Synthesis, structure and reactivity of aliphatic primary nitrosamines stabilized by coordination to [IrCl$_5$]$^{2-}$.

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Table S1. Experimental (I) DFT (a) – (l) (B3LYP, DZVP bases set for N, O, C, H, Cl; LANL2DZ bases set and pseudopotential for Ir) optimized structural parameters of coordinated nitrosamines (a) – (f) and diazoic acids (g) – (l) for different primary nitrosamines. Distances are in Å and angles in degrees.

<table>
<thead>
<tr>
<th>R</th>
<th>d(IrN)</th>
<th>d(NN)</th>
<th>d(NO)</th>
<th>d(NH)</th>
<th>d(NC)</th>
<th>d(IrCltrans)</th>
<th>(\angle)(IrNO)</th>
<th>(\angle)(IrNN)</th>
<th>(\angle)(CNN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenyl (a)</td>
<td>1.992</td>
<td>1.362</td>
<td>1.225</td>
<td>1.039</td>
<td>1.386</td>
<td>2.422</td>
<td>127.7</td>
<td>115.3</td>
<td>129.6</td>
</tr>
<tr>
<td>2,2,2-trifluoroethyl (b)</td>
<td>1.977</td>
<td>1.383</td>
<td>1.223</td>
<td>1.036</td>
<td>1.438</td>
<td>2.425</td>
<td>127.1</td>
<td>116.8</td>
<td>117.1</td>
</tr>
<tr>
<td>benzyl (c)</td>
<td>2.003</td>
<td>1.344</td>
<td>1.228</td>
<td>1.038</td>
<td>1.436</td>
<td>2.427</td>
<td>128.3</td>
<td>115.5</td>
<td>121.8</td>
</tr>
<tr>
<td>n-butyl (d)</td>
<td>1.994</td>
<td>1.353</td>
<td>1.229</td>
<td>1.036</td>
<td>1.448</td>
<td>2.433</td>
<td>127.2</td>
<td>116.7</td>
<td>119.6</td>
</tr>
<tr>
<td>cyclopropylamine (e)</td>
<td>2.007</td>
<td>1.341</td>
<td>1.228</td>
<td>1.036</td>
<td>1.419</td>
<td>2.431</td>
<td>128.5</td>
<td>115.4</td>
<td>122.1</td>
</tr>
<tr>
<td>9-methyladenyl (f)</td>
<td>1.969</td>
<td>1.412</td>
<td>1.211</td>
<td>1.041</td>
<td>1.344</td>
<td>2.420</td>
<td>128.5</td>
<td>115.3</td>
<td>128.2</td>
</tr>
<tr>
<td>2,2,2-trifluoroethyl (l)</td>
<td>2.026</td>
<td>1.326</td>
<td>1.140</td>
<td>0.880</td>
<td>1.478</td>
<td>2.353</td>
<td>123.86</td>
<td>114.24</td>
<td>121.12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>syn- [Cl₂Ir(-ONNHR)]²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
</tr>
<tr>
<td>phenyl (g)</td>
</tr>
<tr>
<td>2,2,2-trifluoroethyl (h)</td>
</tr>
<tr>
<td>bencyl (i)</td>
</tr>
<tr>
<td>n-butyl (j)</td>
</tr>
<tr>
<td>cyclopropylamine (k)</td>
</tr>
<tr>
<td>9-methyladenyl (l)</td>
</tr>
</tbody>
</table>
Table S2. X-ray Diffraction Selected Bond Lengths (Å) and Angles (°) for 1 and 2.

<table>
<thead>
<tr>
<th>Distances (Å) and angles (°)</th>
<th>Compound (1)</th>
<th>Compound (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(N1—N2)</td>
<td>1.326</td>
<td>1.316</td>
</tr>
<tr>
<td>d(N1—O1)</td>
<td>1.140</td>
<td>1.232</td>
</tr>
<tr>
<td>d(N2—C)</td>
<td>1.478</td>
<td>1.459</td>
</tr>
<tr>
<td>d(N1—Ir1)</td>
<td>2.026</td>
<td>2.000</td>
</tr>
<tr>
<td>d(Ir—Cl1)</td>
<td>2.353</td>
<td>2.362</td>
</tr>
<tr>
<td>d(Ir—Cl2)</td>
<td>2.356</td>
<td>2.357</td>
</tr>
<tr>
<td>d(Ir—Cl3)</td>
<td>2.353</td>
<td>2.373</td>
</tr>
<tr>
<td>d(Ir—Cl4)</td>
<td>2.359</td>
<td>2.350</td>
</tr>
<tr>
<td>d(Ir—Cl5)</td>
<td>2.367</td>
<td>2.366</td>
</tr>
<tr>
<td>d(N2—H2)</td>
<td>0.880</td>
<td>0.880</td>
</tr>
<tr>
<td>∠(N2N1O1)</td>
<td>121.77</td>
<td>116.78</td>
</tr>
<tr>
<td>∠(N2N1Ir1)</td>
<td>114.24</td>
<td>117.38</td>
</tr>
<tr>
<td>∠(IrN1O1)</td>
<td>123.86</td>
<td>125.84</td>
</tr>
<tr>
<td>∠(N2N1C)</td>
<td>121.12</td>
<td>122.09</td>
</tr>
<tr>
<td>∠dihedral(C1N2N1O1)</td>
<td>-4.0</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Table S3: Vibrational frequencies (cm⁻¹) of coordinated nitrosamines KRNH₃[IrCl₅(RNHNO)] calculated by DFT normal mode analysis (B3LYP, DZVP bases set for N, O, C, H, Cl; LANL2DZ bases set and pseudopotential for Ir).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ν(N–H)</td>
</tr>
<tr>
<td>phenyl (a)</td>
<td>3192</td>
</tr>
<tr>
<td>2,2,2-trifluoroethyl (b)</td>
<td>3256</td>
</tr>
<tr>
<td>benzyl (c)</td>
<td>3205</td>
</tr>
</tbody>
</table>
\[ n\text{-butyl (d)} \quad 3267 \quad 1600 \text{ and } 1429 \quad 1168 \text{ and } 1030 \]

\[ \text{cyclopropyl (e)} \quad 3249 \quad 1588 \text{ and } 1451 \quad 1137 \]

\[ 9\text{-octyladenyl}^a \text{(f)} \quad 3184 \quad 1630 \text{ and } 1616 \quad 893 \text{ and } 876 \]

\(^a\) Calculations were performed using 9-methyladenyl substituent as model for this compound.

**Table S4**: Most relevant UV-visible absorption signals (nm) of coordinated nitrosamines KRNH\(_3\)[IrCl\(_5\)(RNHNO)].

<table>
<thead>
<tr>
<th>R (nitrosamine)</th>
<th>(\lambda) (nm), (\varepsilon) (M(^{-1})cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2,2-trifluoroethyl (1)(^a)</td>
<td>195, 23000; 321, 1600; 384, 1000; 436, 650</td>
</tr>
<tr>
<td>benzyl (2)(^b)</td>
<td>198, 142000; 310, 12000; 377, 6000; 429, 3000</td>
</tr>
<tr>
<td>(n)-btyl (3)(^b)</td>
<td>260, 2000; 358, 300</td>
</tr>
<tr>
<td>cyclopropyl (4)(^b)</td>
<td>260, 2000; 326, 700; 343, 700; 373, 600; 408, 300</td>
</tr>
<tr>
<td>9-octyladenyl (5)(^a)</td>
<td>263, 4500; 271, 4000; 325, 2000; 384, 1000; 427, 700</td>
</tr>
</tbody>
</table>

\(^a\) in water. \(^b\) in DMSO

**Figure S1**: DFT calculated conformer difference energy (E(anti – syn) in kcal/mol) in acetonitrile for the nitrosamines (1) to (4) (B3LYP, DZVP bases set for N, O, C, H, Cl; LANL2DZ bases set and pseudopotential for Ir, for in vacuo values.
Table S5: DFT calculated energies (kcal/mol) in acetonitrile (PCM model) for the proposed intermediates of the nitrosation reaction.

<table>
<thead>
<tr>
<th>R</th>
<th>Intermediates</th>
<th>$E$ (kcal/mol) relative to the trifluoroethyl nitrosamine</th>
<th>$E$ (kcal/mol) relative to each nitrosamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>[IrCl$_3$(PhNHNO)]$^{2-}$ + H$_2$O</td>
<td>90800.856</td>
<td>0.000</td>
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<tr>
<td></td>
<td>[IrCl$_3$(PhNNOH)]$^{2-}$ + H$_2$O</td>
<td>90808.348</td>
<td>7.492</td>
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<tr>
<td></td>
<td>[IrCl$_3$(PhNNO)]$^{2-}$ + H$_2$O$^+$</td>
<td>90856.411</td>
<td>55.555</td>
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<tr>
<td></td>
<td>[IrCl$_3$(PhN$_2$)]$^+$ + H$_2$O + OH$^-$</td>
<td>90850.982</td>
<td>50.127</td>
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<tr>
<td></td>
<td>[IrCl$_3$(N$_2$)]$^{2-}$ + PhOH + H$_2$O</td>
<td>90751.132</td>
<td>-49.724</td>
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<tr>
<td>CF$_3$CH$_2$</td>
<td>[IrCl$_3$(CF$_3$CH$_2$NHNO)]$^{2-}$ + H$_2$O</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>[IrCl$_3$(CF$_3$CH$_2$NNOH)]$^{2-}$ + H$_2$O</td>
<td>3.715</td>
<td>3.715</td>
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<tr>
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<td>[IrCl$_3$(CF$_3$CH$_2$NNO)]$^{2-}$ + H$_2$O$^+$</td>
<td>49.454</td>
<td>49.454</td>
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<td>[IrCl$_3$(CF$_3$CH$_2$N$_2$)]$^+$ + H$_2$O + OH$^-$</td>
<td>61.594</td>
<td>61.591</td>
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<tr>
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<td>[IrCl$_3$(N$_2$)]$^{2-}$ + CF$_3$CH$_2$OH + H$_2$O</td>
<td>-91.521</td>
<td>-91.521</td>
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<tr>
<td>PhCH$_3$</td>
<td>[IrCl$_3$(PhCH$_2$NHNO)]$^{2-}$ + H$_2$O</td>
<td>66116.166</td>
<td>0.000</td>
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<td>[IrCl$_3$(PhCH$_2$NNOH)]$^{2-}$ + H$_2$O</td>
<td>66122.224</td>
<td>6.058</td>
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<td>[IrCl$_3$(PhCH$_2$NNO)]$^{2-}$ + H$_2$O$^+$</td>
<td>66169.665</td>
<td>53.499</td>
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<td>[IrCl$_3$(PhCH$_2$N$_2$)]$^+$ + H$_2$O + OH$^-$</td>
<td>66168.885</td>
<td>52.719</td>
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<td>[IrCl$_3$(N$_2$)]$^{2-}$ + PhCH$_2$OH + H$_2$O</td>
<td>66073.403</td>
<td>-42.763</td>
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<tr>
<td>C$_4$H$_9$</td>
<td>[IrCl$_3$(C$_4$H$_4$NHNO)]$^{2-}$ + H$_2$O</td>
<td>137080.715</td>
<td>0.000</td>
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<tr>
<td></td>
<td>[IrCl$_3$(C$_4$H$_4$NNOH)]$^{2-}$ + H$_2$O</td>
<td>137087.804</td>
<td>7.089</td>
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<td>[IrCl$_3$(C$_4$H$_4$NNO)]$^{2-}$ + H$_2$O$^+$</td>
<td>137139.241</td>
<td>58.527</td>
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<td>[IrCl$_3$(C$_4$H$_4$N$_2$)]$^+$ + H$_2$O + OH$^-$</td>
<td>137131.097</td>
<td>50.382</td>
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<td>[IrCl$_3$(N$_2$)]$^{2-}$ + C$_4$H$_4$OH + H$_2$O</td>
<td>137039.146</td>
<td>-41.569</td>
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<tr>
<td>C$_3$H$_5$</td>
<td>[IrCl$_3$(c-C$_3$H$_5$NHNO)]$^{2-}$ + H$_2$O</td>
<td>162561.881</td>
<td>0.000</td>
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<td>[IrCl$_3$(c-C$_3$H$_5$NNOH)]$^{2-}$ + H$_2$O</td>
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<td>3.737</td>
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<tr>
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<td>[IrCl$_3$(c-C$_3$H$_5$NNO)]$^{2-}$ + H$_2$O$^+$</td>
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<td>[IrCl$_3$(c-C$_3$H$_5$N$_2$)]$^+$ + H$_2$O + OH$^-$</td>
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<td>52.566</td>
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<td>[IrCl$_3$(N$_2$)]$^{2-}$ + c-C$_3$H$_5$OH + H$_2$O</td>
<td>162518.717</td>
<td>-43.164</td>
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<tr>
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<td>[IrCl$_3$(N$_2$)]$^{2-}$ + CH$_2$CH$_2$CH$_2$OH + H$_2$O</td>
<td>162511.892</td>
<td>-49.989</td>
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<tr>
<td>C$<em>{12}$H$</em>{19}$N$_4$</td>
<td>[IrCl$<em>3$(C$</em>{12}$H$_{19}$N$_4$NHNO)]$^{2-}$ + H$_2$O</td>
<td>-46645.738</td>
<td>0.000</td>
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<tr>
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<td>[IrCl$<em>3$(C$</em>{12}$H$_{19}$N$_4$NNOH)]$^{2-}$ + H$_2$O</td>
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<td>17.503</td>
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<td>[IrCl$<em>3$(C$</em>{12}$H$_{19}$N$_4$NNO)]$^{2-}$ + H$_2$O$^+$</td>
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<td>83.982</td>
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<td>66.142</td>
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<tr>
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<td>[IrCl$<em>3$(N$<em>2$)]$^{2-}$ + C$</em>{12}$H$</em>{20}$N$_4$CO (hypoxantine) + H$_2$O</td>
<td>-46658.859</td>
<td>-104.642</td>
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