Supporting Information

Mesoionic Imines (MIIs): Strong Donors and Versatile Ligands for Transition Metals and Main Group Substrates

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1. General Remarks

Manipulations were carried out using Schlenk-line techniques under the inert atmosphere of argon (Air liquide, ALPHAGAZTM 1, purity ≥ 99.999%). Phenylazide[1], Mesitylazide[2], 1a[3] and 1d[4] were prepared using published methods. Commercially available chemicals were used without further purification. Dry solvents were taken from solvent systems (GS GLOVEBOX or Innovative Technology PURESOLV) and degassed by ultra-sonication before use. NMR-spectra were recorded on either an Avance 250, Avance 400, Avance 500 or Avance 700 from Bruker. Chemical shifts in 1H-NMR-spectra are reported in ppm with reference to the residual solvents peaks (δ(CHCl₃) = 7.26 ppm, δ(C₆D₅H) = 7.0 ppm, δ(HCDCl₂) = 5.32 ppm, δ((HD₂C)₂CO) = 2.05 ppm, δ(HD₂CCN) = 1.94 ppm) relative to Me₄Si.[5] Heteronuclear NMR-spectra were calibrated using the Ξ-method[6]: ¹¹B-NMR: 80 MHz/128 MHz, external standard: BF₃∙OEt₂, δ = 0.0 ppm. ¹³C-NMR: 63 MHz/101 MHz/126 MHz/ 176 MHz, external standard: Me₄Si, δ = 0.0 ppm. ¹⁹F-NMR: 376 MHz, external standard: CFCl₃, δ = 0.0 ppm. Coupling constants are given in Hz. Multiplets are denoted as follows: singlet (s), duplet (d), triplet (t), quartet (q), not-resolved multiplet (m), broad signal (br.) and combinations thereof. IR-spectrum were recorded on a Nicolet iS5 from Thermo Fisher Scientific with an iD5 ATR-unit or with a liquid-cuvette (CaF₂-windows). Wavenumbers ν are reported in cm⁻¹. Mass spectrometry was performed on a microTOFQ Bruker Daltonics. Elemental analysis was performed on an Elementar VarioMICRO cube. X-ray diffractometry was carried out on either an Apex II Duo from Bruker with or a STADIVARI from STOE with molybdenum radiation (λKα = 0.71073 Å). Structures were solved by using SHELXL and refined using SHELXT.[7]

2. Synthesis

Synthesis of 1b

Potassium butoxide (0.56 g, 5.02 mmol, 1.2 eq) and copper(I)-iodide were dissolved in DMSO (9 mL). The reaction vessel was placed into an ice-water bath and benzyl cyanide (0.49 g, 4.18 mmol, 1 eq) was added immediately dropwise. After complete addition 2,4,6-trimethylphenylazide (0.81 g, 5.02 mmol, 1.2 eq) was added dropwise into the solution. The solution was stirred for another 15 minutes after complete addition while still submerged in icy water. The solution was allowed to warm up to room temperature and stirring was continued for 2 hours. The reaction was quenched by the addition of icy water (100 mL), while the product precipitated as an orange solid. The solid was filtered off and washed with generous amounts of water (3x 100 mL). The combined organic layers were dried (Na₂SO₄) and filtrated. The solvents were removed under reduced pressure yielding an orange oil. The crude product was dissolved in CH₂Cl₂ (20 mL) and washed with aqueous NH₄OH-EDTA solution until the aqueous layer was colourless. The combined organic layers were dried (Na₂SO₄) and filtrated. The solvents were removed under reduced pressure yielding an orange oil. The crude product was dissolved in Et₂O (5 mL). The addition of hexane resulted in the deposition of the product as a red oil. Decantation of the liquid and removing of volatiles on high vacuum yielded the desired product as an orange solid, which was used without further purification (1.69 mmol, 48%, 559 mg).

¹H-NMR (500 MHz, CDCl₃) δ: 7.79 (d, J = 7.27 Hz, Phenyl-o-H, 2H), 7.46 (t, J = 7.76 Hz, Phenyl-m-H, 2H), 7.29 (d, J = 7.36 Hz, Phenyl-p-H, 1H), 7.03 (s, Aryl-H, 2H), 3.85 (s, Trz-NH₂, 2H), 2.36 (s, Aryl-p-C₃H₃, 3H), 2.04 (s, Aryl-o-C₃H₃, 6H).

¹³C-NMR (126 MHz, CDCl₃) δ: 140.7 (Aryl-o-C), 138.0, 136.6 (Aryl-p-C), 132.0, 129.7, 129.5 (Aryl-m-C), 129.0 (Phenyl-m-C), 128.6 (Phenyl-i-C), 126.7 (Phenyl-p-C), 125.2 (Phenyl-o-C), 21.2 (Aryl-p-C₃H₃), 17.4 (Aryl-o-C₃H₃).

EA: calc. (C_{17}H_{18}N₄) m/z = 279.16 mg/mol C 73.35, H 6.52, N 20.13; found C 72.95, H 6.61, N 19.21.

MS (ESI): m/z = 279.16 [M+H]+, 301.14 [M+Na]+.

HRMS (ESI): calc. (C_{17}H_{18}N₄) m/z = 279.1604 [M+H]+; found m/z = 279.1604 [M+H]+.
Synthesis of 1c

2,4,6-Trimethylphenylacetonitrile (1.05 g, 6.59 mmol, 1 eq) was submitted into an oven dried Schlenk flask. THF (50 mL) was added under a flow of argon and the solution was cooled to -40 °C. A solution of n-butyllithium in hexanes (2.64 mL, 2.5 M, 1 eq) was added dropwise to the stirring solution and the solution was stirred for 10 minutes. 2,4,6-Trimethylphenylazide was added dropwise into the solution and the solution was over night while slowly heating up to room temperature. The solution was slowly poured into icy water (150 mL) and stirred for another 30 minutes at room temperature until all ice melted. The solution was extracted with EtOAc (3x 100 mL). The combined organic layers were washed with brine (2x 100 mL), dried (Na$_2$SO$_4$) and filtrated over a pad of wool. After removal of the solvent under reduced pressure the crude product was obtained as an orange oil. The oil was dissolved in the least amount of boiling ethanol (~ 10 mL) as possible. After the solution was allowed to cool to room temperature crystallisation was induced by adding a few seed crystals from an earlier batch. The vessel was placed into a freezer for 2-3 days (-20 °C) for quantitative crystallisation. The product was obtained after filtration and washing of the filter cake with ice-cold ethanol as colourless needles. Seed crystals could be obtained by placing the oversaturated ethanol-solution in the fridge (6 °C) for several days. (1.98 mmol, 42%, 0.80 g).

Single crystals suitable for X-ray diffractometry were obtained by slow diffusion of hexane into a saturated solution of the product in CH$_2$Cl$_2$ at room temperature over the course of several days.

$^1$H-NMR (700 MHz, CDCl$_3$) δ: 7.02 (s, Aryl-m-\(\text{H}\), 2H), 6.96 (s, Aryl-m-\(\text{H}\), 2H), 3.39 (s, -NH$_2$, 2H), 2.35 (s, Aryl-p-\(\text{CH}_3\), 3H), 2.32 (s, Aryl-p-\(\text{CH}_3\), 3H), 2.16 (s, Aryl-o-\(\text{CH}_3\), 6H), 2.06 (s, Aryl-o-\(\text{CH}_3\), 6H).

$^{13}$C-NMR (126 MHz, CDCl$_3$) δ: 140.4, 138.9, 138.3, 138.2, 136.4, 130.2 (Aryl-m-\(\text{C}\)), 129.4 (Aryl-m-\(\text{C}\)), 127.7, 126.3, 21.22 (Aryl-p-\(\text{CH}_3\)), 20.12 (Aryl-o-\(\text{CH}_3\)), 17.32 (Aryl-o-\(\text{CH}_3\)).

EA: calc. (C$_{20}$H$_{24}$N$_4$, 320.20 g/mol) C 74.97, H 7.55, N 17.48; found C 74.89, H 7.86, N 17.07.

MS (ESI): m/z = 321.21 [M+H]$^+$, 343.19 [M+Na]$^+$.

HRMS (ESI): calc. (C$_{20}$H$_{24}$N$_4$) m/z = 321.2076 [M+H]$^+$, found m/z = 321.2074 [M+H]$^+$.

Generation of 1d-O

According to a literature-known procedure$^8$, the triazole 1d (307 mg, 1.29 mmol, 1 eq) and m-CPBA (380 mg, 2.59 mmol, 2 eq) were submitted to a roundbottom flask and dissolved in CHCl$_3$ (20 mL). The solution was stirred under reflux for 30 minutes. The solution was allowed to cool to room temperature. The solution was washed with an aqueous Na$_2$S$_2$O$_3$-solution. The organic layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (1x 20 mL). The combined organic layer were washed with aqueous NaOH-solution. The organic layer was separated, dried (Na$_2$SO$_4$) and filtrated over a pad of wool. The volume was reduced to ~2 mL and the solution was overlayered with EtOH yielding orange single crystals suitable for X-ray diffractometry after several days. Further investigation of the thus obtained crystals by NMR shows that the crystalline material does not appear to be a well-defined product (Figure S7). A mixture was obtained. Besides diffractometric methods the product composition was confirmed by HRMS

MS (ESI): m/z = 254.10 [M+H]$^+$, 276.09 [M+Na]$^+$.

HRMS (ESI): calc. (C$_{13}$H$_{11}$N$_5$O) m/z = 276.0854 [M+Na]$^+$, found m/z = 276.0854 [M+H]$^+$.

General procedure for triazolium iodides 2a-c (GP I)
According to a literature-known procedure [9], the appropriate triazole 1a-c was submitted into an oven-dried Schlenk flask. MeCN and methyl iodide were added under a flow of argon. The Schlenk flask was sealed with a stopcock and the mixture was heated to 60 °C. The stopper was lifted to release pressure and the solution was stirred for 3 days at 60 °C in a sealed flask. After 3 days, the reaction mixture was allowed to cool to room temperature and volatiles were removed under reduced pressure. The residue was extracted with CH₂Cl₂. Under intense stirring the desired triazolium iodides 2a-c were precipitated as a fine powder by the addition of Et₂O. Filtration and removal of all volatiles under high vacuum yielded the desired product as white to yellowish powders.

Synthesis of 2a according to GP I

\[
\text{N} \quad \text{N} \quad \text{NH}_2
\]

- 1a (406 mg, 1.72 mmol, 1 eq)
- MeCN (15 mL)
- MeI (1.35 g, 12.0 mmol, 7 eq)

Yield: 635 mg (1.68 mmol, 98%) as a yellow powder. Single crystals suitable for X-ray diffractometry were obtained by slow diffusion of Et₂O into a saturated solution of the product in CH₂Cl₂ at -7 °C over night.

\[ ^1H-NMR \ (250 MHz, \text{CDCl}_3) \delta: 7.89-7.83 \text{ (m, Aryl-H, 2H)}, 7.80-7.74 \text{ (m, Aryl-H, 2H)}, 7.63-7.54 \text{ (m, Aryl-H, 6H), 5.07 (s, -NH}_2, 2\text{H)}, 4.15 \text{ (s, Trz-C}_H_3, 3\text{H)}. \]

\[ ^1H-NMR \ (400 MHz, \text{CD}_3\text{CN}) \delta: 7.76-7.70 \text{ (m, Aryl-H, 5H)}, 7.68-7.61 \text{ (m, Aryl-H, 5H), 5.47 (s, -NH}_2, 2\text{H)}, 4.05 \text{ (s, Trz-C}_H_3, 3\text{H)}. \]

\[ ^13C-NMR \ (126 MHz, \text{CDCl}_3) \delta: 143.3, 132.2, 131.9, 130.6, 130.4, 130.1, 125.7, 125.4, 121.9, 39.1 \text{ (N-CH}_3\text{)}. \]

FTIR (ATR, solid) \( \nu \): 1613 (C Trz-Nexo). EA: calc. (C_{15}H_{15}N_{4}I, 378.22 g/mol): C 47.64, H 4.00, N 14.81; found C 47.52, H 4.14, N 14.80.

MS (ESI): \( m/z = 251.15 \) [M]+.

HRMS (ESI): calc. (C_{15}H_{15}N_{4}I) \( m/z = 251.1291 \) [M+H]+, found \( m/z = 251.1283 \) [M+H]+.

Synthesis of 2b according to GP I

\[
\text{N} \quad \text{N} \quad \text{NH}_2
\]

- 1b (264 mg, 0.95 mmol, 1 eq)
- MeCN (10 mL)
- MeI (0.74 g, 6.64 mmol, 7 eq)

Yield: 251 mg (0.69 mmol, 63%) as an off-white powder.

\[ ^1H-NMR \ (500 MHz, \text{CDCl}_3) \delta: 7.80 \text{ (d, J = 6.9 Hz, Phenyl-H, 2H), 7.63 (t, J = 7.6 Hz, Phenyl-H, 2H), 7.58 (d, J = 7.6 Hz, Phenyl-p-H, 1H), 7.09 (s, Aryl-m-H, 2H), 5.40 (s, -NH}_2, 2\text{H)}, 4.29 (s, NTrz-CH_3, 3\text{H}), 2.40 (s, Aryl-p-CH_3, 3\text{H}), 2.15 (s, Aryl-o-CH_3, 6\text{H}). \]

\[ ^13C-NMR \ (126 MHz, \text{CDCl}_3) \delta: 143.6, 143.2, 135.8, 131.7 \text{ (Aryl-m-C)}, 130.4, 130.3, 130.0, 126.8, 124.4 \text{ (CTrz-NH}_2\text{)}, 121.6, 39.8 \text{ (NTrz-CH}_3\text{)}, 21.3 \text{ (Aryl-o-CH}_3\text{)}, 18.0 \text{ (Aryl-p-CH}_3\text{)}. \]

EA: calc. (C_{18}H_{21}N_{4}I, 420.30 g/mol): C 51.44, H 5.04, N 13.33; found C 51.31, H 5.08, N 13.03.

MS (ESI): \( m/z = 293.18 \) [M]+.
SUPPORTING INFORMATION

HRMS (ESI): calc.(C_{21}H_{27}N_{4}I) m/z = 335.22 [M]+, found m/z = 335.2239 [M]+.

Synthesis of 2c according to GP I

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Yield: 472 mg (1.02 mmol, 78%) as a yellow powder.

Single crystals suitable for X-ray diffractometry were obtained by slow diffusion of Et_{2}O into a saturated solution of the product in CH_{2}Cl_{2} at -7 °C over night.

H-NMR (500 MHz, CDCl_{3}) δ: 7.07 (s, Aryl-m- H, 2H), 7.02 (s, Aryl-m- H, 2H), 5.28 (br. s, -NH_{2}, 2H), 3.98 (s, N-Trz-C_{H}3, 3H), 2.35 (s, Aryl-p-C_{H}3, 3H), 2.32 (s, Aryl-p-C_{H}3, 3H), 2.13 (s, Aryl-o-C_{H}3, 6H), 2.10 (s, Aryl-o-C_{H}3, 6H).

C-NMR (126 MHz, CDCl_{3}) δ: 144.1, 143.2, 142.8, 139.0, 135.5, 130.4 (Aryl-m-C), 129.7 (Aryl-m-C), 126.9, 123.3 (C_{Trz-NH_{2}}), 116.7, 38.7 (N-Trz-C_{H}3), 21.4 (Aryl-p-C_{H}3), 21.3 (Aryl-p-C_{H}3), 20.1 (Aryl-o-C_{H}3), 17.5 (Aryl-o-C_{H}3).

EA: calc. (C_{21}H_{27}N_{4}I, 462.38 g/mol): C 54.55, H 5.89, N 12.12; found C 54.32, H 6.00, N 11.47.

MS (ESI): m/z = 335.22 [M]+.

HRMS (ESI): calc.(C_{21}H_{27}N_{4}I) m/z = 335.2230 [M]+, found m/z = 335.2239 [M]+.

Synthesis of 3a

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Triazolium salt 2a (300 mg, 0.79 mmol, 1 eq) and potassium hexamethyldisilazide (158 mg, 0.79 mmol, 1 eq) were submitted into an oven-dried Schlenk flask and cooled to -78 °C. THF (30 mL) was added. The reaction mixture was stirred for 30 minutes, warmed to room temperature and then stirred for 1 hour at room temperature. Volatiles were removed under reduced pressure. The residue was suspended in toluene (10 mL) and filtrated over a pad of cellite. The filter cake was extracted with toluene (2x 10 mL). Removal of the solvent under reduced pressure yielded the product as a bright yellow solid (0.64 mmol, 81 %, 160 mg). Pure product was obtained after trituration of the product with small amounts of toluene.

Single crystals suitable for X-ray diffractometry were obtained by storage of a saturated solution of the product in benzene at 4 °C for several weeks.

H-NMR (250 MHz, C_{6}D_{6}) δ: 8.79-8.68 (m, Aryl-H, 2H), 7.15-7.07 (m, Aryl-H, 2H), 6.92-6.88 (m, Aryl-H, 4H), 6.86-6.78 (m, Aryl-H, 2H), 5.49 (s, br., =NH, 1H), 2.60 (s, Trz-CH_{3}, 3H).

H-NMR (500 MHz, CD_{3}CN) δ: 8.25 (dd, J = 7.6 Hz, J = 1.3 Hz, Aryl-H, 2H), 7.58-7.49 (m, Aryl-H, 6H), 7.43 (tm, J = 6.6 Hz, Aryl-H, 1H), 7.33 (tm, J = 7.6 Hz, Aryl-H, 1H), 4.78 (s, br., =NH, 1H), 3.91 (s, N-Trz-CH_{3}, 3H).

H-NMR (250 MHz, CD_{2}Cl_{2}) δ: 8.15-8.08 (m, Aryl-H, 2H), 7.48-7.29 (m, Aryl-H, 7H), 7.27-7.19 (m, Aryl-H, 1H), 4.71 (s, br., =NH, 1H), 3.83 (s, Trz-CH_{3}, 3H).

C-NMR (126 MHz, CD_{3}CN) δ: 154.8, 137.3, 128.9, 128.6, 128.1, 127.9, 127.3, 126.0, 120.6, 128.1, 37.8 (N-Trz-CH_{3}).
SUPPORTING INFORMATION

FTIR (ATR, solid) \(\nu\): 1719 (C-Trz-N-exo).

EA: calc. (C\(_{15}\)H\(_{14}\)N\(_4\)) C 71.98, H 5.64, N 22.38; found. C 71.68, H 5.60, N 22.19.

MS (ESI): m/z = 251.13 [M+H]*.

HRMS (ESI): calc. (C\(_{15}\)H\(_{14}\)N\(_4\)) m/z = 251.1291 [M+H]*, found. m/z = 251.1284 [M+H]*.

Synthesis of 3b

Triazolium salt 2b (154 mg, 0.37 mmol, 1 eq) and potassium hexamethyldisilazide (73 mg, 0.37 mmol, 1 eq) were submitted into an oven-dried Schlenk flask and cooled to -78 °C. THF (10 mL) was added. The reaction mixture was stirred for 30 minutes, warmed to room temperature and then stirred for 1 hour at room temperature. Volatiles were removed under reduced pressure. The residue was suspended in Et\(_2\)O (5 mL) and filtered over celite. The filtrate was discarded. The filter cake was extracted with toluene (3x 10 mL). Removal of the solvent under reduced pressure yielded the product as an orange solid (0.21 mmol, 56 %, 60 mg).

Single crystals suitable for X-ray diffractometry were obtained by storage of a saturated solution of the product in toluene at -16 °C for several weeks. The obtained structure shows that 3b and 2b co-crystallised.

\(^1\)H-NMR (500 MHz, C\(_6\)D\(_6\)) \(\delta\): 7.73 (br, Phenyl-H, 2H), 7.07 (t, J = 7.6 Hz, Phenyl-H, 2H), 6.90 (t, J = 7.6 Hz, Phenyl-o-H, 2H), 6.59 (s, Aryl-m-H, 2H), 4.30 (br, Trz=N-H, 1H), 2.93 (s, Trz-C-H\(_3\), 3H), 2.06 (s, Aryl-o-C-H\(_3\), 6H), 1.92 (s, Aryl-p-C-H\(_3\), 3H).

\(^1\)C-NMR (126 MHz, C\(_6\)D\(_6\)) \(\delta\): 139.5 (Aryl-p-C-H), 137.3 (Aryl-o-C), 129.6, 129.2 (Aryl-m-C), 128.7 (Aryl-m-C), 127.5, 126.9 (C-Trz=NH), 117.0 (C-Trz-Phenyl), 38.4 (N-C-H\(_3\)), 21.1 (Aryl-o-C-H\(_3\)), 18.0 (Aryl-p-C-H\(_3\)).

EA: calc. (C\(_{18}\)H\(_{20}\)N\(_4\)) C 73.94, H 6.89, N 19.16; found C 72.96, H 6.55, N 18.75.

CHN-Analysis shows a major deviation from the calculated values. This can be explained by contamination of the starting material 2b which could not be removed.

MS (ESI): m/z = 293.18 [M+H]*.

HRMS (ESI): calc. (C\(_{18}\)H\(_{20}\)N\(_4\)) m/z = 293.1761 [M+H]*, found m/z = 293.1765 [M+H]*.

Synthesis of 3c

Triazolium salt 2c (230 mg, 0.50 mmol, 1 eq) and potassium hexamethyldisilazide (99 mg, 0.50 mmol, 1 eq) were submitted into an oven-dried Schlenk flask and cooled to -78 °C. THF (15 mL) was added. The reaction mixture was stirred for 30 minutes, warmed to room temperature and then stirred for 1 hour at room temperature. Volatiles were removed under reduced pressure. The residue was suspended in Et\(_2\)O (10 mL) and filtered over celite. The filter cake was extracted with Et\(_2\)O (3x 15 mL). Removal of the solvent under reduced pressure yielded the product as an orange solid (0.30 mmol, 60 %, 100 mg). Pure 3c was obtained after trituration with n-pentane.

Single crystals suitable for X-ray diffractometry were obtained by slow solvent-evaporation of a solution of the product in C\(_6\)D\(_6\) at room temperature.

\(^1\)H-NMR (500 MHz, C\(_6\)D\(_6\)) \(\delta\): 6.77 (s, Aryl-H, 4H), 3.48 (s, br., =N-H, 1H), 2.86 (s, Trz-C-H\(_3\), 3H), 2.30 (s, Aryl-o-C-H\(_3\), 6H), 2.14 (s, Aryl-o-C-H\(_3\), 6H), 2.13 (s, Aryl-p-C-H\(_3\), 3H), 2.08 (s, Aryl-p-C-H\(_3\), 3H).
**SUPPORTING INFORMATION**

**1H-NMR** (500 MHz, CD<sub>3</sub>CN) δ: 9.07 (d, J = 6.3 Hz, Pyridyl-H, 1H), 8.75 (t, J = 7.6 Hz, Pyridyl-H, 1H), 8.34 (d, J = 8.2 Hz, Pyridyl-H, 1H), 8.31 (t, J = 7.3 Hz, Pyridyl-H, 1H), 7.81-7.73 (m, Phenyl-H, 5H), 6.30 (s, br., Trz-NH<sub>2</sub>, 2H), 4.35 (s, N<sub>Py</sub>-C<sub>H</sub>₃, 3H), 4.13 (s, N<sub>Trz</sub>-C<sub>H</sub>₃, 3H).

**13C-NMR** (126 MHz, CD<sub>3</sub>CN) δ: 149.2, 146.8, 145.8, 133.3, 132.2, 131.4, 130.5, 130.4, 125.5, 120.4 (q, J<sub>CF</sub> = 320 Hz, SO₃C<sub>F</sub>₃), 46.6 (N<sub>Py</sub>-C<sub>H</sub>₃), 39.4 (N<sub>Trz</sub>-C<sub>H</sub>₃).

**19F-NMR** (235 MHz, CD<sub>3</sub>CN) δ: - 78.3 (s, SO₃C<sub>F</sub>₃)

**EA:** calc. (C₁₇H₁₇F₆N₅O₆S₂, 565.46 g/mol) C 36.11, H 3.03, N 12.39; found C 36.11, H 3.21, N 12.45.

**MS (ESI):** m/z = 236.1182 [M]<sup>2+</sup>, found m/z = 236.1180 [M]<sup>2+</sup>.

**Preparation of 1d-O single crystals suitable for X-ray diffraction**

According to a reported protocol, a round-bottom flask was equipped with a stir bar, the triazole 1d (307 mg, 1.29 mmol, 1 eq) and mCPBA (580 mg, 2.59 mmol, 2 eq). Distilled chloroform (20 mL) was added and the solution was stirred under reflux for 30 Min. The solution was allowed to cool to room temperature. The organic phase was washed with aqueous Na₂SO₃-solution, followed by washing with aqueous NaOH-solution. The combined aqueous layers were extracted with CH₂Cl₂ (2x 10 mL). The combined organic layers were dried (Na₂SO₄) and filtrated. A crude product mixture was obtained after removal of the solvent under reduced pressure as a highly viscous red oil. Single crystals were obtained after several days by over layering a concentration solution of the crude product in CH₂Cl₂ with EtOH at room temperature.

**Synthesis of 5a**

![Synthesis of 5a](image)
The ligand precursor 2a (18 mg, 0.05 mmol, 1 eq), NaOAc (23 mg, 0.29 mmol, 6 eq) and [Ir(Cp*)Cl₂] (19 mg, 0.02 mmol, 0.5 eq) were submitted into an oven-dried Schlenk flask. Under a flow of argon, MeCN (6 mL) was added and the flask was sealed. The mixture was heated to 65 °C, the stop-cock was lifted to release pressure and the mixture was stirred at 65 °C in the sealed flask for three days. The mixture was allowed to cool to room temperature. The suspension was filtered through a pad of cellite and the solvent in the filtrate was removed under reduced pressure. The residue was suspended in Et₂O (10 mL) and sonicated with ultra-sound for 1 hour. The resulting red solid was filtrated and washed with small amounts of ice-cold Et₂O. The product was obtained in a pure form as red needles after crystallisation through slow diffusion of n-pentane at room temperature into a concentrated solution of the crude product in CH₂Cl₂ over the course of several days (0.04 mmol, 75%, 25 mg).

Single crystals suitable for X-ray diffraction were obtained in the same way.

**SUPPORTING INFORMATION**

**Synthesis of 5b**

The ligand precursor 2b (28 mg, 0.07 mmol, 1 eq), NaOAc (33 mg, 0.40 mmol, 6 eq) and [Ir(Cp*)Cl₂] (27 mg, 0.03 mmol, 0.5 eq) were submitted into an oven-dried Schlenk flask. Under a flow of argon, MeCN (6 mL) was added and the flask was sealed. The mixture was heated to 65 °C, the stop-cock was lifted to release pressure and the mixture was stirred at 65 °C in the sealed flask for three days. The mixture was allowed to cool to room temperature. The suspension was filtered through cellite and the solvent in the filtrate was removed under reduced pressure. The residue was suspended in Et₂O (10 mL) and sonicated with ultra-sound for 1 hour. The resulting red solid was filtrated and washed with small amounts of ice-cold Et₂O. The product was obtained in a pure form as red plates after crystallisation through slow diffusion of n-pentane at room temperature into a concentrated solution of the crude product in CH₂Cl₂ over the course of several days (0.03 mmol, 40%, 20 mg).

Single crystals suitable for X-ray diffraction were obtained in the same way.

**1H-NMR** (500 MHz, CD₂Cl₂) δ: 7.87 (d, J = 7.6 Hz, Phenyl-H, 1H), 7.47 (d, J = 7.6 Hz, Phenyl-H, 1H), 7.00 (s, Aryl-m-H, 2H), 6.85-6.77 (m, Phenyl-H, 2H), 4.17 (s, Trz-CH₃, 3H), 2.77 (s, br., =NH, 1H), 2.29 (s, Aryl-p-CH₃, 3H), 2.04 (s, Aryl-o-CH₃, 6H), 1.45 (s, Cp-(CH₃)₅, 15 H).

**1C-NMR** (126 MHz, CD₂Cl₂) δ: 148.8, 146.8, 141.7, 136.9, 130.2, 129.3, 128.5, 126.0, 125.1, 122.4, 119.4, 87.8 (C₅p), 41.9 (Trz-CH₃), 21.3 (Aryl-p-CH₃), 18.0 (Aryl-o-CH₃), 9.4 (Cp-(CH₃)₅).

**EA:** calc. (C₂₈H₂₈IrN₄, 743.71 g/mol) C 45.10, H 4.60, N 7.51; found C 43.79, H 4.53, N 7.13.

The low carbon content in CHN-analysis is presumably affiliated with the formation of iridium carbides during the combustion method as the hydrogen/nitrogen content fit the calculated values and no impurities were detected spectroscopically.

**HRMS (ESI):** m/z = 619.24 [M-I]⁺, 293.18 [2b]⁺.

**HRMS (ESI):** calc. (C₂₈H₂₈IrN₄), m/z = 619.2408 [M-I]⁺, found. m/z = 619.2412 [M-I]⁺.
Synthesis of 5d

The ligand precursor 2d (147 mg, 0.26 mmol, 1 eq), NaOAc (128 mg, 1.56 mmol, 6 eq) and [Ir(Cp*)Cl]₂ (104 mg, 0.13 mmol, 0.5 eq) were submitted into an oven-dried Schlenk flask. Under a flow of argon, MeCN (15 mL) was added and the flask was sealed. The mixture was heated to 65 °C, the stop-cock was lifted to release pressure and the mixture was stirred at 65 °C in the sealed flask over night. The mixture was allowed to cool to room temperature. The suspension was filtered through cellite. The solvent in the filtrate was reduced to ~2 mL and the product obtained in a pure form after precipitation by addition of Et₂O as an orange powder (0.17 mmol, 66%, 160 mg).

Single crystals suitable for X-ray diffractometry were obtained as red needles by slow diffusion of Et₂O at room temperature into a concentrated solution of the product in MeCN over night.

1H-NMR (700 MHz, CD₃CN) δ: 9.00 (d, J = 6.1 Hz, Aryl-H, 1H), 8.68 (dt, J = 7.9 Hz, J = 1.9 Hz, Aryl-H, 1H), 8.28 (dd, J = 7.8 Hz, J = 1.2 Hz, Aryl-H, 1H), 8.21-8.18 (m, Aryl-H, 1H), 7.81-7.78 (m, Aryl-H, 1H), 7.69-7.67 (m, Aryl-H, 2H), 4.86 (s, =N-H, 1H), 4.22 (s, NPy-C₃H₃, 3H), 3.98 (s, NTrz-C₃H₃, 3H), 1.96 (s, MeCN), 1.53 (s, Cp-(C₅H₅), 15 H).

13C-NMR (176 MHz, CD₃CN) δ: 149.7, 148.1, 147.2, 143.3, 140.4, 135.9, 135.0, 133.2, 129.8, 128.6, 125.5, 121.6 (q, JCF = 321 Hz, SO₃CF₃), 116.4, 112.1, 90.3 (C₅Cp*), 47.3 (NPy-C₃H₃), 39.8 (Trz-C₃H₃), 8.5 (Cp-(C₅H₅)).

EA: calc. (C₂₉H₃₃F₆IrN₆O₆S₂, 931.95 g/mol) C 37.38, H 3.57, N 9.02; found C 37.35, H 3.61, N 8.80.

MS (ESI): m/z = 742.16 [M-(OTf)-(MeCN)]⁺, 594.22 [M-OTf-MeCN+H]⁺, 296.61 [M-(OTf)₂-MeCN]⁺. HRMS (ESI): calc. (C₂₉H₃₃F₆IrN₆O₆S₂), m/z = 742.1645 [M-(OTf)-(MeCN)]⁺, found. m/z = 742.1646 [M-(OTf)-(MeCN)]⁺.

The auxiliary MeCN-ligand could be removed by solving 5 in acetone followed by precipitation with Et₂O as a green powder. Crystallisation by diffusion of either Et₂O or n-pentane at room temperature into a concentrated solution of 5d-acetone in acetone over the course of several days yielded a pure product in the form of green plates. Single crystals suitable for X-ray diffractometry were obtained as green plates following the same procedure.

1H-NMR (500 MHz, (D₃)₂CO) δ: 11.30 (s, br., =NH, 1H), 9.44 (d, J = 6.3 Hz, Aryl-H, 1H), 9.16 (d, J = 7.8 Hz, Aryl-H, 1H), 8.93 (t, J = 7.8 Hz, Aryl-H, 1H), 8.72 (d, J = 7.7 Hz, Aryl-H, 1H), 8.58 (d, J = 8.4 Hz, Aryl-H, 1H), 8.47 (t, J = 6.8 Hz, Aryl-H, 1H), 7.75 (t, J = 7.7 Hz, Aryl-H, 1H), 7.52 (t, J = 7.3 Hz, Aryl-H, 1H), 4.63 (s, NPy-C₃H₃, 3H), 4.45 (s, NTrz-C₃H₃, 3H), 1.90 (s, Cp-(C₅H₅), 15 H).

EA: calc. (C₂₉H₃₀F₃IrN₆O₆S₂, 890.89 g/mol) C 36.40, H 3.39, N 7.86; found C 36.55, H 3.45, N 7.71.
Synthesis of 3c-Rh(CO)₂Cl

The ligand 3c (62 mg, 0.19 mmol, 1 eq) and [Rh(CO)₂Cl]₂ (36 mg, 0.09 mmol, 0.5 eq) were submitted into an oven-dried Schlenk flask. Under a flow of argon, THF (5 mL) was added and the solution was stirred at room temperature over night. The solvent was removed under reduced pressure and the residue was suspended in Et₂O (5 mL). The solution was filtrated over celite. The filter cake was extracted with Et₂O (2x 5 mL). The solvent in the residue was removed under reduced pressure yielding 3c-Rh(CO)₂Cl a pale yellow powder in a pure form (0.04 mmol, 41%, 40 mg).

Single crystals suitable for X-ray diffractometry were obtained as yellow plates by slow diffusion of n-pentane at room temperature into a concentrated solution of the product in toluene over the course of several weeks.

**1H-NMR** (250 MHz, C₆D₆) δ: 6.83 (s, Aryl-H, 2H), 6.68 (s, Aryl-H, 2H), 2.96 (s, br., =NH, 1H), 2.68 (s, Trz-CH₃, 3H), 2.18 (s, Aryl-o-CH₃, 12H), 2.14 (s, Aryl-p-CH₃, 3H), 2.03 (s, Aryl-p-CH₃, 3H).

**13C-NMR** (63 MHz, C₆D₆) δ: 184.7 (d, JCRH = 65 Hz, Rh-CO), 180.8 (d, JCRH = 74 Hz, Rh-CO), 151.7, 140.1, 140.0, 139.0, 135.7, 128.8, 128.1, 128.0, 120.4, 119.2, 35.0, 20.1, 19.9, 19.1, 16.7.

**EA:** calc. (C₂₃H₂₂ClN₄O₂Rh, 528.84 g/mol) C 52.24, H 4.96, N 10.59; found C 52.23, H 4.98, N 10.51.

**MS (EI):** m/z = 528.1 [M]+.
**Supporting Information**

Figure S1. $^1$H-NMR-spectrum of 1b (CDCl$_3$, 500 MHz).

Figure S2. $^{13}$C($^1$H)NMR-spectrum of 1b (CDCl$_3$, 126 MHz).
Figure S3. $^1$H-NMR-spectrum of 1c (CDCl$_3$, 700 MHz).

Figure S4. $^{13}$C($^1$H)-NMR-spectrum of 1c (CDCl$_3$, 176 MHz).
Figure S5. $^1$H-NMR-spectrum of 1d (CDCl$_3$, 250 MHz).

Figure S6. $^{13}$C($^1$H)-NMR-spectrum of 1d (CDCl$_3$, 63 MHz).
Figure S7. $^1$H-NMR-spectrum of the reaction of 1d with m-CPBA (CDCl$_3$, 250 MHz).

Figure S8. $^1$H-NMR-spectrum of 2a (CDCl$_3$, 500 MHz).
Figure S9. $^{13}$C($^1$H)-NMR-spectrum of 2a (CDCl$_3$, 126 MHz).

Figure S10. $^1$H-NMR-spectrum of 1d (CD$_3$CN, 700 MHz).
Figure S11. $^1$H-NMR-spectrum of 2b (CDCl$_3$, 500 MHz).

Figure S12. $^{13}$C[$^1$H]-NMR-spectrum of 2b (CDCl$_3$, 126 MHz).
Figure S13. $^1$H-NMR-spectrum of 2c (CDCl$_3$, 700 MHz).

Figure S14. $^{13}$C[1H]-NMR-spectrum of 2c (CDCl$_3$, 176 MHz).
Figure S15. $^1$H-NMR-spectrum of 2d (CD$_3$CN, 500 MHz).
Figure S16. $^{13}$C($^1$H)-NMR-spectrum of 2d (CD$_3$CN, 126 MHz).

Figure S17. $^{19}$F-NMR-spectrum of 2d (CD$_3$CN, 235 MHz).
Figure S18. $^1$H-NMR-spectrum of 3a ($C_6D_6$, 250 MHz).

Figure S19. $^{13}$C($^1$H)-NMR-spectrum of 3a ($C_6D_6$, 126 MHz).
Figure S20. $^1$H-NMR-spectrum of 3a (CD$_3$CN, 400 MHz).

Figure S21. $^{13}$C($^1$H)-NMR-spectrum of 3a (CD$_3$CN, 126 MHz).
Figure S22. $^1$H-NMR-spectrum of 3a (CD$_2$Cl$_2$, 250 MHz).

Figure S23. $^1$H-NMR-spectrum of 3b (CD$_6$D$_6$, 500 MHz).
Figure S24. $^{13}$C($^1$H)-NMR-spectrum of $3b$ (CD$_6$D$_6$, 126 MHz).

Figure S25. $^1$H-NMR-spectrum of $3c$ (CD$_6$D$_6$, 500 MHz).
Figure S26. $^{13}$C($^1$H)-NMR-spectrum of 3c (C6D6, 126 MHz).

Figure S27. $^1$H-NMR-spectrum of 5a (CD2Cl2, 700 MHz).
Figure S28. $^{13}$C($^1$H)-NMR-spectrum of 5a (CD$_2$Cl$_2$, 176 MHz).

Figure S29. $^1$H-NMR-spectrum of 5b (CD$_2$Cl$_2$, 500 MHz).
Figure S30. $^{13}$C($^1$H)-NMR-spectrum of 5b (CD$_2$Cl$_2$, 126 MHz).

Figure S31. $^1$H-NMR-spectrum of 5d (CD$_3$CN, 700 MHz).
Figure S32. $^{13}$C($^{1}$H)-NMR-spectrum of 5d (CD$_3$CN, 176 MHz).

Figure S33. $^{1}$H-NMR-spectrum of 5d-acetone (acetone-d$_6$, 500 MHz).
Figure S34. $^{13}$C($^1$H)-NMR-spectrum of 5d-acetone (acetone-d6, 126 MHz).

Figure S35. $^1$H-NMR-spectrum of 3c-Rh(CO)$_2$Cl (C$_6$D$_6$, 250 MHz).
Figure S36. $^{13}$C($^1$H)-NMR-spectrum of 3c-Rh(CO)$_2$Cl (C$_6$D$_6$, 63 MHz).

4. IR-Spectra

Figure S37. FTIR-spectrum of 1a (powder ATR-unit).
Figure S38. FTIR-spectrum of 2a (powder ATR-unit).

Figure S39. FTIR-spectrum of 3a (powder ATR-unit).
Figure S40. FTIR-spectrum of 3c-Rh(CO)$_2$Cl (CH$_2$Cl$_2$, CaF$_2$-windows).

\[
\nu_{av} = \frac{1985 \text{ cm}^{-1} + 2067 \text{ cm}^{-1}}{2} = 2026 \text{ cm}^{-1}
\]

\[
\text{TEP} = 0.8001 \cdot \nu_{av} + 420.0 \text{ cm}^{-1} = 2041 \text{ cm}^{-1}
\]

5. Detailed discussion of the crystallographic and spectroscopic data of 1-3

The crystallographic data shows (Table 1), that the relevant C1-N4 bond length is in the same range for the respective 1,4-diphenyl (1a-3a) and 1,4-dimesityl (1c-3c) substituted triazole-compounds indicating that the in the manuscript aforementioned hydrogen bonding interactions have no influence on the C1-N4 bond order. A structural similarity is also observed between the precursors (1a,c and 2a,c) when comparing the relevant chemical shift of the N-H proton (Table 1). The imines 3a and 3c on the other hand show significant differences in the shift of the N-H proton in the $^1$H-NMR-spectra. Compared to the bisphenyl substituted imine 3a (4.78/5.49 ppm (CD$_3$CN/C$_6$D$_6$)) the N-H proton in 3c (2.33/3.48 ppm (CD$_3$CN/C$_6$D$_6$)) resonates at higher frequencies. This behaviour is attributed to the intermolecular N4-H4⋯N4'-H4'⋯ interactions found in 3a.

Compared to the triazolium salt 2a, the $^1$H-NMR-spectrum of 3a shows one signal with an integral of 2 (relative to $^6$H(N-CH$_3$)) shifted to significantly higher frequencies while two distinct signals with a relative integral of 1 in each case are shifted towards lower frequencies (Figure S41). This behaviour is explained by the previously illustrated intramolecular interactions of the respective ortho-hydrogen atoms in the phenyl moieties with the exocyclic N-fragment. Breaking of the C$_2$-symmetry in the phenyl substituents is a direct result of these interactions. Hence the downfield-shifted signals are assigned to the C10/C8-H8A/H10⋯N4 protons. The upfield-shifted signals are assigned accordingly to the remaining set of ortho-hydrogen atoms, which are not facing the exocyclic N-fragment.
6. Complexation reactions

6.1 Preparation of 3a-CO₂ solutions

The ligand 3a (10 mg, 0.04 mmol, 1 eq) was submitted into an oven-dried Schlenk-flask. Under a flow of argon the ligand was dissolved in CD₃CN (1.5 mL) and then transferred into two NMR-tubes (0.5 mL respectively). ¹H and ¹³C-NMR-measurements were conducted with the first sample. The second sample was gassed with a mild flow of CO₂-Gas for 10 minutes (0.5 bar) until the solution was colourless. ¹H and ¹³C-NMR-spectra were recorded with this sample:

¹H-NMR (400 MHz, CD₃CN) δ: 7.76 (m, Aryl-H, 2H), 7.59-7.47 (m, Aryl-H, 8H), 3.96 (s, Trz-CH₃, 3H).

¹³C-NMR (101 MHz, CD₃CN) δ: 134.8, 130.2, 129.5, 129.4, 129.0, 124.2, 123.53, 38.4 (N-CH₃).
Figure S42. $^1$H-NMR-spectrum of (CD$_3$CN, 400 MHz). Bottom: 3a. Top: 3a after gassing with CO$_2$-gas.

Figure S43. $^{13}$C($^1$H)-NMR-spectrum (CD$_3$CN). Bottom: 3a (126 MHz). Top: 3a after gassing with CO$_2$-gas (101 MHz).

The sample was then flushed with argon-gas for 10 minutes resulting in a bright yellow coloured solution. $^1$H and $^{13}$C-NMR-spectra were recorded again with this sample yielding the native spectrum of the first sample.
The ligand 3a (20 mg, 0.08 mmol, 1 eq) was submitted into an oven-dried Schlenk-flask. Under a flow of argon the ligand was dissolved in a mixture of toluene (3 mL) and n-pentane (3 mL). CO$_2$-gas (1 bar) was bubbled through the solution for 1 hour. The formed precipitated was separated from the solution by transfer onto a frit via CO$_2$-pressure and Teflon tubing. The filter cake was washed n-pentane (2x 3 mL) and then dried by a mild flow of CO$_2$-Gas for 1 hour. IR-measurements of the solid with an ATR-unit were conducted immediately.

Figure S44. FTIR-spectrum of 3a and 3a-CO$_2$ (powder ATR-unit).

6.2 Preparation of 3a-B(C$_6$F$_5$)$_3$

Synthesis of 3a-B(C$_6$F$_5$)$_3$

The ligand 3a (16 mg, 0.06 mmol, 1 eq) and B(C$_6$F$_5$)$_3$ (33 mg, 0.06 mmol, 1 eq) were submitted into an oven-dried Schlenk-flask and cooled to 0 °C. C$_6$D$_6$ (1 mL) was added under a flow of argon and the solution was stirred for 10 minutes. The solution was allowed to warm to room temperature and was stirred over night at room temperature. The resulting colourless solution was investigated.

Single crystals suitable for X-ray diffractometry were obtained by slow diffusion of hexane into a solution of 3a-B(C$_6$F$_5$)$_3$ in toluene at room temperature of the course of several days.

$^1$H-NMR (400 MHz, C$_6$D$_6$) δ: 7.02-6.83 (m, Phenyl-H, 6H), 6.72-6.63 (m, Phenyl-H, 2H), 4.93 (s, Trz=N(H)-BAryl, 1H), 2.43 (s, N-CH$_3$, 3H).

One set of signals can not be assigned as they collapse with the residual solvent signal.
SUPPORTING INFORMATION

$^{11}$B-NMR (128 MHz, C$_6$D$_6$) δ: -9.1 (s).

$^{13}$C-NMR (101 MHz, C$_6$D$_6$) δ: 146.9, 132.1, 131.4, 130.3, 130.1, 129.0, 128.5, 125.2, 123.7, 122.2, 37.1.

$^{13}$C-NMR (176.1 MHz, C$_6$D$_6$) δ: 168.9, 147.5 (dm, $^1$J$_{CF}$ = 241 Hz), 138.6 (dm, $^1$J$_{CF}$ = 248 Hz), 136.2 (ddd, $^1$J$_{CF}$ = 248 Hz, $^2$J = 20 Hz, $^3$J = 12 Hz).

$^{19}$F-NMR (376 MHz, C$_6$D$_6$) δ: -134.2 (d, $^3$J$_{FF}$ = 20 Hz), -159.3 (t, $^3$J$_{FF}$ = 21 Hz), -164.5 (dt, $^3$J$_{FF}$ = 22 Hz, $^4$J$_{FF}$ = 8 Hz).

MS (ESI): m/z = 251.13 [PhPh=NH+H]$^+$, 761.10 [M-H$^-$], 785.10 [M+Na$^+$].

HRMS (ESI): calc. (C$_{33}$H$_{14}$BF$_{15}$N$_4$), m/z = 761.1005 [M-H$^-$], 785.0970 [M+Na$^+$], found m/z = 761.1003 [M-H$^-$], 785.0964 [M+Na$^+$].

IR-measurements were conducted of the resulting residue after removal of the solvent under reduced pressure.

FTIR (ATR, solid) ν: 1644 (C$_{Trz}$-N$_{exo}$).

Figure S45. $^1$H-NMR-spectrum of 3a-B(C$_{6}$F$_5$)$_3$ (C$_6$D$_6$, 400 MHz).
Figure S46. $^{11}$B($^1$H)-NMR-spectrum of 3a-B(C$_6$F$_5$)$_3$ (C$_6$D$_6$, 80 MHz).

Figure S47. $^{13}$C($^1$H)-NMR-spectrum of 3a-B(C$_6$F$_5$)$_3$ (C$_6$D$_6$, 101 MHz).
Figure S48. $^{19}$F-NMR-spectrum of 3a-B(C$_6$F$_5$)$_3$ (C$_6$D$_6$, 376 MHz).

Figure S49. FTIR-spectrum of 3a-B(C$_6$F$_5$)$_3$ (powder ATR-unit).
6.3 Crystallographic data of Ir half sandwich complexes

Table S1. Selected crystallographic parameters for Ir-Cp* complexes, the ligand 3a, the precursor 2a and the adduct 3a-B(C,F)3.

|                  | 2a  | 3a  | 3a-B(C,F)3 | 5a  | 5b  | 5d  |
|------------------|-----|-----|------------|-----|-----|-----|
| C1-N4 [Å]        | 1.353(3) | 1.296(2) | 1.343(6) | 1.312(3) | 1.307(3) | 1.322(2) |
| N4-Ir1 [Å]       | -   | -   | -          | 2.068(2) | 2.055(2) | 2.096(2) |
| Cp-Ir1 [Å]       | -   | -   | -          | 1.820(1) | 1.820(1) | 1.808(1) |
| C_{Phenyl}-Ir1 [Å]| -   | -   | -          | 2.053(2) | 2.062(3) | 2.062(3) |
| C1-N4-Ir1 [°]    | -   | -   | -          | 123.6(2) | 123.1(2) | 117.4(2) |

6.4 Preparation of 4/4' solutions

The Ligand 3a (11 mg, 0.04 mmol, 1 eq) was submitted into an oven-dried Schlenk-flask. Under a flow of argon, the ligand was dissolved in THF (7 mL). The solution was degassed by bubbling argon-gas through the solution for 10 minutes. [Ir(COD)Cl]2 (16 mg, 0.02 mmol, 0.5 eq) was added as a solid and the solution was stirred over night at room temperature. The solvent was removed under reduced pressure and the residue was dissolved in CD2Cl2 (2 mL). The solution was transferred into three different NMR-tubes (0.5 mL respectively). Into the first two samples either a drop of Et3N or a drop ethereal HCl-solution were submitted. 1H-NMR-measurments were conducted immediately. Temperature-dependent 1H-NMR-measurments were conducted on an Avance 400 from Bruker with the third sample.

Scheme S1. Proposed reaction of 3a with [Ir(COD)Cl]2 according to found fragments by HRMS.
Figure S51. HRMS-spectrum of 3a-Ir(COD)Cl.
Figure S52. HRMS-spectrum of 3a-Ir(COD)Cl.
Figure S53. $^1$H-NMR-spectra of 3a and [Ir(COD)Cl]$_2$ (CD$_2$Cl$_2$, 400 MHz). a) native. b) + Et$_3$N. c) + HCl in EtO.

Scheme S2. Determined equilibrium between 4 and 4'.
Figure S54. Selected parts of temperature-dependant ¹H-NMR-measurements from the reaction mixture of 3a with [Ir(COD)Cl]₂ in CD₂Cl₂ (400 MHz). Left: Region of the exocyclic protons. Right: Region of N-CH₃.

The equilibrium constant $K = \frac{[\text{I}]}{[\text{II}]}$ for the equilibrium according to scheme 2 can be calculated by the relative integrals of either the exocyclic protons ($K_{\text{exo}}$) and the CH₃-protons ($K_{\text{Me}}$). The values are summarised in the following table:

**Table S2. Temperature-dependant equilibrium constants.**

| $T$ (K) | $\frac{1}{T}$ | $K_{\text{exo}}$ | $\ln K_{\text{exo}}$ | $K_{\text{Me}}$ | $\ln K_{\text{Me}}$ |
|---------|----------------|------------------|----------------------|----------------|------------------|
| 303     | 3.30           | 1.26             | 0.23                 | 1.26           | 0.23             |
| 283     | 3.53           | 1.20             | 0.18                 | 1.21           | 0.19             |
| 263     | 3.80           | 1.13             | 0.12                 | 1.09           | 0.09             |
| 243     | 4.12           | 1.03             | 0.03                 | 1.03           | 0.03             |
| 223     | 4.48           | 0.94             | -0.06                | 0.91           | -0.09            |
| 203     | 4.93           | 0.88             | -0.13                | 0.86           | -0.15            |
| 183     | 5.46           | 0.75             | -0.29                | 0.75           | -0.29            |

According to van't Hoff the equilibrium constant and temperature can be set in a relation to

$$\ln K = -\frac{\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R}$$
with $\Delta H$: enthalpy and $\Delta S$: entropy.

Linear regression of the resulting van’t Hoff plots:

**Figure S55.** Van’t-Hoff plot of the equilibrium shown in scheme 2 according to the exocyclic protons

**Figure S56.** Van’t-Hoff plot of the equilibrium shown in scheme 2 according to the methyl protons
Examination of the van’t Hoff plot leads to:

Table S3. Determined thermodynamic data for the equilibrium shown in scheme 2.

|       | $\Delta H$ [J mol$^{-1}$] | $\Delta S$ [J mol$^{-1}$ K$^{-1}$] |
|-------|--------------------------|----------------------------------|
| Fehler! | 1966 ± 0.90               | 8.42 ± 0.004                    |
| Fehler! | 2004 ± 1.36               | 8.48 ± 0.006                    |

6.5 Preparation of 2a(Cl)

The triazolium chloride of 2a was generated by the reaction of 3a (5 mg, 0.02 mmol) with one drop of ethereal HCl-solution using CD$_2$Cl$_2$ (0.5 mL) as the solvent in an NMR-tube. $^1$H-NMR-measurements were conducted before and after addition of ethereal HCl.
7. Computational details

All calculations were performed using the ORCA 4.2.1 program.\textsuperscript{[11]} Geometry optimizations were carried out using the PBE0 functional\textsuperscript{[12]} with def2-SVP basis sets\textsuperscript{[13]} on all atoms, starting from the X-ray determined structures, except for the 3a-CO\textsubscript{2} adduct. The optimized structures were used for single point and frequency calculations with the PBE0 functional and def2-TZVP basis sets. For complex 3a-B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, the optimized structure was employed in single-point (but not frequency) calculations, using the PBE0 functional and def2-TZVP basis sets, in order to calculate the electron density difference between the full complex and its 3a and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} fragments, according to a methodology previously reported by our group.\textsuperscript{[14]} Implicit solvation by CH\textsubscript{2}Cl\textsubscript{2} was taken into account using the SMD method\textsuperscript{[14]} together with the CPCM model.\textsuperscript{[15]} The resolution-of-the-identity (RI) approximation\textsuperscript{[16]} with matching basis sets (def2/J),\textsuperscript{[17]} as well as the RJCOSX approximation (combination of RI and chain-of-spheres algorithm for exchange integrals) were used to reduce the time of calculations. The optimized structures were confirmed to be minima by the absence of imaginary vibrational frequencies. Orbital and electron density isosurfaces were plot with Chemcraft.\textsuperscript{[18]}

Frontier orbitals for the studied molecules

Figures S55 to S61 show the HOMO and LUMO orbitals of each of the calculated molecules.
Figure S58. Isosurfaces corresponding to the HOMO (top) and LUMO (bottom) orbitals of the cation in compound 2a. Isovalue = 0.03.
Figure S59. Isosurfaces corresponding to the HOMO (top) and LUMO (bottom) orbitals of 3a. Isovalue = 0.03
**Figure S60.** Isosurfaces corresponding to the HOMO (top) and LUMO (bottom) orbitals of 1a. Isovalue = 0.03
Figure S61. Isosurfaces corresponding to the HOMO (top) and LUMO (bottom) orbitals of MIC-a. Isovalue = 0.03.
Figure S62. Isosurfaces corresponding to the HOMO (top) and LUMO (bottom) orbitals of 3c. Isovalue = 0.03.
Figure S63. Isosurfaces corresponding to the HOMO (left) and LUMO (right) orbitals of 3a-B(C6F5)3. Isovalue = 0.03.
Figure S64. Isosurfaces corresponding to the HOMO (top) and LUMO (bottom) orbitals of 3a-CO$_2$. Isovalue = 0.03.

Table S4. Single-point and Gibbs Free Energies (in Ha) and absolute HOMO and LUMO energies, as well as their difference $\Delta_{HL}$ in cm$^{-1}$, for selected compounds studied computationally.

|       | HOMO (cm$^{-1}$) | LUMO (cm$^{-1}$) | $\Delta_{HL}$ (cm$^{-1}$) | Gibbs (Ha) |
|-------|-----------------|-----------------|--------------------------|------------|
| (2a)  | -57353          | -16750          | 40602                    | -798.632   |
| (3a)  | -42821          | -11458          | 31363                    | -798.165   |
| (1a)  | -48425          | -7238           | 41186                    | -758.948   |
| (MIC-a)| -52296          | -11579          | 40717                    | -742.829   |
| (3a-B(C$_6$F$_3$)$_3$) | -51056          | -13634          | 37422                    | -3001.746$^a$ |
### Optimized Geometries

#### 2a – I

|   |   |   |   |
|---|---|---|---|
| N  | -3.209478000000 | 2.880808000000 | -2.607647000000 |
| N  | -3.302668000000 | 1.748533000000 | -1.956927000000 |
| C  | -3.871451000000 | 2.180166000000 | -0.653340000000 |
| N  | -3.611861000000 | 3.518356000000 | -0.672256000000 |
| C  | -3.677782000000 | 4.438761000000 | 0.414194000000 |
| C  | -4.825487000000 | 4.863380000000 | 1.205093000000 |
| C  | -2.587174000000 | 5.275232000000 | 0.649928000000 |
| C  | -4.870056000000 | 5.386300000000 | 1.205093000000 |
| C  | -2.653984000000 | 6.181524000000 | 1.704286000000 |
| C  | -3.789704000000 | 6.235630000000 | 2.513810000000 |
| H  | -5.677370000000 | 3.838580000000 | 0.989750000000 |
| H  | -1.703016000000 | 5.209540000000 | 0.013371000000 |
| H  | -5.762777000000 | 5.437164000000 | 2.892551000000 |
| H  | -1.807605000000 | 6.843801000000 | 1.898787000000 |
| N  | -4.319454000000 | 1.502520000000 | 0.418191000000 |
| C  | -2.826710000000 | 3.017285000000 | -4.000004000000 |
| H  | -1.752835000000 | 2.819846000000 | -4.113198000000 |
| H  | -3.408387000000 | 2.309200000000 | -4.600429000000 |
| H  | -3.050272000000 | 4.045800000000 | -4.306905000000 |

#### 3a

|   |   |   |   |
|---|---|---|---|
| N  | -2.909383000000 | 2.751155000000 | -2.443031000000 |
| N  | -2.895989000000 | 3.805171000000 | -1.692850000000 |
| C  | -3.549694000000 | 1.687117000000 | -1.956927000000 |
| C  | -4.015514000000 | 2.124344000000 | -0.816124000000 |
| N  | -3.550993000000 | 3.454278000000 | -0.578924000000 |
| C  | -3.694421000000 | 4.421621000000 | 0.437829000000 |
| C  | -4.399519000000 | 4.131618000000 | 1.613113000000 |
| C  | -3.119588000000 | 5.689933000000 | 0.259292000000 |
| C  | -4.522272000000 | 5.112450000000 | 2.596917000000 |
| C  | -3.254701000000 | 6.653741000000 | 1.253057000000 |
| C  | -3.955826000000 | 6.374010000000 | 2.427950000000 |
| H  | -4.833685000000 | 3.138900000000 | 1.727426000000 |
| H  | -2.570973000000 | 5.911807000000 | -0.856482200000 |
| H  | -5.074167000000 | 4.877991000000 | 3.510934000000 |
| H  | -2.803840000000 | 7.638041000000 | 1.103720000000 |
| H  | -4.058149000000 | 7.135754000000 | 3.204520000000 |
| H  | -3.735759000000 | 6.382730000000 | -2.528850000000 |
| C  | -2.723907000000 | -0.255232000000 | -3.269803000000 |
| C  | -4.963798000000 | -0.286347000000 | -2.361637000000 |
| C  | -2.943349000000 | -1.506346000000 | -3.839330000000 |
| C  | -5.172521000000 | -1.542273000000 | -2.924079000000 |
| C  | -4.165809000000 | -2.157050000000 | -3.669454000000 |
| H  | -1.746522000000 | 0.216614000000 | -3.381742000000 |
| H  | -1.769667000000 | 0.196363000000 | -1.803717000000 |
| H  | -2.143547000000 | -1.983786000000 | -4.411532000000 |
| Atom | X-Coord  | Y-Coord  | Z-Coord  |
|------|----------|----------|----------|
| H    | -6.135516 | -2.040384 | -2.786604 |
| H    | -4.331531 | -3.141947 | -4.112369 |
| N    | -4.673483 | 1.548349  | 0.337732  |
| H    | -4.858158 | 0.580584  | 0.077579  |
| C    | -2.278221 | 2.850571  | -3.742766 |
| H    | -1.250339 | 2.466882  | -3.697558 |
| H    | -2.859320 | 2.267922  | -4.474204 |
| H    | -2.630720 | 3.909659  | -4.022377 |

| Atom | X-Coord  | Y-Coord  | Z-Coord  |
|------|----------|----------|----------|
| N    | -4.392309 | 2.841426  | -2.563545 |
| N    | -4.389963 | 3.867250  | -1.826215 |
| C    | -4.764473 | 1.715352  | -1.814207 |
| C    | -4.648965 | 2.121743  | -0.478839 |
| N    | -4.743287 | 3.478011  | -0.542305 |
| C    | -4.709866 | 4.432655  | 0.499800  |
| C    | -4.345829 | 4.221002  | 1.704998  |
| N    | -3.532410 | 6.536120  | 2.509292  |
| C    | -4.939184 | 3.317436  | 1.853777  |
| H    | -2.418812 | 5.745728  | -0.661072 |
| H    | -4.789455 | 5.014980  | 2.898520  |
| H    | -2.302100 | 7.477504  | -2.710234 |
| H    | -2.363434 | 2.813281  | -4.474204 |

| Atom | X-Coord  | Y-Coord  | Z-Coord  |
|------|----------|----------|----------|
| N    | -2.928387 | 2.795120  | -2.503191 |
| N    | -2.915703 | 3.842249  | -1.735610 |
| C    | -3.614348 | 1.753964  | -1.930138 |
| C    | -4.099845 | 2.183950  | -0.685937 |
| N    | -4.601171 | 3.462888  | -0.867436 |
| C    | -3.770185 | 4.412080  | 0.831019  |
| C    | -4.811076 | 1.045185  | -4.175080 |
| H    | -2.691505 | 2.823251  | -1.789918 |
| H    | -4.823975 | 5.018500  | -5.257265 |
| H    | -3.778860 | 5.343520  | -4.109784 |
| H    | -3.076357 | 1.880870  | 1.461787  |

| Atom | X-Coord  | Y-Coord  | Z-Coord  |
|------|----------|----------|----------|
| H    | -3.343996 | 0.447041  | 0.613544  |
| N    | -3.923960 | 2.841426  | -2.563545 |
| N    | -3.899632 | 3.867250  | -1.826215 |
| C    | -3.764473 | 1.715352  | -1.814207 |
| C    | -3.648965 | 2.121743  | -0.478839 |
| N    | -3.743287 | 3.478011  | -0.542305 |
| C    | -3.670986 | 4.432655  | 0.499800  |
| C    | -4.345829 | 4.221002  | 1.704998  |
| N    | -3.532410 | 6.536120  | 2.509292  |
| C    | -4.939184 | 3.317436  | 1.853777  |
| H    | -2.418812 | 5.745728  | -0.661072 |
| H    | -4.789455 | 5.014980  | 2.898520  |
| H    | -2.302100 | 7.477504  | -2.710234 |
| H    | -2.363434 | 2.813281  | -4.474204 |

| Atom | X-Coord  | Y-Coord  | Z-Coord  |
|------|----------|----------|----------|
| C    | -3.804677 | 6.961479  | 3.261915  |
| C    | -3.804677 | 6.961479  | 3.261915  |
| C    | -2.812791 | -0.192284 | -3.325960 |
| C    | -5.021910 | -0.228358 | -2.347571 |
| C    | -3.042530 | -1.450631 | -3.879154 |
| C    | -5.245184 | -1.486260 | -2.898533 |
| C    | -4.258445 | -2.100649 | -3.671922 |
| H    | -1.839858 | 0.279670  | -3.470004 |
| H    | -5.790592 | 0.256698  | -1.743055 |
| H    | -2.257313 | -1.930330 | -4.468859 |
| H    | -6.199610 | -1.989670 | -2.726179 |
| H    | -4.435089 | -3.087389 | -4.106797 |
| C    | -2.284014 | 2.890128  | -3.796657 |
| H    | -2.854831 | 2.307560  | 4.529105  |
### SUPPORTING INFORMATION

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | -2.270034  | 3.945293   | -4.091455  |
| H    | -1.254044  | 2.512290   | -3.741461  |
| C    | -3.882438  | 2.945859   | -2.652887  |
| N    | -3.894864  | 4.000326   | -1.900681  |
| C    | -3.809771  | 1.771872   | -1.977392  |
| C    | -3.757282  | 2.125722   | -0.589047  |
| C    | -4.818042  | 4.491284   | 1.342376   |
| C    | -2.608146  | 5.239387   | 0.571826   |
| C    | -4.721261  | 5.387670   | 2.408410   |
| H    | -5.547807  | 5.445401   | 3.122675   |
| C    | -3.784717  | 0.432734   | -2.576785  |
| C    | -2.684980  | -0.005633  | -3.344286  |
| C    | -4.867902  | -0.445959  | -2.327141  |
| C    | -2.697313  | -1.305340  | -3.864936  |
| H    | -1.840895  | -1.643678  | -4.456007  |
| C    | -3.680553  | 1.467566   | 0.527251   |
| H    | -3.609953  | 0.472056   | 0.314142   |
| C    | -3.964636  | 3.123502   | -4.086589  |
| H    | -2.983921  | 3.413440   | -4.486233  |
| C    | -3.539401  | 7.171863   | 3.733280   |
| H    | -4.374130  | 7.890689   | 3.702114   |
| C    | -3.613759  | 6.638350   | 4.695162   |
| C    | -2.600371  | 7.743099   | 3.733010   |
| C    | -1.471275  | 5.153108   | 0.851671   |
| C    | -5.728275  | 2.560920   | 1.305799   |
| C    | -6.808796  | 3.873691   | 1.882288   |
| C    | -3.593401  | 7.171863   | 3.733280   |
| H    | -4.374130  | 7.890689   | 3.702114   |
| C    | -3.613759  | 6.638350   | 4.695162   |
| C    | -2.600371  | 7.743099   | 3.733010   |
| C    | -1.471275  | 5.153108   | 0.851671   |
| C    | -5.728275  | 2.560920   | 1.305799   |
| C    | -6.808796  | 3.873691   | 1.882288   |

### 3a-B(CF₃)₂

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| F    | 11.073570  | 4.168614   | 10.263553  |
| F    | 7.088866   | 5.070043   | 11.862261  |
| F    | 8.305268   | 0.779643   | 8.449576   |
| F    | 9.813045   | 5.289750   | 7.907728   |
| F    | 9.193618   | 2.863628   | 6.613640   |
| F    | 10.208909  | 7.893740   | 8.445363   |
| F    | 9.051403   | 9.100727   | 10.593680  |
| F    | 7.489815   | 7.642065   | 12.274377  |
| F    | 5.475790   | 4.399160   | 9.120990   |
| F    | 7.763988   | 3.050970   | 4.413092   |
| F    | 12.865488  | 0.032627   | 9.113050   |
| F    | 4.057575   | 4.549899   | 6.886575   |
|   |   |   |   |
|---|---|---|---|
| F | 5.175393000000 | 3.885141000000 | 4.492246000000 |
| C | 8.856326000000 | 7.806919000000 | 10.370323000000 |
| C | 7.872670000000 | 5.699469000000 | 10.986180000000 |
| C | 5.447799000000 | 5.031858000000 | 9.903148000000 |
| C | 9.480361000000 | 1.263237000000 | 8.873625000000 |
| C | 8.065140000000 | 7.059422000000 | 11.228933000000 |
| C | 6.088771000000 | 4.036812000000 | 7.981269000000 |
| C | 7.420434000000 | 5.835178000000 | 9.963538000000 |
| C | 9.220434000000 | 5.835178000000 | 9.963538000000 |
| C | 9.561018000000 | 2.566518000000 | 9.364123000000 |
| C | 10.562881000000 | 0.397777000000 | 8.775490000000 |
| C | 10.840248000000 | 2.962522000000 | 9.750739000000 |
| C | 5.317778000000 | 4.139228000000 | 6.828995000000 |
| C | 7.204231000000 | 3.367070000000 | 5.573740000000 |
| C | 5.884877000000 | 3.799650000000 | 5.606863000000 |
| B | 8.201580000000 | 0.957071000000 | 11.782930000000 |
| N | 6.627951200000 | -0.503084000000 | 11.782930000000 |
| N | 7.215576000000 | -0.093500000000 | 11.292130000000 |
| H | 5.867118000000 | 1.256940000000 | 10.341881000000 |
| C | 3.723320000000 | 0.530190000000 | 10.954746000000 |
| H | 3.723320000000 | 1.095352000000 | 8.222180000000 |
| C | 2.546360000000 | 0.301884000000 | 10.177288000000 |
| H | 1.613668000000 | 0.028965000000 | 10.676291000000 |
| C | 2.530260000000 | 0.742808000000 | 8.853790000000 |
| H | 1.583660000000 | 0.812340000000 | 8.312440000000 |
| H | 1.583660000000 | 1.095352000000 | 7.184536000000 |
| C | 6.111769000000 | -1.790322000000 | 11.948910000000 |
| H | 6.911779000000 | -2.509276000000 | 12.127840000000 |
| H | 5.550630000000 | -2.094926000000 | 12.786790000000 |
| H | 5.439476000000 | -2.094926000000 | 12.786790000000 |
| C | 11.774184000000 | 2.615884000000 | 13.238293000000 |
| H | 12.706769000000 | 3.049360000000 | 13.605120000000 |
| C | 11.742720000000 | 1.286271000000 | 12.818076000000 |
| H | 12.647845000000 | 0.675990000000 | 12.854749000000 |

3a-CO₂

| N | -3.724742000000 | 2.936328000000 | -2.598506000000 |
| N | -3.795793000000 | 3.987345000000 | -1.841123000000 |
| C | -3.635950000000 | 1.773302000000 | -1.897524000000 |
| C | -3.655191000000 | 2.167024000000 | -0.555137000000 |
| N | -3.734805000000 | 3.534604000000 | -0.605368000000 |
| C | 3.713917000000 | 4.814340000000 | 0.461438000000 |
| C | -4.553142000000 | 5.588617000000 | 0.389870000000 |
| C | -2.823086000000 | 4.305763000000 | 1.517669000000 |
| C | -4.497934000000 | 6.543009000000 | 1.403568000000 |
| C | -2.782982000000 | 5.263650000000 | 2.526412000000 |
| C | -3.617334000000 | 6.381281000000 | 2.473135000000 |
| H | 5.244693000000 | 5.694924000000 | -0.447531000000 |
| H | 4.718864000000 | 3.426729000000 | 1.554891000000 |
| H | 5.154657000000 | 7.414833000000 | 1.358359000000 |
| H | -2.089755000000 | 5.134701000000 | 3.360839000000 |
| H | -3.581335000000 | 7.128710000000 | 3.269280000000 |
8. Crystallographic data

Crystal data and structure refinement for 1a

![Figure S65. X-ray solid-state structure of 1a. Ellipsoids are all set at 50 % probability. Selected bond parameters in [Å] and [°]. C1-N4 1.362(2).](image)

Empirical formula: C_{14}H_{12}N_{4}

Formula weight: 236.28

CCDC Deposit Number: 2082293

Temperature: 140.0 K

Wavelength: 0.71073 Å

Crystal system: Orthorhombic

Space group: Pnma

Unit cell dimensions:

- \( a = 6.3776(5) \) Å, \( \alpha = 90^\circ \)
- \( b = 25.2845(19) \) Å, \( \beta = 90^\circ \)
- \( c = 7.1474(5) \) Å, \( \gamma = 90^\circ \)

Volume: 1152.55(15) Å³

Z: 4

Density (calculated): 1.362 g/m³

Absorption coefficient: 0.086 mm⁻¹
**SUPPORTING INFORMATION**

| Description                                      | Value                              |
|--------------------------------------------------|------------------------------------|
| F(000)                                           | 496                                |
| Crystal size                                     | 0.364 x 0.31 x 0.18 mm³            |
| Theta range for data collection                  | 1.611 to 28.338°                   |
| Index ranges                                     | -8 ≤ h ≤ 8, -33 ≤ k ≤ 19, -9 ≤ l ≤ 9 |
| Reflections collected                            | 10625                              |
| Independent reflections                          | 1475 [R(int) = 0.0273]             |
| ComPLEteness to theta = 25.242°                  | 99.9 %                             |
| Refinement method                                | Full-matrix least-squares on F²    |
| Data / restraints / parameters                    | 1475 / 52 / 96                     |
| Goodness-of-fit on F²                             | 1.087                              |
| Final R indices [I>2σ(I)]                        | R₁ = 0.0385, wR₂ = 0.0987          |
| R indices (all data)                             | R₁ = 0.0457, wR₂ = 0.1039          |
| Extinction coefficient                            | 0.012(2)                           |
| Largest diff. peak and hole                      | 0.310 and -0.166 eÅ⁻³              |

Crystal data and structure refinement for **1c**

![Chemical structure of 1c](image)

**Figure S66.** X-ray solid-state structure of **1c.** Ellipsoids are all set at 50 % probability. Selected bond parameters in [Å] and [°]. C1-N4 1.359(4).

| Property                             | Value                              |
|--------------------------------------|------------------------------------|
| Empirical formula                    | C₂₀H₄N₄                             |
| Formula weight                       | 320.43                             |
| CCDC Deposit Number                  | 2120117                            |
| Temperature                          | 139.99 K                           |
| Wavelength                           | 0.71073 Å                          |
| Crystal system                       | Monoclinic                         |
| Space group                          | P21/c                              |
| Unit cell dimensions                 | a = 16.110(2) Å, b = 7.5688(9) Å,  |
|                                     | c = 17.043(2) Å                    |
| Volume                               | 1854.5(5) Å³                       |
| Z                                    | 4                                  |
| Density (calculated)                 | 1.148 g/m³                         |
### Crystal data and structure refinement for 1d

| Property                                    | Value                        |
|---------------------------------------------|------------------------------|
| Empirical formula                          | C_{13}H_{11}N_{5}            |
| Formula weight                             | 237.266                      |
| CCDC Deposit Number                        | 2082294                      |
| Temperature                                | 140.01 K                     |
| Wavelength                                 | 0.71073 Å                    |
| Crystal system                             | Monoclinic                   |
| Space group                                | P2_1                         |
| Unit cell dimensions: a                    | 12.7186(13) Å               |
| Unit cell dimensions: b                    | 6.2494(6) Å                  |
| Unit cell dimensions: c                    | 15.5100(16) Å               |
| Volume                                      | 1131.5(2) Å³                |

**Figure S67.** X-ray solid-state structure of 1d. Ellipsoids are all set at 50 % probability.
SUPPORTING INFORMATION

Z 4
Density (calculated) 1.393 g/m³
Absorption coefficient 0.090 mm⁻¹
F(000) 496
Crystal size $0.419 \times 0.303 \times 0.188$ mm³
Theta range for data collection 12.86 to 52.68°.
Index ranges $-15 \leq h \leq 14$, $-6 \leq k \leq 7$, $-19 \leq l \leq 19$
Reflections collected 12808
Independent reflections 4147 [R_int = 0.0467, R_sigma = 0.0476]
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4147 / 109 / 328
Goodness-of-fit on F² 1.042
Final R indices [I≥2σ(I)] $R_1 = 0.1017$, $wR_2 = 0.2520$
R indices (all data) $R_1 = 0.1075$, $wR_2 = 0.2563$
Extinction coefficient 0.012(2)
Largest diff. peak and hole 0.45 and -0.67 eÅ⁻³

Crystal data and structure refinement for 1d-O

![Crystal structure diagram](image)

Figure S68. X-ray solid-state structure of 1d-O. Ellipsoids are all set at 50 % probability. Selected bond parameters in [Å] and [%]. C1-N4 1.345(3), N5-O1 1.342(2), O1-H4B 2.087(2), N5-O1-H4B 110.0(1).

**Empirical formula**
C₁₃H₁₁N₅O

**Formula weight**
253.27

**CCDC Deposit Number**
2082105

**Temperature**
140.01 K

**Wavelength**
0.71073 Å

**Crystal system**
Orthorhombic

**Space group**
P2₁2₁2₁

**Unit cell dimensions**

\[
\begin{align*}
a &= 8.5740(3) \text{ Å} & \alpha &= 90°. \\
b &= 10.3820(3) \text{ Å} & \beta &= 90°. \\
c &= 12.9176(4) \text{ Å} & \gamma &= 90°. \\
\end{align*}
\]

**Volume**
1149.86(6) Å³
Z 4
Density (calculated) 1.463 g/m³
Absorption coefficient 0.100 mm⁻¹
F(000) 528
Crystal size 0.283 × 0.232 × 0.082 mm³
Theta range for data collection 5.034 to 56.714°.
Index ranges -11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -16 ≤ l ≤ 17
Reflections collected 13138
Independent reflections 2866 [R_int = 0.0332, R_sigma = 0.0341]
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 2866 / 0 / 172
Goodness-of-fit on F² 1.046
Final R indices [I≥2σ(I)] R₁ = 0.0392, wR₂ = 0.0843
R indices (all data) R₁ = 0.0535, wR₂ = 0.0905
Largest diff. peak and hole 0.23 and -0.23 e.Å⁻³

Crystal data and structure refinement for 2a

Figure 69. X-ray solid-state structure of 1d-O. Ellipsoids are all set at 50 % probability. Selected bond parameters in [Å] and [°]. C1-N4 1.345(3), N5-O1 1.342(2), O1-H4B 2.087(2), N5-O1-H4B 110.0(1).

Empirical formula C₁₅H₁₅IN₄
Formula weight 378.21
CCDC Deposit Number 2082308
Temperature 293(2) K
Wavelength 0.71073 Å
Crystal system Monoclinic
Space group P2₁/c
Unit cell dimensions a = 10.6295(4) Å α = 90°.
b = 13.3791(4) Å β = 109.305(3)°.
SUPPORTING INFORMATION

Volume 1541.91(10) Å³
Z 4
Density (calculated) 1.629 Mg/m³
Absorption coefficient 2.073 mm⁻¹
F(000) 744
Crystal size n/a
Theta range for data collection 2.030 to 32.216°.
Index ranges -15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -17 ≤ l ≤ 17
Reflections collected 53467
Independent reflections 5174 [R(int) = 0.0838]
Completeness to theta = 25.242° 100.0 %
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 5174 / 0 / 190
Goodness-of-fit on F² 1.019
Final R indices [I>2σ(I)] R₁ = 0.0435, wR₂ = 0.1023
R indices (all data) R₁ = 0.0648, wR₂ = 0.1086
Extinction coefficient n/a
Largest diff. peak and hole 1.305 and -1.307 e Å⁻³

Crystal data and structure refinement for 2c

Empirical formula C₂₁H₂₇I₄N₄
Formula weight 462.36
CCDC Deposit Number 2085140
Temperature 140.00 K
Wavelength 0.71073 Å
Crystal system Orthorhombic
Space group Pbca
Unit cell dimensions a = 16.1756(7) Å α = 90°.
b = 14.5456(5) Å β = 90°.
c = 18.0224(8) Å γ = 90°.
Volume 4240.4(3) Å³
Z 8
Density (calculated) 1.449 g/m³
Absorption coefficient 1.522 mm⁻¹
F(000) 1872.0
Crystal size 0.328 × 0.189 × 0.074 mm³
Theta range for data collection 4.392 to 52.854°.
Index ranges -20 ≤ h ≤ 20, -17 ≤ k ≤ 18, -19 ≤ l ≤ 22
Reflections collected 41190
Independent reflections 4351 [R(int) = 0.0346, Rσ = 0.0252]
### Crystal data and structure refinement for $3a$

- **Empirical formula**: C$_{15}$H$_{14}$N$_4$
- **Formula weight**: 250.30
- **CCDC Deposit Number**: 2082090
- **Temperature**: 140.0 K
- **Wavelength**: 0.71073 Å
- **Crystal system**: Triclinic
- **Space group**: P-1
- **Unit cell dimensions**:
  - $a = 9.7738(6)$ Å
  - $b = 10.2222(7)$ Å
  - $c = 13.3134(10)$ Å
  - $\alpha = 102.721(3)^\circ$
  - $\beta = 99.497(3)^\circ$
  - $\gamma = 91.146(3)^\circ$
- **Volume**: 1277.51(15) Å$^3$
- **Z**: 4
- **Density (calculated)**: 1.301 Mg/m$^3$
- **Absorption coefficient**: 0.081 mm$^{-1}$
- **F(000)**: 528
- **Crystal size**: 0.266 x 0.24 x 0.11 mm$^3$
- **Theta range for data collection**: 1.592 to 28.349°
- **Index ranges**: $-12 \leq h \leq 13$, $-13 \leq k \leq 13$, $-17 \leq l \leq 17$
- **Reflections collected**: 27649
- **Independent reflections**: 6300 [R(int) = 0.0202]
- **Completeness to theta = 25.242°**: 99.5 %
- **Absorption correction**: Semi-empirical from equivalents
- **Max. and min. transmission**: 0.7457 and 0.7090
- **Refinement method**: Full-matrix least-squares on F$^2$
- **Data / restraints / parameters**: 6300 / 0 / 455
- **Goodness-of-fit on F$^2$**: 1.031
- **Final R indices [I>2sigma(I)]**: $R_1 = 0.0402$, $wR_2 = 0.0955$
- **R indices (all data)**: $R_1 = 0.0512$, $wR_2 = 0.1017$
- **Extinction coefficient**: n/a
- **Largest diff. peak and hole**: 0.292 and -0.229 e.Å$^{-3}$

### Crystal data and structure refinement for the co-crystallised system $3b-2b$
**Figure S70.** X-ray solid-state structure of the co-crystallised system 3b-2b. Ellipsoids are all set at 50 % probability. Selected bond parameters in [Å] and [°]. C1-N4 1.310(3), N4-H8A 1.918(2), C19-N8 1.332(3).

Empirical formula $C_{18}H_{20.5}I_{0.5}N_4$
Formula weight 356.33
CCDC Deposit Number 2082106
Temperature 140.0 K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group P-1
Unit cell dimensions
\[a = 11.3554(6) \text{ Å}, \quad \alpha = 110.781(3)^\circ,\]
\[b = 11.9738(6) \text{ Å}, \quad \beta = 100.372(2)^\circ,\]
\[c = 13.5185(7) \text{ Å}, \quad \gamma = 95.304(2)^\circ.\]

Volume 1665.82(15) Å$^3$
Z 4
Density (calculated) 1.421 g/m$^3$
Absorption coefficient 1.00 mm$^{-1}$
F(000) 732.0
Crystal size 0.286 × 0.263 × 0.12 mm$^3$
Theta range for data collection 3.31 to 56.726°.
Index ranges $-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-17 \leq l \leq 18$
Reflections collected 31570
Independent reflections 8210 [R(int) = 0.0362, R(sigma) = 0.0492]
Refinement method Full-matrix least-squares on F$^2$
Data / restraints / parameters 8210 / 0 / 417
Goodness-of-fit on F$^2$ 1.041
SUPPORTING INFORMATION

Final R indices \([I \geq 2\sigma(I)]\)

\[ R_1 = 0.0344, \text{ wR}_2 = 0.0619 \]

R indices (all data)

\[ R_1 = 0.0561, \text{ wR}_2 = 0.0685 \]

Largest diff. peak and hole

0.59 and -0.53 e Å\(^{-3}\)

Crystal data and structure refinement 3c

Empirical formula \( \text{C}_21\text{H}_{26}\text{N}_4 \)

Formula weight 334.46

CCDC Deposit Number 2093977

Temperature 139.99 K

Wavelength 0.71073 Å

Crystal system Triclinic

Space group P-1

Unit cell dimensions

\[ a = 7.727(1) \text{ Å} \quad \alpha = 79.150(8)^\circ. \]
\[ b = 8.394(2) \text{ Å} \quad \beta = 87.771(8)^\circ. \]
\[ c = 14.744(2) \text{ Å} \quad \gamma = 82.346(9)^\circ. \]

Volume 930.7(3) Å\(^3\)

Z 2

Density (calculated) 1.193 g/m\(^3\)

Absorption coefficient 0.072 mm\(^{-1}\)

\( F(000) \) 360.0

Crystal size 0.488 × 0.482 × 0.148 mm\(^3\)

Theta range for data collection 2.812 to 52.774°.

Index ranges \(-8 \leq h \leq 9, -10 \leq k \leq 10, -12 \leq l \leq 18\)

Reflections collected 14652

Independent reflections 3802 \([\text{R}_{\text{int}} = 0.0345, \text{ R}_{\text{sigma}} = 0.0358]\)

Data / restraints / parameters 3802 / 0 / 237

Goodness-of-fit on \( F^2 \) 1.076

Final R indices \([I \geq 2\sigma(I)]\)

\[ R_1 = 0.0631, \text{ wR}_2 = 0.1754 \]

R indices (all data)

\[ R_1 = 0.0828, \text{ wR}_2 = 0.1875 \]

Largest diff. peak and hole 0.34 and -0.35 e Å\(^{-3}\)

Crystal data and structure refinement for 3a-B(C\(_6\)F\(_5\))\(_3\)

Empirical formula \( \text{C}_{33}\text{H}_{14}\text{BF}_{15}\text{N}_4 \)

Formula weight 762.29

CCDC Deposit Number 2082091

Temperature 139.99 K

Wavelength 0.71073 Å

Crystal system Monoclinic

Space group \( \text{P2}_1/c \)

Unit cell dimensions

\[ a = 17.4558(7) \text{ Å} \quad \alpha = 90^\circ. \]
\[ b = 11.8190(5) \text{ Å} \quad \beta = 115.868(3)^\circ. \]
\[ c = 15.7702(6) \text{ Å} \quad \gamma = 90^\circ. \]

Volume 2927.5(2) Å\(^3\)

Z 4

Density (calculated) 1.730 g/m\(^3\)
Absorption coefficient: 1.527 mm$^{-1}$
F(000): 1520.0
Crystal size: 0.103 × 0.103 × 0.097 mm$^3$
Theta range for data collection: 5.626° to 125.99°
Index ranges: -19 ≤ h ≤ 20, -13 ≤ k ≤ 13, -15 ≤ l ≤ 18
Reflections collected: 15156
Independent reflections: 4589 [R$_{int}$ = 0.0447, R$_{sigma}$ = 0.0435]
Refinement method: Full-matrix least-squares on F$^2$
Data / restraints / parameters: 4589 / 0 / 479
Goodness-of-fit on F$^2$: 1.097
Final R indices [I≥2σ(I)]: R$_1$ = 0.0669, wR$_2$ = 0.1679
R indices (all data): R$_1$ = 0.0922, wR$_2$ = 0.2031
Largest diff. peak and hole: 0.98 and -0.38 e.A$^{-3}$

Crystal data and structure refinement for 4

**Figure S71.** X-ray solid-state structure of 4. Ellipsoids are all set at 50 % probability. Selected bond parameters in [Å] and [°]: C1-N4 1.29(2), N4-Ir1 2.02(2), C1-N4-Ir1 132(2), C10-N4-Ir1 87(1), C10-Ir1 2.08(2), C16/17-Ir1 2.01(1), C20/21-Ir1 2.01(1), C1-N3-C9-C10 4(2).

Empirical formula: C$_{23}$H$_{25}$IrN$_4$
Formula weight: 549.67
CCDC Deposit Number: 208378
Temperature: 293(3) K
Wavelength: 0.71073 Å
Crystal system: orthorhombic
Space group: Pna2$_1$
**SUPPORTING INFORMATION**

| Property                                      | Value                          |
|-----------------------------------------------|--------------------------------|
| Unit cell dimensions                          |                                |
| a = 7.3070(2) Å                               | α = 90°.                        |
| b = 26.2885(10) Å                             | β = 90°.                        |
| c = 10.1595(4) Å                             | γ = 90°.                        |
| Volume                                        | 1951.54(12) Å³                 |
| Z                                             | 4                              |
| Density (calculated)                         | 1.871 g/m³                     |
| Absorption coefficient                       | 6.858 mm⁻¹                     |
| F(000)                                        | 1072.0                         |
| Crystal size                                 | 1.0 × 0.3 × 0.2 mm³            |
| Theta range for data collection              | 3.098 to 64.204°.              |
| Index ranges                                 | -10 ≤ h ≤ 10, -38 ≤ k ≤ 37, -15 ≤ l ≤ 15 |
| Reflections collected                        | 32541                          |
| Independent reflections                      | 6178 [R_{int} = 0.0997, R_{sigma} = 0.0983] |
| Refinement method                            | Full-matrix least-squares on F² |
| Data / restraints / parameters                | 6178 / 25 / 243                |
| Goodness-of-fit on F²                         | 1.022                          |
| Final R indices [I≥2σ(I)]                    | R₁ = 0.0532, wR₂ = 0.1121     |
| R indices (all data)                         | R₁ = 0.1027, wR₂ = 0.1324     |
| Largest diff. peak and hole                  | 3.82 and -2.18 e.A⁻³           |

**Crystal data and structure refinement for 5a**

| Property                                      | Value                          |
|-----------------------------------------------|--------------------------------|
| Empirical formula                            | C₂₅H₂₈IrN₄                      |
| Formula weight                                | 703.61                         |
| CCDC Deposit Number                          | 2082129                        |
| Temperature                                  | 140.01 K                       |
| Wavelength                                   | 0.71073 Å                      |
| Crystal system                               | triclinic                      |
| Space group                                   | P-1                            |
| Unit cell dimensions                          |                                |
| a = 9.0988(17) Å                             | α = 84.348(8)°.                |
| b = 11.2121(19) Å                            | β = 75.139(9)°.                |
| c = 12.662(2) Å                              | γ = 87.321(8)°.                |
| Volume                                        | 1242.1(4) Å³                   |
| Z                                             | 2                              |
| Density (calculated)                         | 1.881 g/m³                     |
| Absorption coefficient                       | 6.636 mm⁻¹                     |
| F(000)                                        | 672.0                          |
| Crystal size                                 | 0.75 × 0.334 × 0.283 mm³       |
| Theta range for data collection              | 3.342 to 66.484°.              |
| Index ranges                                 | -13 ≤ h ≤ 14, -17 ≤ k ≤ 8, -19 ≤ l ≤ 19 |
| Reflections collected                        | 40477                          |
| Independent reflections                      | 9418 [R_{int} = 0.0295, R_{sigma} = 0.0246] |
| Refinement method                            | Full-matrix least-squares on F² |
| Data / restraints / parameters                | 9418 / 0 / 290                 |
| Goodness-of-fit on F²                         | 1.060                          |
| Final R indices [I≥2σ(I)]                    | R₁ = 0.0198, wR₂ = 0.0432      |
SUPPORTING INFORMATION

R indices (all data)  \( R_1 = 0.0233, wR_2 = 0.0446 \)

Largest diff. peak and hole  1.18 and -1.39 e.Å\(^{-3}\)

Crystal data and structure refinement for 5b

Empirical formula  \( \text{C}_{14.5}\text{H}_{18.95}\text{Cl}_{0.95}\text{Ir}_{0.5}\text{N}_{2} \)

Formula weight  413.62

CCDC Deposit Number  2082128

Temperature  140.01 K

Wavelength  0.71073 Å

Crystal system  triclinic

Space group  P-1

Unit cell dimensions
\[ a = 10.8224(5) \text{ Å} \quad \alpha = 82.449(2)^\circ. \]
\[ b = 11.3562(5) \text{ Å} \quad \beta = 70.549(2)^\circ. \]
\[ c = 14.2993(6) \text{ Å} \quad \gamma = 84.804(2)^\circ. \]

Volume  1640.67(13) Å\(^3\)

Z  4

Density (calculated)  1.675 g/m\(^3\)

Absorption coefficient  5.188 mm\(^{-1}\)

\( F(000) \)  801.0

Crystal size  0.686 × 0.388 × 0.371 mm\(^3\)

Theta range for data collection  3.622 to 66.572°.

Index ranges  -16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22

Reflections collected  53931

Independent reflections  12500 [\( R_{int} = 0.0303, R_{sigma} = 0.0261 \)]

Refinement method  Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters  12500 / 0 / 348

Goodness-of-fit on \( F^2 \)  1.056

Final R indices \([I≥2σ(I)]\)  \( R_1 = 0.0243, wR_2 = 0.0576 \)

R indices (all data)  \( R_1 = 0.0308, wR_2 = 0.0609 \)

Largest diff. peak and hole  2.29 and -1.85 e.Å\(^{-3}\)

Crystal data and structure refinement for 5d

Empirical formula  \( \text{C}_{29}\text{H}_{33}\text{F}_{6}\text{IrN}_{6}\text{O}_{6}\text{S}_{2} \)

Formula weight  931.93

CCDC Deposit Number  2082093

Temperature  139.99 K

Wavelength  0.71073 Å

Crystal system  Monoclinic

Space group  C2/c

Unit cell dimensions
\[ a = 35.8233(15) \text{ Å} \quad \alpha = 90^\circ. \]
\[ b = 18.3547(4) \text{ Å} \quad \beta = 90.215(4)^\circ. \]
\[ c = 23.0390(9) \text{ Å} \quad \gamma = 90^\circ. \]

Volume  6895.4(5) Å\(^3\)

Z  8
Density (calculated) 1.798 g/m³
Absorption coefficient 4.077 mm⁻¹
F(000) 3680.0
Crystal size 0.204 × 0.131 × 0.12 mm³
Theta range for data collection 3.536 to 61.168°.
Index ranges -50 ≤ h ≤ 51, -11 ≤ k ≤ 11, -32 ≤ l ≤ 32
Reflections collected 109215
Independent reflections 10570 \([R_{int} = 0.0484, R_{sigma} = 0.0315]\]
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 10570 / 324 / 502
Goodness-of-fit on F² 1.038
Final R indices \([I \geq 2\sigma(I)]\) R₁ = 0.0266, wR₂ = 0.0507
R indices (all data) R₁ = 0.0434, wR₂ = 0.0553
Largest diff. peak and hole 0.95 and -0.67 e.Å⁻³

Crystal data and structure refinement for 5d-acetone

Empirical formula C₂₇H₃₀F₆IrN₅O₆S₂
Formula weight 890.88
CCDC Deposit Number 2114162
Temperature 139.99 K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group P-1
Unit cell dimensions a = 10.7638(8) Å α = 109.485(3°.
b = 10.9663(7) Å β = 92.013(5)°.
c = 14.220(1) Å γ = 100.650(4)°.
Volume 1546.7(2) Å³
Z 2
Density (calculated) 1.913 g/m³
Absorption coefficient 4.538 mm⁻¹
F(000) 876.0
Crystal size 0.242 × 0.155 × 0.065 mm³
Theta range for data collection 3.054 to 52.974°.
Index ranges -13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -16 ≤ l ≤ 17
Reflections collected 27169
Independent reflections 6336 \([R_{int} = 0.0675, R_{sigma} = 0.0774]\]
Data / restraints / parameters 6336 / 282 / 435
Goodness-of-fit on F² 1.059
Final R indices \([I \geq 2\sigma(I)]\) R₁ = 0.0573, wR₂ = 0.1574
R indices (all data) R₁ = 0.0804, wR₂ = 0.1754
Largest diff. peak and hole 3.42 and -2.42 e.Å⁻³
Figure S72. X-ray solid-state structure 3c-Rh(CO)$_2$Cl.

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