

Supporting information

Experimental

Bis-NHC complexes were prepared according to the literature employing the alkoxide route.¹ Mono-NHCs have been prepared and characterized according to previously reported literature methods.^{1,2} All experiments were carried out under dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under nitrogen. ¹H, ¹⁹F and ¹³C-NMR spectra were recorded on a JEOL-JMX-GX 400 MHz spectrometer at room temperature and referenced to the residual ¹H and ¹³C signals of the solvents and ¹⁹F to C₆F₆. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, q = quartet, t = triplet, sept. = septet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. IR spectra were recorded on a Jasco 460 spectrometer. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Mass spectra were performed at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 spectrometer using FAB technique.

1,1'-Methyl-3,3'-propylene-dibenzimidazoliumdibromid

Methylbenzimidazole (10 mmol) and 1,3-dibromopropane (5 mmol) was dissolved in 3.5 mL THF. The solution was then heated for 30 min in a pressure sealed tube in the microwave reactor at 130 °C. The resulting viscous oil is treated in 2 mL THF resulting in the formation of a white solid. The white product was washed three times with 5 mL acetone, ether and THF. Yield: 62 %.

¹H-NMR (400 MHz, 25°C, DMSO-d₆): δ = 9.97 (s, 2H, NCHN), 8.15 (d, ³*J* = 8.4 Hz, 2H, CH-Ar), 8.14 (d, ³*J* = 8.4 Hz, 2H, H-Ar), 7.70 (m, 4H, H-Ar), 4.75 (t, 4H, NCH₂-Linker), 4.09 (s, 6H, NCH₃) 2.62 (m, 2H, NCH₂CH₂-Linker).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.5 MHz, 25°C, DMSO- d_6): δ = 142.8 (NCHN), 131.7, 130.8, 126.3, 113.5 (C-Ar), 43.7 (NCH₂-Linker), 33.2, 28.1 (NCH₂CH₂-Linker, NCH₃).

MS (FAB): m/z = 386.9 [M - Br]⁺, 305.0 [M - 2Br - H]⁺.

General procedure for the preparation of biscarbene complexes of the type (η^4 -1,5-cyclooctadiene)bis(azolinylidene)iridium(I) iodide

A solution of sodium hydride (0.6 mmol) in 3 ml of EtOH is added drop wise to a suspension of [Ir(COD)Cl]₂ (0.15 mmol) in EtOH (2 mL) and the resulting mixture is stirred for 45 min, while a colour change from orange to yellow is observed. After the addition of 0.35 mmol bis-azolium salt (1.2 mmol mono-azolium salt) the suspension is stirred for an additional 12 h and 1.2 mmol NaI is added. After stirring for another 12 h the volatiles are removed in vacuum and the crude product is purified by column chromatography (silica gel, 4:1 → 2:1 dichloromethane / acetone). The iodine salts of iridium(I) are employed in an ion exchange reaction without further characterization unless otherwise stated.

General procedure for the ion exchange with bis-NHC complexes of iridium(I)

In 5 mL acetonitrile 0.1 mmol iridium iodide complex is dissolved and 0.1 mmol of the silver salt AgX is added, resulting in the formation of AgI. The resulting suspension is stirred for 30 min at room temperature and the orange-red product solution is filtered off. Volatiles are removed in vacuum, and the resulting red-orange viscous oil is redissolved in dichloromethane. The product is precipitated with pentane and the resulting orange solid dried *in vacuo*.

(η^4 -1,5-cyclooctadiene)bis(1,3-dimethylbenzimidazol-2-ylidene)iridium(I)

trifluoroacetate 2^{TFA}

The iodide complex was prepared from 1,3-dimethylbenzimidazolium iodide. The ion exchange is performed with 0.1 mmol 2^{I} and AgTFA. Yield: 69 %.

$^1\text{H-NMR}$ (400 MHz, 25°C, DMSO- d_6): δ = 7.55 (m, 4H, CH-Ar), 7.30 (m, 4H, CH-Ar), 4.18 (s, 12H, NCH₃), 4.04 (br s, 4H, CH-COD), 2.38 (br s, 4H, CH₂-COD), 2.02 (m, 4H, CH₂-COD).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (100.5 MHz, 25°C, DMSO- d_6): δ = 187.2 (Carbene), 157.7 (q, $^2J_{\text{CF}}$ = 29.9 Hz, CO), 117.3 (q, $^1J_{\text{CF}}$ = 301.5 Hz, CF₃), 134.8; 122.6; 110.2 (Aryl-C), 77.5 (CH-COD), 34.9 (NCH₃), 30.6 (CH₂-COD).

$^{19}\text{F-NMR}$ (376.2 MHz, 25 °C, DMSO- d_6) δ = -72.8 (CF₃).

MS (FAB): m/z = 593 [M]⁺, 484.0 [M - COD - H]⁺.

(η^4 -1,5-cyclooctadiene)bis(1,4-dimethyltriazol-5-ylidene)iridium(I)

trifluoroacetate 3^{TFA}

The iodide complex was prepared from 1,2,4-dimethyltriazoliumiodide. The ion exchange is performed with 0.1 mmol 3^{I} and AgTFA. Yield: 80 %.

$^1\text{H-NMR}$ (400 MHz, 25°C, CD₂Cl₂): δ = 8.60 (s, 2H, NCHN), 4.03 (br s, 12H, CH₃), 3.91 (br s, 4 H, CH-COD), 2.28 (m, 4H, CH-COD), 2.03 (m, 4H, CH₂-COD).

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (100.5 MHz, 25°C, CD₂Cl₂): δ = 180.0 (Carbene), 160.1 (q, $^2J_{\text{CF}}$ = 31.2 Hz, CO) 118.0 (q, $^1J_{\text{CF}}$ = 325.2 Hz, CF₃), 145.25 (NCHN), 79.4 (CH-COD), 79.3 (CH-COD), 78.9 (CH-COD), 78.8 (CH-COD), 40.2 (NCH₃), 35.4 (NCH₃), 31.8 (CH₂-COD), 31.5 (CH₂-COD), 31.4 (CH₂-COD), 31.2 (CH₂-COD).

^{19}F -NMR (376.2 MHz, 25 °C, CD_2Cl_2) δ = -75.1 (CF_3).

MS (FAB): m/z = 555.3 $[\text{M}]^+$.

**(η^4 -1,5-cyclooctadiene)(1,1'-methyl-3,3'-propylene-diimidazol-2,2'-
diylidene)iridium(I) trifluoroacetate **6**^{TFA}**

The ion exchange is performed with 0.1 mmol **6**^I and AgTFA. Yield: 72 %.

^1H -NMR (400 MHz, 25°C, DMSO-d_6): δ = 7.29 (d, 2H, NCHCHN), 7.22 (d, 2H, NCHCHN), 4.58 (t, 2H, $\text{NCH}_2\text{-Linker}$), 4.30 (m, 2H, $\text{NCH}_2\text{-Linker}$), 4.06 (br s, 2H, CH-COD), 3.99 (br s, 2H, CH-COD), 3.80 (s, 6H, NCH_3), 2.26 (m, 6H, $\text{CH}_2\text{-COD}$, $\text{NCH}_2\text{CH}_2\text{-Linker}$), 1.96 (m, 4H, $\text{CH}_2\text{-COD}$).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.5 MHz, 25°C, DMSO-d_6): δ = 176.6 (Carbene), 157.6 (q, $^2J_{\text{CF}}$ = 27.5 Hz, CO), 117.0 (q, $^1J_{\text{CF}}$ = 299.7 Hz, CF_3), 122.2, 122.1 (NCHCHN), 75.4, 74.15 (CH-COD), 51.3 ($\text{NCH}_2\text{-Linker}$), 36.9 (NCH_3), 33.0, 30.7 ($\text{NCH}_2\text{CH}_2\text{-Linker}$, $\text{CH}_2\text{-COD}$).

^{19}F NMR (376.17 MHz, 25 °C, DMSO-d_6): δ = -72.7 (CF_3).

MS (FAB): m/z = 505.0 $[\text{M}]^+$.

**(η^4 -1,5-cyclooctadiene)(1,1'-methyl-3,3'-butylene-diimidazol-2,2'-
diylidene)iridium(I) trifluoroacetate **7**^{TFA}**

The iodide complex was prepared from 1,1'-methyl-3,3'-butylenediimidazolium dibromide. The ion exchange is performed with 0.1 mmol **7**^I and AgTFA. Yield: 81 %.

^1H -NMR (400 MHz, 25°C, DMSO-d_6): δ = 7.28 (d, 2H, NCHCHN), 7.22 (d, 2H, NCHCHN), 4.58 (m, 2H $\text{NCH}_2\text{-Linker}$), 4.30 (m, 2H $\text{NCH}_2\text{-Linker}$), 4.08 (m, 2H, CH-COD), 3.92 (m, 2H, CH-COD), 3.79 (s, 6H, NCH_3), 2.27 (m, 8H, $\text{CH}_2\text{-COD}$, $\text{CH}_2\text{-Linker}$), 1.96 (m, 4H, $\text{CH}_2\text{-COD}$).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.5 MHz, Aceton- d_6 , 25 °C): δ = 177.9 (Carbene), 124.2, 122.0 (NCHCHN), 77.0, 75.9 (CH-COD), 46.4 (NCH₂-Linker), 38.1 (NCH₃), 31.9, 26.9 (NCH₂CH₂-Linker, CH₂-COD).

^{19}F -NMR (376.2 MHz, 25 °C, DMSO- d_6): δ = -72.7 (CF₃).

MS (FAB): m/z = 519.0 [M]⁺, 409.0 [M - COD - 2H]⁺.

(η^4 -1,5-cyclooctadiene)(1,1'-methyl-3,3'-propylene-dibenzimidazol-2,2'-diylidene)iridium(I) trifluoroacetate **9^{TFA}**

The iodide complex was prepared from 1,1'-methyl-3,3'-propylenedibenzimidazolium dibromide. The ion exchange is performed with 0.1 mmol **9**^I and AgTFA. Yield: 69 %.

^1H -NMR (400 MHz, 25°C, DMSO- d_6): δ = 7.61 (m, 2H, CH-Ar), 7.48 (m, 2H, CH-Ar), 7.24 (m, 4H, CH-Ar), 4.94 (m, 4H, NCH₂-Linker), 4.32 (br s, 4H, CH-COD), 4.09 (s, 6H, NCH₃), 2.41 (m, 6H, CH₂-COD, NCH₂CH₂-Linker), 1.60 (m, 4H, CH₂-COD).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.5 MHz, 25°C, DMSO- d_6): δ = 188.1 (Carbene), 134.6, 134.1, 122.8, 122.5, 110.7, 109.8 (C-Ar), 78.3, 77.6 (CH-COD), 48.6 (NCH₂-Linker), 34.6, 30.8 (NCH₂CH₂-Linker, CH₂-COD).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.5 MHz, 25°C, CD₂Cl₂): δ = 189.1 (Carbene), 160.1 (q, $^2J_{\text{CF}}$ = 33.7 Hz, CO) 118.0 (q, $^1J_{\text{CF}}$ = 302.8 Hz, CF₃), 135.4, 134.9, 123.9, 123.6, 110.5, 109.9 (C-Ar), 80.2, 79.5 (CH-COD), 49.53 (NCH₂-Linker), 35.5, 31.5 (NCH₂CH₂-Linker, CH₂-COD).

^{19}F -NMR (376.17 MHz, 25 °C, CD₂Cl₂): δ = -75.1 (CF₃).

MS (FAB): m/z = 605.0 [M]⁺, 494.9 [M - COD - 2H]⁺.

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