

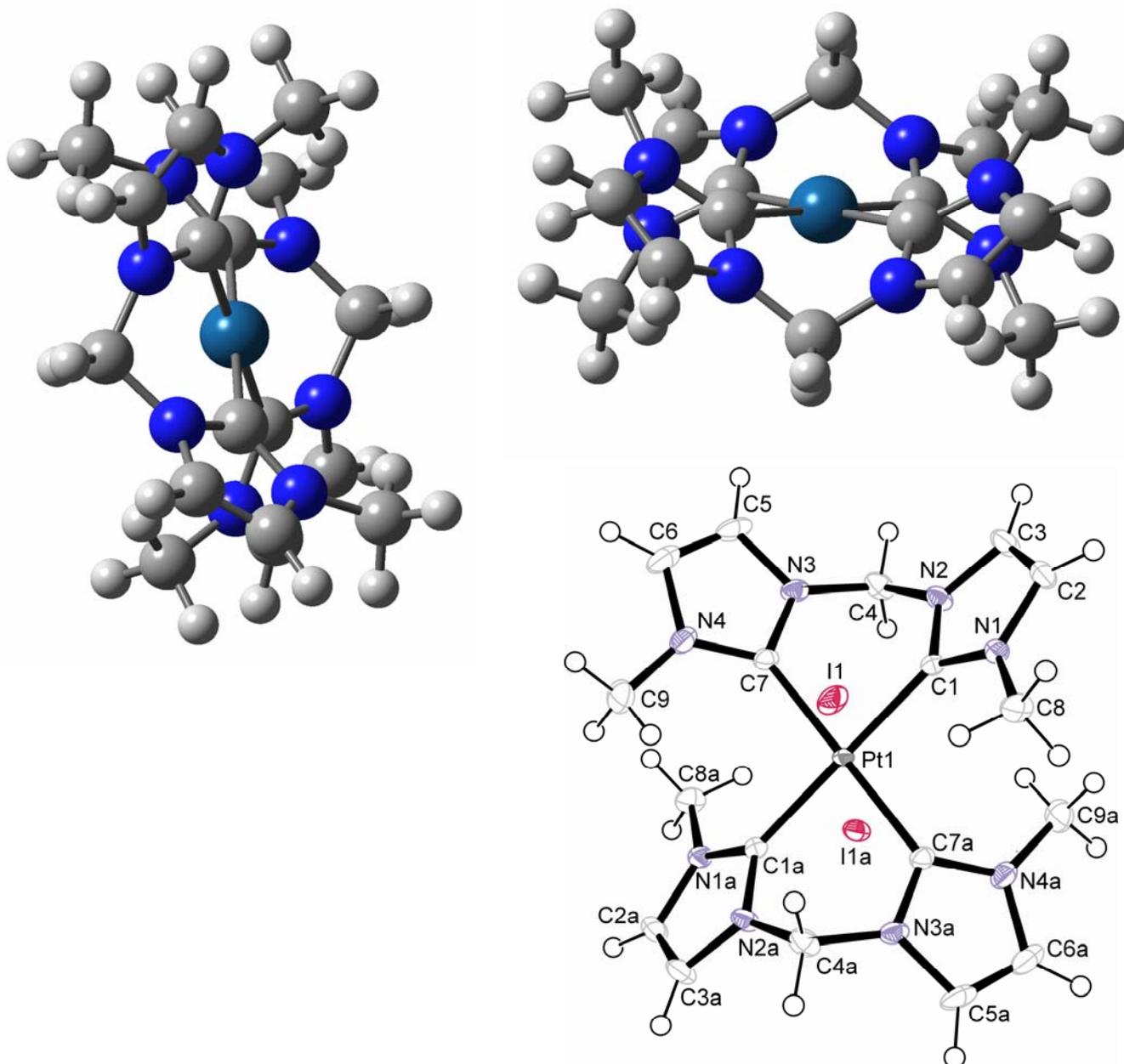
Supplementary Information

Blue phosphorescent emitters: new *N*-heterocyclic platinum(II) tetracarbene complexes

Yvonne Unger, Alexander Zeller, Sebastian Ahrens[‡] and Thomas Strassner*

E-mail: thomas.strassner@chemie.tu-dresden.de
[‡]*X-ray analysis.*

3D-views



Experimental Details

Solvents of 99.5% purity were used throughout this study. All other chemicals and platinum(II) chloride were obtained from common suppliers and used without further purification. The *N*-substituted imidazoles are commercially available (1-methylimidazole, 1-*n*-butylimidazole) or were prepared according to literature procedure (1-isopropylimidazole, 1-cyclohexylimidazole).¹ The ¹H- and ¹³C-NMR spectra were recorded with a Bruker AC 300P or Bruker DRX 500 spectrometer. The spectra were referenced internally to the references of the solvent (DMSO). Elemental analysis were performed by the microanalytical laboratory at our institute using an Eurovektor Hekatech EA-3000 Elemental Analyzer. The melting points were measured with an Electrothermal 9100 melting-point apparatus and are uncorrected.

Synthesis of the bisimidazolium salts

1,1'-Dimethyl-3,3'-methylene-diimidazolium diiodide (1a)

1-methylimidazole (0.024 mol, 2.000 g, 1.94 mL) and diiodomethane (0.012 mol, 3.214 g, 0.97 mL) were dissolved in 5 mL tetrahydrofuran in a sealed tube. The reaction mixture was stirred for 20 h at 110 °C until a white precipitate was formed. The solid was filtered off and washed three times with tetrahydrofuran (5 mL). After that the product was dried in vacuo and obtained as a white powder.

Yield: 5.198 g (99.9%). Mp: decomposition > 277 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): δ = 9.35 (s, 2H, NCHN); 7.96 (t, 2H, *J* = 1.7 Hz, NCHCHN); 7.80 (t, 2H, *J* = 1.7 Hz, NCHCHN); 6.64 (s, 2H, NCH₂N); 3.90 (s, 6H, CH₃) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): δ = 137.84 (NCHN); 124.24 (NCHCHN); 121.76 (NCHCHN); 58.01 (NCH₂N); 36.15 (CH₃) ppm. EA: Anal. Calc. for C₉H₁₄N₄I₂ (432.042 g/mol): C 25.02; H 3.27; N 12.97%. Found: C 25.17; H 3.25; N 12.97%.

1,1'-Di-isopropyl-3,3'-methylene-diimidazolium diiodide (1b)

1-isopropylimidazole (0.027 mol, 3.000 g) and diiodomethane (0.0135 mol, 3.616 g, 1.09 mL) were dissolved in 7 mL tetrahydrofuran in a sealed tube. The reaction mixture was stirred for 17 h at 80 °C until a white precipitate was formed. The solid was filtered off and washed three times with tetrahydrofuran (5 mL). After that the product was dried in vacuo and obtained as a white powder.

Yield: 4.832 g (73.3%). Mp: decomposition > 247 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): δ = 9.50 (s, 2H, NCHN); 8.04 (s, 4H, NCHCHN); 6.59 (s, 2H, NCH₂N); 4.72 (sept, 2H, *J* = 6.6 Hz, (CH₃)₂CHN); 1.50 (d, 12H, *J* = 6.6 Hz, CH₃) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): δ = 136.28 (NCHN); 122.23 (NCHCHN); 121.20 (NCHCHN); 58.12 (NCH₂N); 52.66 ((CH₃)₂CHN); 21.91 (CH₃) ppm. EA: Anal. Calc. for C₁₃H₂₂N₄I₂ (488.146 g/mol): C 31.98; H 4.54; N 11.48%. Found: C 31.96; H 4.47; N 11.39%.

1,1'-Dicyclohexyl-3,3'-methylene-diimidazolium diiodide (1c)

1-cyclohexylimidazole (0.013 mol, 2.000 g) and diiodomethane (0.0065 mol, 1.741 g, 0.52 mL) were dissolved in 5 mL tetrahydrofuran in a sealed tube. The reaction mixture was stirred for 3 h at 80 °C until a white precipitate was formed. The solid was filtered off and washed three times with tetrahydrofuran (5 mL). After that the product was dried in vacuo and obtained as a white powder.

Yield: 0.891 g (24.1%). Mp: decomposition > 286 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): δ = 9.45 (s, 2H, NCHN); 8.01 (dd, 4H, *J* = 1.6 Hz, NCHCHN); 6.58 (s, 2H, NCH₂N); 4.36 (t, 2H, *J* = 11.7 Hz, CH); 2.09 (d, 4H, *J* = 9.7 Hz, CH₂); 1.85 (d, 4H, *J* = 13.3 Hz, CH₂); 1.68 (d, 4H, *J* = 12.3 Hz, CH₂); 1.40 (quart, 4H, *J* = 12.7 Hz, CH₂); 1.23 (t, 4H, *J* = 12.5 Hz, CH₂) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): δ = 136.20 (NCHN); 122.13 (NCHCHN); 121.40 (NCHCHN); 58.84 (CH); 58.19 (NCH₂N); 32.02 (CH₂); 24.15 (CH₂) ppm. EA: Anal. Calc. for C₁₉H₃₀N₄I₂ (568.270 g/mol): C 40.16; H 5.32; N 9.86%. Found: C 40.46; H 5.42; N 9.99%.

1,1'-Di-n-butyl-3,3'-methylene-diimidazolium diiodide (1d)

1-n-butylimidazole (0.024 mol, 3.000 g, 3.17 mL) and diiodomethane (0.012 mol, 3.214 g, 0.97 mL) were dissolved in 7 mL tetrahydrofuran in a sealed tube. The reaction mixture was stirred for 5 d at rt and 72 h at 80 °C in which a white precipitate was formed. The solid was filtered off and washed three times with tetrahydrofuran (5 mL). After that the product was dried in vacuo and obtained as a white powder.

Yield: 5.929 g (95.7%). Mp = 151.4 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): δ = 9.44 (s, 2H, NCHN); 8.00 (s, 2H, NCHCHN); 7.92 (s, 2H, NCHCHN); 6.63 (s, 2H, NCH₂N); 4.23 (t, 4H, *J* = 7.2 Hz, NCH₂CH₂CH₂CH₃); 1.79 (quint, 4H, *J* = 7.3 Hz, NCH₂CH₂CH₂CH₃); 1.31 (sext, 4H, *J* = 7.4 Hz, NCH₂CH₂CH₂CH₃); 0.91 (t, 6H, *J* = 7.3 Hz, NCH₂CH₂CH₂CH₃) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): δ = 137.48 (NCHN); 123.24 (NCHCHN); 122.23 (NCHCHN); 58.43 (NCH₂N); 49.10 (NCH₂CH₂CH₂CH₃); 31.11 (NCH₂CH₂CH₂CH₃); 18.80

(NCH₂CH₂CH₂CH₃); 13.35 (NCH₂CH₂CH₂CH₃) ppm. EA: Anal. Calc. for C₁₅H₂₆N₄I₂ (516.198 g/mol): C 34.90; H 5.08; N 10.86%. Found: C 34.95; H 5.01; N 10.81%.

Synthesis of the complexes

A) Biscarbenes

General Procedure

1 eq Platinum(II) chloride, 1 eq diimidazolium diiodide (**1**), 2 eq sodium acetate trihydrate and 2 eq potassium iodide were dissolved in 5 mL dimethylsulfoxide and stirred for 2 h at 60 °C, 2 h at 80 °C and 5 h at 110 °C. The solvent was removed in vacuo and the residue was washed twice with 3 mL methanol and 3 mL tetrahydrofuran. The product was dried under high vacuum to obtain a white powder.

1,1'-Di-isopropyl-3,3'-methylene-diimidazoline-2,2'-diylidene platinum(II) diiodide (2b)

This complex was prepared according to the general procedure. Yield: 0.116 g (68.1%). Mp : decomposition > 340 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): δ = 7.56 (d, 2H, *J* = 2.1 Hz, NCHCHN); 7.51 (d, 2H, *J* = 2.2 Hz, NCHCHN); 6.07 (AB, 1H, *J* = 13.1 Hz, NCH₂N); 5.98 (AB, 1H, *J* = 13.1 Hz, NCH₂N); 5.47 (sept, 2H, *J* = 6.8 Hz, (CH₃)₂CHN); 1.46 (d, 6H, *J* = 6.7 Hz, CH₃); 1.17 (d, 6H, *J* = 6.8 Hz, CH₃) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): δ = 149.22 (NCN); 121.26 (NCHCHN); 117.61 (NCHCHN); 62.02 (NCH₂N); 52.06 ((CH₃)₂CHN); 23.23 (CH₃); 20.98 (CH₃) ppm. EA: Anal. Calc. for C₁₃H₂₀N₄PtI₂ (681.207 g/mol): C 22.92; H 2.96; N 8.23%. Found: C 22.45; H 2.88; N 8.17%.

1,1'-Dicyclohexyl-3,3'-methylene-diimidazoline-2,2'-diylidene platinum(II) diiodide (2c)

This complex was prepared according to the general procedure. Yield: 0.221 g (72.6%). Mp: decomposition > 382 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): δ = 7.59 (s, 2H, NCHCHN); 7.57 (s, 2H, NCHCHN); 6.11 (AB, 1H, *J* = 13.2 Hz, NCH₂N); 5.99 (AB, 1H, *J* = 13.2 Hz, NCH₂N); 5.21 (t, 2H, *J* = 11.6 Hz, CH); 2.13 (d, 4H, *J* = 10.9 Hz, CH₂); 1.84 (d, 4H, *J* = 13.0 Hz, CH₂); 1.59 (d, 4H, *J* = 11.9 Hz, CH₂); 1.39 (t, 4H, *J* = 11.8 Hz, CH₂); 1.28 (t, 4H, *J* = 12.6 Hz, CH₂) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): δ = 143.56 (NCN); 120.93

(NCHCHN); 118.10 (NCHCHN); 61.72 (NCH₂N); 57.76 (CH); 33.25 (CH₂); 32.24 (CH₂); 25.29 (CH₂); 24.76 (CH₂); 24.51 (CH₂) ppm. EA: Anal. Calc. for C₁₉H₂₈N₄PtI₂ (761.332 g/mol): C 29.97; H 3.71; N 7.36%. Found: C 30.11; H 3.58; N 7.51%.

1,1'-Di-n-butyl-3,3'-methylene-diimidazoline-2,2'-diylidene platinum(II) diiodide (2d)

This complex was prepared according to the general procedure. The crude product was washed twice with 3 mL water, 3 mL methanol and 3 mL tetrahydrofuran. Yield: 0.232 g (65.4%). Mp = 249.8 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): δ = 7.51 (d, 2H, *J* = 1.8 Hz, NCHCHN); 7.37 (d, 2H, *J* = 1.9 Hz, NCHCHN); 6.10 (AB, 1H, *J* = 13.0 Hz, NCH₂N); 5.94 (AB, 1H, *J* = 13.0 Hz, NCH₂N); 4.83 (m, 2H, *J* = 7.5 Hz, NCH₂CH₂CH₂CH₃); 3.96 (m, 2H, *J* = 6.6 Hz, NCH₂CH₂CH₂CH₃); 1.74 (quint, 4H, *J* = 7.2 Hz, NCH₂CH₂CH₂CH₃); 1.18 (sext, 4H, *J* = 7.2 Hz, NCH₂CH₂CH₂CH₃); 0.86 (t, 6H, *J* = 7.4 Hz, NCH₂CH₂CH₂CH₃) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): δ = 143.11 (NCN); 121.19 (NCHCHN); 120.36 (NCHCHN); 61.79 (NCH₂N); 48.69 (NCH₂CH₂CH₂CH₃); 32.42 (NCH₂CH₂CH₂CH₃); 19.09 (NCH₂CH₂CH₂CH₃); 13.49 (NCH₂CH₂CH₂CH₃) ppm. EA: Anal. Calc. for C₁₅H₂₄N₄PtI₂ (709.260 g/mol): C 25.40; H 3.41; N 7.90%. Found: C 25.32; H 3.47; N 8.08%.

B) Homoleptic tetracarbenes

General procedures

Path 1: 1 eq Platinum(II) chloride, 2.5 eq diimidazolium diiodide (**1**) and 2 eq sodium acetate trihydrate were dissolved in dimethylsulfoxide. The reaction mixture was stirred for 2 h at 60 °C, 2 h at 80 °C and 1 h at 110 °C. At this temperature 2 eq sodium acetate trihydrate was added again and the mixture was stirred for further 5 h at 110 °C. The solvent was removed in vacuo and the residue was washed. The product was dried under high vacuum to obtain a white powder.

Path 2: 1 eq Diimidazoline-2,2'-diylidene platinum(II) diiodide (**2**), 1 eq diimidazolium diiodide (**1**) and 2 eq sodium acetate trihydrate were dissolved in dimethylsulfoxide. The reaction mixture was stirred for 2 h at 60 °C, 2 h at 80 °C and 5 h at 110 °C. The solvent was removed in vacuo and the residue was washed twice with a methanol tetrahydrofuran mixture. The product was dried under high vacuum to obtain a white powder.

Bis-(1,1'-dimethyl-3,3'-methylene-diimidazoline-2,2'-diylidene)platinum(II) diiodide (3aa)

This complex was prepared according to path 1. The residue was washed with 10 mL water and 5 mL tetrahydrofuran. Yield: 0.137 g (68.4%). Mp: decomposition > 360 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): δ = 7.75 (d, 4H, *J* = 1.8 Hz, NCHCHN); 7.47 (d, 4H, *J* = 1.8 Hz, NCHCHN); 6.54 (AB, 2H, *J* = 13.2 Hz, NCH₂N); 6.43 (AB, 2H, *J* = 13.2 Hz, NCH₂N); 3.32 (s, 12H, CH₃) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): δ = 162.74 (NCN); 123.01 (NCHCHN); 122.09 (NCHCHN); 62.66 (NCH₂N); 36.69 (CH₃) ppm. EA: Anal. Calc. for C₁₈H₂₄N₈PtI₂ (801.330 g/mol): C 26.98; H 3.02; N 13.97%. Found: C 26.99; H 3.06; N 13.93%.

Bis-(1,1'-di-isopropyl-3,3'-methylene-diimidazoline-2,2'-diylidene)platinum(II) diiodide (3bb)

This complex was prepared according to path 2. Yield: 0.020 g (21.9%). Mp: decomposition > 350 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): δ = 7.80 (d, 4H, *J* = 1.8 Hz, NCHCHN); 7.67 (d, 4H, *J* = 1.9 Hz, NCHCHN); 6.52 (AB, 2H, *J* = 13.5 Hz, NCH₂N); 6.33 (AB, 2H, *J* = 13.4 Hz, NCH₂N); 3.90 (sept, 4H, *J* = 6.6 Hz, (CH₃)₂CHN); 1.28 (d, 12H, *J* = 6.8 Hz, CH₃); 1.12 (d, 12H, *J* = 6.6 Hz, CH₃) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): δ = 162.98 (NCN); 122.90 (NCHCHN); 118.46 (NCHCHN); 63.14 (NCH₂N); 52.41 ((CH₃)₂CHN); 24.94 (CH₃); 20.20 (CH₃) ppm.

Bis-(1,1'-dicyclohexyl-3,3'-methylene-diimidazoline-2,2'-diylidene)platinum(II) diiodide (3cc)

This complex was prepared according to path 2. Yield: 0.028 g (24.8%). Mp: decomposition > 393 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): δ = 7.89 (s, 4H, NCHCHN); 7.70 (s, 4H, NCHCHN); 6.68 (AB, 2H, *J* = 13.4 Hz, NCH₂N); 6.11 (AB, 2H, *J* = 13.7 Hz, NCH₂N); 3.34 (t, 4H, *J* = 11.8 Hz, CH); 1.81 (d, 8H, *J* = 12.1 Hz, CH₂); 1.68 (d, 8H, *J* = 11.7 Hz, CH₂); 1.35 (d, 8H, *J* = 11.5 Hz, CH₂); 1.15 (t, 8H, *J* = 11.9 Hz, CH₂); 0.84 (t, 8H, *J* = 12.1 Hz, CH₂) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): δ = 162.68 (NCN); 122.91 (NCHCHN); 118.98 (NCHCHN); 60.25 (NCH₂N); 58.80 (CH); 35.47 (CH₂); 30.33 (CH₂); 25.02 (CH₂); 24.84 (CH₂); 24.21 (CH₂) ppm.

*Bis-(1,1'-di-*n*-butyl-3,3'-methylene-diimidazoline-2,2'-diylidene)platinum(II) diiodide (3dd)*

This complex was prepared according to path 1. The residue was washed twice with 3 mL methanol, 3 mL tetrahydrofuran and 1 mL water. Yield: 0.136 g (28.1%). Mp: decomposition > 370 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): δ = 7.87 (s, 4H, NCHCHN); 7.63 (s, 4H, NCHCHN); 6.80 (AB, 2H, *J* = 13.4 Hz, NCH₂N); 6.17 (AB, 2H, *J* = 13.6 Hz, NCH₂N); 3.81

(m, 4H, $J = 6.8$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 3.23 (m, 4H, $J = 6.9$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.56 (quint, 8H, $J = 7.2$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 0.98 (sext, 8H, $J = 7.4$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 0.70 (t, 12H, $J = 7.2$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) ppm. ^{13}C -NMR (d_6 -DMSO, 75.475 MHz): $\delta = 162.05$ (NCN); 122.43 (NCHCHN); 122.02 (NCHCHN); 62.67 (NCH_2N); 49.35 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 32.33 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 19.04 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 13.25 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) ppm.

C) Heteroleptic tetracarbenes

General procedure

1 eq Diimidazoline-2,2'-diylidene platinum(II) diiodide (**2**), 1 eq diimidazolium diiodide (**1**) and 2 eq sodium acetate trihydrate were dissolved in dimethylsulfoxide. The reaction mixture was stirred for 2 h at 60 °C, 2 h at 80 °C and 5 h at 110 °C. The solvent was removed in vacuo and the residue was washed twice with a methanol tetrahydrofuran mixture followed by water. The product was dried under high vacuum to obtain a white powder.

(1,1'-Di-isopropyl-3,3'-methylene-diimidazoline-2,2'-diylidene)(1'',1'''-dimethyl-3'',3'''-methylene-diimidazoline-2'',2'''-diylidene)platinum(II) diiodide (3ab)

This complex was prepared according to the general procedure. The residue was washed twice with 1 mL methanol. Yield: 0.017 g (15.3%). Mp: decomposition > 360 °C. ^1H -NMR (d_6 -DMSO, 300.13 MHz): $\delta = 7.80$ (d, 2H, $J = 1.8$ Hz, NCHCHN); 7.75 (d, 2H, $J = 1.8$ Hz, NCHCHN); 7.71 (d, 2H, $J = 1.9$ Hz, NCHCHN); 7.47 (d, 2H, $J = 1.7$ Hz, NCHCHN); 6.58 (AB, 1H, $J = 13.1$ Hz, NCH_2N); 6.47 (AB, 1H, $J = 13.6$ Hz, NCH_2N); 6.43 (AB, 1H, $J = 13.3$ Hz, NCH_2N); 6.35 (AB, 1H, $J = 13.4$ Hz, NCH_2N); 3.97 (sept, 2H, $J = 6.6$ Hz, $(\text{CH}_3)_2\text{CHN}$); 3.29 (s, 6H, CH_3); 1.28 (d, 6H, $J = 6.8$ Hz, CH_3); 1.10 (d, 6H, $J = 6.6$ Hz, CH_3) ppm. ^{13}C -NMR (d_6 -DMSO, 75.475 MHz): $\delta = 162.95$ (NCN); 123.18 (NCHCHN); 122.85 (NCHCHN); 122.32 (NCHCHN); 118.26 (NCHCHN); 62.80 (NCH_2N); 52.51 ($(\text{CH}_3)_2\text{CHN}$); 37.25 (CH_3); 24.76 (CH_3); 20.31 (CH_3) ppm.

(1,1'-Dicyclohexyl-3,3'-methylene-diimidazoline-2,2'-diylidene)(1'',1'''-dimethyl-3'',3'''-methylene-diimidazoline-2'',2'''-diylidene)platinum(II) diiodide (3ac)

This complex was prepared according to the general procedure. Yield: 0.065 g (63.0%). Mp: decomposition > 375 °C. ^1H -NMR (d_6 -DMSO, 300.13 MHz): $\delta = 7.84$ (s, 2H,

NCHCHN); 7.81 (s, 2H, NCHCHN); 7.67 (s, 2H, NCHCHN); 7.52 (s, 2H, NCHCHN); 6.66 (AB, 1H, $J = 13.1$ Hz, NCH₂N); 6.63 (AB, 1H, $J = 13.4$ Hz, NCH₂N); 6.52 (AB, 1H, $J = 13.2$ Hz, NCH₂N); 6.15 (AB, 1H, $J = 13.4$ Hz, NCH₂N); 3.59 (t, 2H, $J = 12.5$ Hz, CH); 3.35 (s, 6H, CH₃); 1.85 (d, 4H, $J = 12.5$ Hz, CH₂); 1.76 (d, 4H, $J = 10.1$ Hz, CH₂); 1.67 (d, 4H, $J = 10.9$ Hz, CH₂); 1.37 (t, 4H, $J = 9.5$ Hz, CH₂); 1.12 (t, 4H, $J = 9.6$ Hz, CH₂) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): $\delta = 163.17$ (NCN); 162.69 (NCN); 123.16 (NCHCHN); 122.66 (NCHCHN); 122.47 (NCHCHN); 118.83 (NCHCHN); 66.99 (CH); 62.82 (NCH₂N); 60.24 (NCH₂N); 37.48 (CH₂); 34.97 (CH₂); 30.61 (CH₂); 25.24 (CH₂); 25.10 (CH₃); 24.24 (CH₂) ppm. EA: Anal. Calc. for C₂₈H₄₀N₈PtI₂ (937.558 g/mol): C 35.87; H 4.30; N 11.95%. Found: C 35.79; H 4.06; N 11.98%.

(1,1'-Di-n-butyl-3,3'-methylene-diimidazoline-2,2'-diylidene)(1'',1'''-dimethyl-3'',3'''-methylene-diimidazoline-2'',2'''-diylidene)platinum(II) diiodide (3ad)

This complex was prepared according to the general procedure. Yield: 0.118 g (78.4%). Mp: decomposition > 356 °C. ¹H-NMR (*d*₆-DMSO, 300.13 MHz): $\delta = 7.83$ (s, 4H, NCHCHN); 7.58 (d, 2H, $J = 1.8$ Hz, NCHCHN); 7.50 (d, 2H, $J = 1.8$ Hz, NCHCHN); 6.57 (AB, 1H, $J = 13.2$ Hz, NCH₂N); 6.51 (AB, 1H, $J = 13.6$ Hz, NCH₂N); 6.45 (AB, 1H, $J = 13.3$ Hz, NCH₂N); 6.17 (AB, 1H, $J = 13.3$ Hz, NCH₂N); 3.87 (m, 2H, $J = 6.5$ Hz, NCH₂CH₂CH₂CH₃); 3.32 (s, 6H, CH₃); 3.24 (m, 2H, $J = 6.6$ Hz, NCH₂CH₂CH₂CH₃); 1.58 (quint, 4H, $J = 6.9$ Hz, NCH₂CH₂CH₂CH₃); 1.01 (sext, 4H, $J = 6.7$ Hz, NCH₂CH₂CH₂CH₃); 0.72 (t, 6H, $J = 7.2$ Hz, NCH₂CH₂CH₂CH₃) ppm. ¹³C-NMR (*d*₆-DMSO, 75.475 MHz): $\delta = 162.49$ (NCN); 162.36 (NCN); 123.22 (NCHCHN); 122.22 (NCHCHN); 121.75 (NCHCHN); 62.72 (NCH₂N); 62.66 (NCH₂N); 49.03 (NCH₂CH₂CH₂CH₃); 36.95 (CH₃); 32.26 (NCH₂CH₂CH₂CH₃); 18.99 (NCH₂CH₂CH₂CH₃); 13.23 (NCH₂CH₂CH₂CH₃) ppm.

Crystallographic data

Single crystals of **3aa** suitable for the X-ray diffraction study were obtained by allowing methanol to condense into a saturated solution of the metal complex in dimethylsulfoxide. The crystals were stored under perfluorinated ether, transferred on a glass capillary and fixed. Preliminary examination and data collection were carried out on an area detecting system (kappa-CCD; Nonius FR590) using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Raw data were corrected for Lorentz, polarization, decay and absorption effects. The absorption correction was applied using SADABS.² After merging the independent reflections were used for all calculations. The structure was solved by a combination of direct methods³ and difference Fourier syntheses.⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions using the SHELXL riding model. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.001. Details of the structure determination are given in Table 1 and selected bond lengths and bond angles are given in Tables 2 and 3. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for Crystallography*.⁵ All calculations were performed with the programs COLLECT,⁶ DIRAX,⁷ EVALCCD,⁸ SIR92,³ SADABS,² the SHELXL-97 package^{4,9} and ORTEP-III.¹⁰

Table 1

Crystallographic data for complex **3aa** (CCDC 680958)

	3aa
Measured by	S. Ahrens
Chemical formula	C ₁₈ H ₂₄ I ₂ N ₈ Pt
Color / shape	Colorless / block
Crystal size (mm)	0.13 x 0.31 x 0.38
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> (Å)	10.422(1)
<i>b</i> (Å)	9.778(1)
<i>c</i> (Å)	12.131(1)
α (°)	90
β (°)	110.15(1)
γ (°)	90

V (Å ³)	1160.6(2)
Z	2
T (K)	183 ± 2
ρ_{calcd} (g/cm ³)	2.293
μ (mm ⁻¹)	8.727
F_{000}	744
Θ -range (deg)	3.05 - 29.40
Data collected (h, k, l)	±14, ±13, ±16
No. of reflections collected	32989
No. of independent reflections / R_{int}	3203 (all) / 0.0420
No. of observed reflections ($I > 2\sigma(I)$)	3070
No. of parameters refined	144
$R_1^{[a]}$ (obsd / all)	0.0185 / 0.0198
$wR_2^{[b]}$ (obsd / all)	0.0482 / 0.0489
GOF ^[c]	1.124
Largest difference in peak and hole (e/Å ³)	0.69 / -2.16

$$[a] R_1 = \sum (||F_0| - |F_c||) / \sum |F_0|, [b] wR_2 = \left(\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2 \right)^{1/2}, [c] GOF = \left(\sum w(F_0^2 - F_c^2)^2 / (NO - NV) \right)^{1/2}$$

Table 2

Selected bond lengths (Å) of complex **3aa**.

3aa	
Pt1-C1	2.025(2)
Pt1-C7	2.028(2)
C1-N1	1.344(3)
C1-N2	1.352(4)
N3-C7	1.350(3)
N4-C7	1.349(3)

Table 3

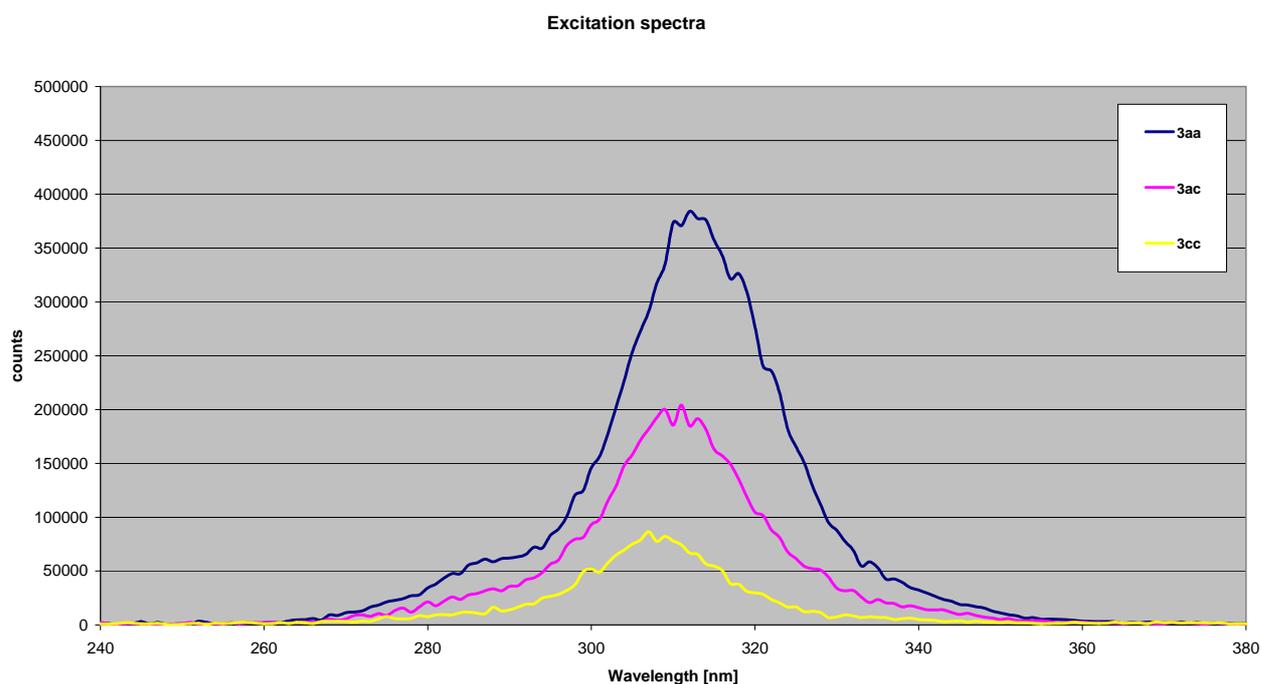
Selected angles (°) of complex **3aa**.

3aa	
C1-Pt1-C7	84.16(11)
C1-Pt1-C7a	95.85(11)
N1-C1-Pt1	133.0(2)
N2-C1-Pt1	122.20(19)
N1-C1-N2	104.8(2)

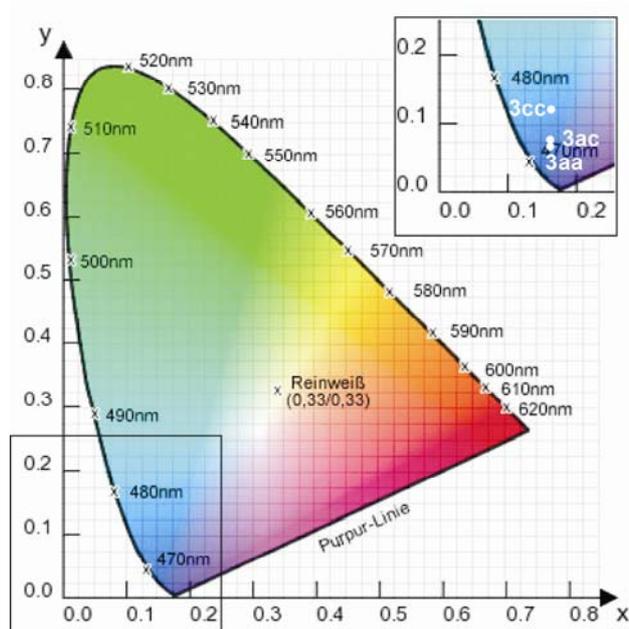
Photoluminescence Measurements

The photoluminescence of the complexes was measured in thin PVA (polyvinyl acetate) films doped with 2% emitter. The films were prepared by doctor blading a solution of emitter (2 mg/L) and PVA in dichloromethane on a substrate with a 60 μm doctor blade. The excitation was carried out vertically to the substrate at a wavelength of 325 nm (HeCd laser) and the emission was detected in a 45° angle with a fiber optics diode array.

Excitation spectra



CIE diagram



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