the tBuOMe initially reacting with a source of "I" to form 2-methylpropene. The 2-methylpropene goes on to react with a source of I⁺ and a molecule of 1 to form complex 4.
Figure S8: The $^1$H NMR spectrum of ligand 1 in CD$_3$CN.
Figure S9: The $^{13}$C NMR spectrum of ligand 1 in CD$_3$CN.
Figure S10: The $^1$H-$^{15}$N HMBC spectrum of ligand 1 in CD$_3$CN.
Figure S11: The $^1$H NMR spectrum of complex 2 in CD$_3$CN.
Figure S12: The $^{13}$C NMR spectrum of complex 2 in CD$_3$CN.
Figure S13: The $^1$H-$^{15}$N HMBC spectrum of complex 2 in CD$_3$CN.
Figure S14: The $^1$H NMR spectrum of complex 3 in CD$_3$CN.
Figure S15: The $^{13}$C NMR spectrum of complex 3 in CD$_3$CN.
Figure S16: The $^1$H-$^{15}$N HMBC spectrum of complex 3 in CD$_3$CN.
Figure S17: The $^2$H NMR spectrum of complex 4 in CD$_3$CN.
Figure S18: The $^{13}$C NMR spectrum of complex 4 in CD$_3$CN.
Figure S19: The $^1$H-$^{15}$N HMBC spectrum of complex 4 in CD$_3$CN.
Figure S20: The $^1$H NMR spectrum of complex 4 in CD$_2$Cl$_2$. 
Figure S21: The $^{13}$C NMR spectrum of complex 4 in CD$_2$Cl$_2$. 
Figure S22: The $^1$H-$^{15}$N HMBC spectrum of complex 4 in CD$_2$Cl$_2$. 
References

1 Agilent Technologies Ltd, 2014, CrysAlisPro.


