

Unexpected Coordination Difference in Geometric-Isomerism Between *N,S*- and *N,N*-Heterocyclic Carbenes in Cyclometallated Platinum(II)

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General Procedures. Unless otherwise stated, all manipulations were performed without taking precautions to exclude air and moisture. All solvents were used as received. Benzothiazole and 2-phenylpyridine was purchased from Sigma-Aldrich® and distilled prior to use. [Pt(C[^]N)(acac)]¹ and 1,3-dibenzylbenzimidazolium bromide² were prepared as reported. ¹H and ¹³C NMR spectra were recorded on a Bruker AC 300 and / or AMX 500 spectrometer using Me₄Si as an internal standard. ¹⁹⁵Pt NMR spectra were recorded on a Bruker AMX 500 spectrometer using 1.2 M K₂PtCl₄ in D₂O as an external standard referenced to -1620 ppm.³ ESI mass spectra were obtained using a Finnigan MAT 731 LCQ spectrometer. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

[Pt(C[^]N)(*N*-benzylbenzothiazolin-2-ylidene)(Br)] (1)

A mixture of 3-benzylbenzothiazolium bromide (0.79 g, 0.26 mmol) and Pt(C[^]N)(acac) (0.11 g, 0.24 mmol) was suspended in DMSO (5 mL) and heated at 70 °C overnight. The solvent was removed under vacuum. Purification by column chromatography using CH₂Cl₂ as eluent gave **1** as a yellow solid. Yellow single crystals of **1** were obtained from a diffusion of Et₂O into a concentrated CH₂Cl₂ solution. Yield: 0.05 g (0.077 mmol, 32%). ¹H NMR (300 MHz, CDCl₃): δ 9.85 (d, ³J_{HH} = 5.3 Hz, 1H, Ar-H), 7.98-6.93 (m, 15H, Ar-H), 6.64 (d, ³J_{HH} = 7.6 Hz, 1H, Ar-H), 6.47 (d, ²J_{HH} = 15.3 Hz, 1H, CH₂), 6.20 (d, ²J_{HH} = 15.3 Hz, 1H, CH₂). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 197.5 (s, NSHC), 165.2, 150.9, 144.8, 143.9, 143.3, 138.9, 135.9, 134.3, 133.8, 130.6, 128.9, 128.2, 127.5, 126.7, 124.9, 123.9, 123.8, 122.6, 122.1, 119.2, 118.3, 115.2 (s, Ar-C), 59.5 (s, CH₂). ¹⁹⁵Pt{¹H} NMR (107 MHz, CDCl₃): δ - 3578. MS (ESI, positive mode) m/z (%): 575 [M-

Br]⁺. Anal. Calc for C₂₅H₁₉BrN₂PtS (M = 654.48): C, 45.88; H, 2.93; N, 4.28; S, 4.90. Found: C, 46.20; H, 3.08; N, 4.13; S, 4.72.

[Pt(C[^]N)(*N*-propylbenzothiazolin-2-ylidene)(Br)] (2)

Complex **2** was prepared as described above for **1** from 3-propylbenzothiazolium bromide (0.08 g, 0.29 mmol) and Pt(C[^]N)(acac) (0.12 g, 0.26 mmol). Yellow single crystals of **2** were obtained from a diffusion of Et₂O into a concentrated CH₂Cl₂ solution. Yield: 0.06 g (0.099 mmol, 38%). ¹H NMR (500 MHz, CDCl₃): δ 9.80 (d, ³J_{HH} = 5.7 Hz, J_{PtH} = ca 22 Hz, 1H, Ar-H), 7.84 (d, ³J_{HH} = 8.9 Hz, 2H, Ar-H), 7.75 (m, 1H, Ar-H), 7.69 (d, ³J_{HH} = 8.2 Hz, 1H, Ar-H), 7.58-7.49 (m, 3H, Ar-H), 7.27 (t, ³J_{HH} = 6.9 Hz, 1H, Ar-H), 7.10 (t, ³J_{HH} = 8.2 Hz, 1H, Ar-H), 6.90 (t, ³J_{HH} = 8.2 Hz, 1H, Ar-H), 6.45 (d, ³J_{HH} = 7.6 Hz, 1H, Ar-H), 4.97 (m, 1H, CHHCH₂CH₃), 4.85 (m, 1H, CHHCH₂CH₃), 2.23 (m, 1H, CH₂CHHCH₃), 2.07 (m, 1H, CH₂CHHCH₃), 1.02 (t, ³J_{HH} = 7.3 Hz, 3H, CH₂CH₂CH₃). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 195.3 (s, NSHC), 165.1, 150.8, 144.8, 143.9, 143.4, 138.9, 135.8, 134.3, 130.2, 128.9, 128.8, 126.7, 124.9, 123.8, 123.1, 118.3, 114.0 (s, Ar-C), 56.2 (s, CH₂CH₂CH₃), 22.7 (s, CH₂CH₂CH₃), 14.1 (s, CH₂CH₂CH₃). ¹⁹⁵Pt{¹H} NMR (107 MHz, CDCl₃): δ - 3581. MS (ESI, positive mode) m/z (%): 527 [M-Br]⁺. Anal. Calc for C₂₁H₁₉BrN₂PtS.2Et₂O (M = 754.68): C, 46.15; H, 5.21; N, 3.71; S, 4.25. Found: C, 45.20; H, 4.16; N, 3.98; S, 2.70.

[Pt(C[^]N)(*N,N*-dibenzylbenzimidazol-2-ylidene)(Br)] (3)

Complex **3** was prepared as described above as described above for **1** from dibenzylbenzimidazolium bromide (0.17 g, 0.44 mmol) and Pt(C[^]N)(acac) (0.16 g, 0.37 mmol). A 20 : 1 mixture of isomers was observed in the ¹H NMR spectrum. Yellow single crystals of **3** were obtained from a diffusion of Et₂O into a concentrated CH₂Cl₂ solution. Yield: 0.15 g (0.20 mmol, 54%). ¹H NMR of major isomer (300 MHz, CDCl₃): δ 8.47 (d, ³J_{HH} = 6.9 Hz, J_{PtH} = 25 Hz, 1H, Ar-H), 7.70-7.62 (m, 2H, Ar-H), 7.51 (d, ³J_{HH} = 7.4 Hz, 1H, Ar-H), 7.46-7.11 (m, 17H, Ar-H), 6.36 (t, ³J_{HH} = 7.31 Hz, 1H, Ar-H), 6.14 (d, ²J_{HH} = 15.3 Hz, 2H, CH₂), 5.95 (d, ²J_{HH} = 15.3 Hz, 2H, CH₂). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 193.7 (s, NHC), 169.2 (s, J_{Pt-C} = 34.9 Hz, Ar-H), 158.2 (s, Ar-C), 150.8 (s, J_{Pt-C} = 18.0 Hz, Ar-C), 145.9, 137.1, 135.7, 135.5, 134.9 (s, Ar-C), 130.5 (s, J_{Pt-C} = 16.4 Hz, Ar-C), 128.4,

127.9, 127.8, 123.8, 123.3, 123.0 (s, Ar-C), 121.9 (s, $J_{\text{Pt-C}} = 22.4$ Hz, Ar-C), 118.9 (s, $J_{\text{Pt-C}} = 22.4$ Hz, Ar-C), 111.5 (Ar-C), 51.7 (s, $J_{\text{Pt-C}} = 8.73$ Hz, CH₂). ¹⁹⁵Pt{¹H} NMR (107 MHz, CDCl₃): δ - 3584. MS (ESI, positive mode) m/z (%): 648 [M-Br]⁺. Anal. Calc for C₃₂H₂₆BrN₃Pt.H₂O (M = 745.57): C, 51.55; H, 3.79; N, 5.64. Found: C, 50.21; H, 3.97; N, 4.89.

X-ray Diffraction Studies

Single crystals of complexes **1-3** were obtained by diffusion of Et₂O into CH₂Cl₂ solution. Suitable crystals were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The collecting frames of date, indexing reflection and determination of lattice parameters and polarization effects were performed with the SMART suite programs.⁴ The integration of intensity of reflections and scaling was performed by SAINT. The empirical absorption correction was performed by SADABS.⁵ The space group determination, structure solution and least-squares refinements on $|F|^2$ were carried out with the SHELXTL.⁶ The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The crystal of **3** contains two independent molecules in the asymmetric unit cell. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions. A selected summary of crystal data for complexes **1-3** are summarized in Tables 1.

Table 1: Selected bond lengths [Å] and angles [deg] of **1-3**.

Bond Lengths	1	2	3
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[Å]	Molecule a			Molecule b	
Pt1-C1	1.939(4)	1.946(4)	2.053(7)	Pt2-C33	2.035(8)
Pt1-N2	2.074(4)	2.080(3)	-	-	-
Pt1-N3	-	-	2.022(6)	Pt2-N6	2.024(6)
Pt1-C21	2.000(4)	1.985(4)	-	-	-
Pt1-C32	-	-	2.037(6)	Pt2-C64	2.025(8)
Pt1-Br1	2.521(5)	2.525(5)	2.443(9)	Pt2-Br4	2.437(9)
S1-C1	1.722(4)	1.725(4)	-	-	-
S1-C7	1.736(5)	1.747(4)	-	-	-
N1-C1	1.346(5)	1.340(5)	1.377(8)	N4-C33	1.346(8)
N1-C2	1.403(5)	1.401(5)	1.391(9)	N4-C34	1.402(10)
N1-C8	1.480(5)	1.471(5)	1.444(9)	N4-C40	1.470(9)
N2-C1	-	-	1.344(9)	N5-C33	1.351(9)
N2-C7	-	-	1.411(8)	N5-C39	1.396(9)
Angles [deg]					
C1-Pt1-C21	93.71(16)	93.29(17)	-	-	-
C1-Pt1-C32	-	-	178.2(3)	C33-Pt2-C64	175.9(3)
C1-Pt1-N2	174.76(14)	170.87(15)	-	-	-
C1-Pt1-N3	-	-	98.1(2)	C33-Pt2-N6	96.2(3)
C21-Pt1-N2	81.08(15)	80.85(16)	-	-	-
C32-Pt1-N3	-	-	80.7(3)	C64-Pt2-N6	80.0(3)
C1-Pt1-Br1	89.58(11)	90.02(12)	86.86(19)	C33-Pt2-Br4	88.03(19)
C21-Pt1-Br1	176.65(11)	173.56(11)	-	-	-
C32-Pt1-Br1	-	-	94.2(2)	C64-Pt2-Br4	95.7(2)
N2-Pt1-Br1	95.62(9)	96.51(11)	-	-	-
N3-Pt1-Br1	-	-	173.60(16)	N6-Pt2-Br4	175.41(19)
C1-N1-C8	122.5(4)	121.2(3)	126.2(6)	C33-N4-C40	123.4(7)
C11-N2-C15	118.4(4)	118.8(4)	-	-	-
C22-N3-C26	-	-	119.2(6)	C54-N6-C58	118.5(7)
C11-N2-Pt1	127.2(3)	125.9(3)	-	-	-
C22-N3-Pt1	-	-	125.3(5)	C54-N6-Pt2	124.0(6)
C15-N2-Pt1	114.3(3)	114.4(3)	-	-	-
C26-N3-Pt1	-	-	115.4(5)	C58-N6-Pt2	117.3(5)
N1-C1-S1	109.2(3)	109.7(3)	-	-	-
N1-C1-N2	-	-	106.8(6)	N4-C33-N5	104.8(7)
N1-C1-Pt1	128.8(3)	126.6(3)	125.5(5)	N4-C33-Pt2	128.8(6)
S1-C1-Pt1	121.9(2)	123.7(2)	-	-	-
N2-C1-Pt1	-	-	127.4(5)	N5-C33-Pt2	126.3(5)

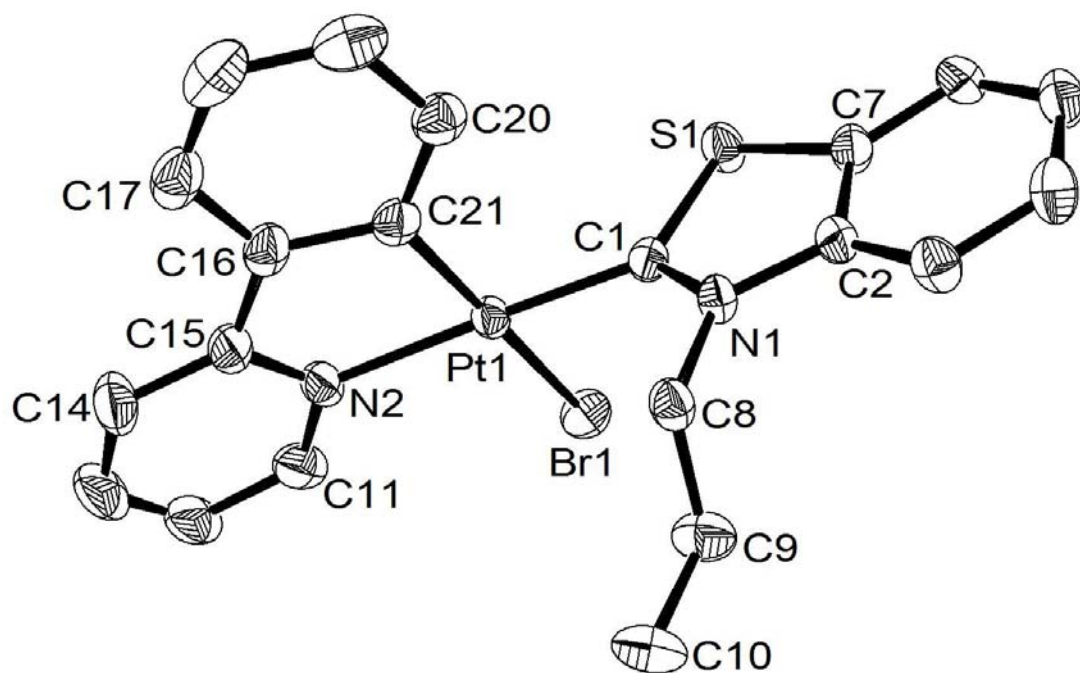


Fig. S1. ORTEP representation of **2** with 50% thermal ellipsoids and labeling scheme; hydrogen atoms are omitted for clarity.

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