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Note

Synthesis and structural characterization of two bis(imidazol-2-ylidene) complexes of Pt(II)

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Abstract

The air stable syntheses of two new chelating N-heterocyclic carbene complexes of Pt(II), bis(1,1′-*n*-butylimidazolium)-3,3′-methylenePtI$_2$ (**2**) and bis[bis(1,1′-*n*-butylimidazolium)-3,3′-methylene]PtI$_2$ (**3**) are described.

1. Introduction

Since the discovery of stable free N-heterocyclic carbene ligands by Arduengo in 1991 [1], many transition metal carbene complexes have been synthesized [2]. However, there are few complexes reported for Pt(II) [3]. All such complexes were synthesized by carbene transfer to platinum [3b,3c], via the free carbene [3e], or in situ in nonaqueous ionic liquids [3a,3d]. Where the Pd systems were easily synthesized using palladium(II) acetate [4], the corresponding Pt complexes were unattainable via an analogous route using platinum(II) acetate. Herein, we report the first synthesis of two bis(imidazol-2-ylidene) complexes of Pt(II) by a previously unpublished route [5,6].

The synthesis of the Pt(II) complexes, bis(1,1′-*n*-butylimidazolium)-3,3′-methylenePtI$_2$ (**2**) and bis[bis(1,1′-*n*-butylimidazolium)-3,3′-methylene]PtI$_2$ (**3**) is illustrated in Scheme 1. The condensation of *n*-butyl imidazole and diiodomethane in THF afforded **1** as a fine white powder in 83% yield [7,8]. Deprotonation of **1** with sodium acetate in wet DMSO at 90 °C in the presence of PtCl$_2$ produced complexes **2** and **3** in 50 and 16% yields, respectively. Even when a precise 1:1 ratio of **1** to PtCl$_2$ was used, a small amount of the tetracarbene **3** was produced. A 2:1 reaction resulted in approximately a 50:50 mixture of the two products. By deprotonating the carbonium sites with KH at -78 °C to generate the free carbene, followed by an addition of PtCl$_2$, the analogous PtCl$_2$ carbene complex was also synthesized. This was confirmed by mass spectrometry, though the yield and purity of the product were extremely low.

The choice of DMSO as solvent proved to be problematic. Mass spectrometric analysis revealed the presence of (DMSO)$_2$PtI$_2$ in the sample. This is believed to be the reason for the low yields of **2** and **3**. By diluting the reaction mixture, the synthesis of **3** can be avoided, thereby increasing the yield of **2** to 69.2%. Other solvents were screened, and acetonititrile seemed to be the next best solvent, though, even in dilute reactions, it afforded a greater percentage of the tetracarbene complex **3**.

The complexes **2** and **3** can be readily separated with acetonitrile. Whereas **3** is very soluble in acetonitrile, **2** is only slightly soluble. Surprisingly, both **2** and **3** were cocrystallized from a solution in acetonitrile. Crystals of **2** alone were obtained from slow evaporation of a saturated solution in chloroform. Crystals of **3** alone have so far been unattainable.

The ^{1}H and ^{13}C spectra are in agreement with the solid state structure for **2** and **3**, as shown in Figs. 1 and 2. In the ^{1}H- and ^{13}C-NMR spectra for **1**, the most notable resonances are the carbonium C–H occurring as a singlet at 9.46 ppm and the methylene linker between the imidazolium units occurring as a singlet at 6.63 ppm. In contrast to the ^{1}H-NMR spectrum of **1**, the two protons on the methylene linker are inequivalent and

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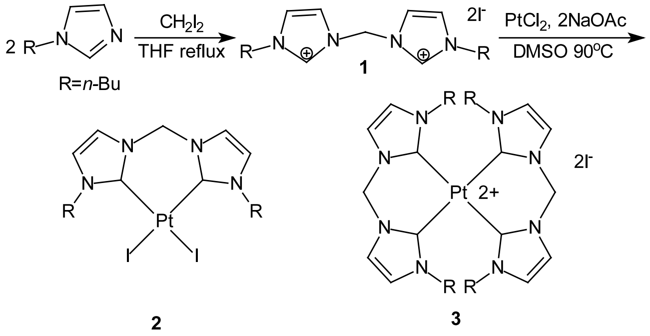

Scheme 1.

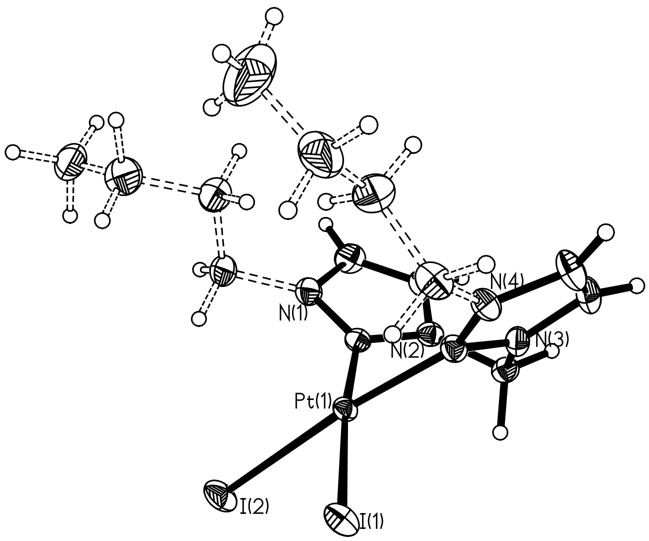

Fig. 1. Thermal ellipsoid plot of **2**. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths and angles: Pt(1)–C(7): 1.983(3); Pt(1)–C(11): 1.991(3); Pt(1)–I(1): 2.6563(3); Pt(1)–I(2): 2.6641(3) Å, C(7)–Pt(1)–I(1): 174.76(10), and C(11)–Pt(1)–I(2) 171.89(10)°.

appear as two doublets at 6.05 ppm ($^1J = 13$ Hz) for **2** and at 6.34 ppm ($^1J = 13$ Hz) for **3**. The inequivalency of the protons can be explained by hindered rotation about the methylene linker due to the presence of the Pt. Also, the protons on the carbon of the butyl chain closest to the nitrogen are split into two multiplets. This occurs because the ligand is twisted relative to the Pt and, therefore, the two protons on that specific carbon atom are no longer equivalent. The absence of a resonance at ca. 9 ppm is diagnostic for the loss of the carbonium proton.

The crystal structure of the co-crystallized mixture of **2** and **3** is reported below. Table 1 summarizes X-ray collection data and final structure refinements. Selected bond distances and angles are summarized in Table 2. The crystals of **2** alone were also characterized by X-ray crystallography. The crystal data and structural refinement of **2** is summarized in Table 3. With the exception of the butyl chains, the distances and angles found for the two forms of **2** are within experimental error.

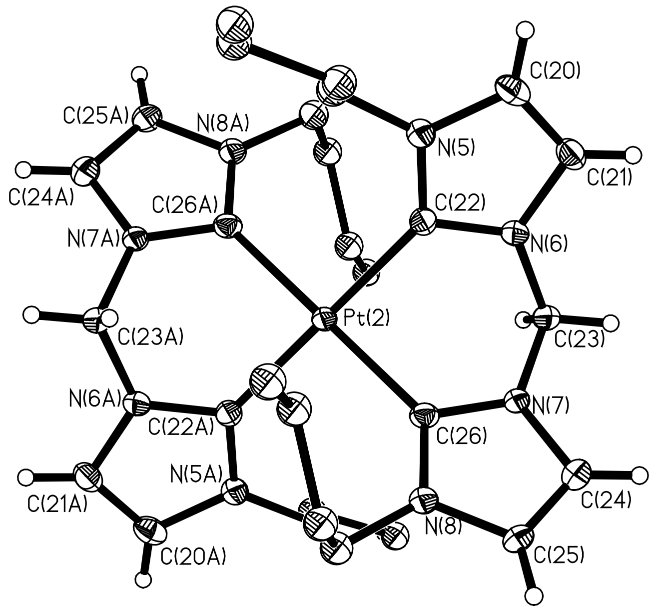

Fig. 2. Thermal ellipsoid plot of **3**, with thermal ellipsoids drawn at 50% probability. Iodide anions and hydrogen atoms on the alkyl chains have been omitted for clarity. Carbons of the alkyl chains were fixed as isotropic with artiffically low displacement parameters for modeling purposes. Selected bond lengths and angles: Pt(2)–C(22): 2.026(3); Pt(2)–C(22a): 2.026(3); Pt(2)–C(26): 2.030(3); Pt(2)–C(26a): 2.030(3) Å, C(22)–Pt(2)–C(22a): 180.0, and C(26)–Pt(2)–C(26a): 180.0°.

Table 1
Crystal data and structure refinement for **2** and **3**

Compound	**2** and **3**
Empirical formula	$C_{32}H_{51}I_3N_9Pt_{1.50}$
Formula weight	1235.15
Temperature (K)	100(2)
λ (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	10.1145(6)
b (Å)	13.1692(8)
c (Å)	16.548(1)
α (°)	109.022(1)
β (°)	95.856(1)
γ (°)	92.796(1)
V (Å^3)	2065.1(2)
Z	2
D_{calc} (Mg m^{-3})	1.986
Crystal size (mm)	0.20 × 0.10 × 0.09
θ Range (°)	1.64–27.49
Reflections collected	25 314
Reflections unique (R_{int})	9127 (0.0272)
Data/restraint/parameters	9127/0/565
R_1, wR_2 [$I > 2\delta(I)$]	0.0247, 0.0559
R_1, wR_2 (all data)	0.0273, 0.0569
Goodness-of-fit	1.060

Compound **2** (Fig. 1) is neutral with two coordinating iodides balancing the charge of the metal. In this

Table 2
Selected bond lengths (Å) and angles (°) for **2** and **3**

2		**3**	
Bond lengths			
Pt(1)–C(7)	1.983(3)	Pt(2)–C(22)	2.026(3)
Pt(1)–C(11)	1.991(3)	Pt(2)–C(26)	2.030(3)
Pt(1)–I(1)	2.6563(3)	N(5)–C(22)	1.352(4)
Pt(1)–I(2)	2.6641(3)	N(6)–C(22)	1.352(4)
N(1)–C(7)	1.354(4)	N(5)–C(19)	1.473(5)
N(1)–C(5)	1.389(5)	N(5)–C(20)	1.387(4)
N(1)–C(4)	1.492(5)	N(6)–C(21)	1.390(4)
N(2)–C(7)	1.355(4)	N(6)–C(23)	1.464(4)
N(2)–C(6)	1.389(5)	C(20)–C(21)	1.337(5)
N(2)–C(8)	1.462(4)		
C(5)–C(6)	1.343(5)		
Bond angles			
C(7)–Pt(1)–C(11)	84.2(1)	C(22)–Pt(2)–C(26)	84.0(1)
I(1)–Pt(1)–I(2)	89.892(9)	N(5)–C(22)–Pt(2)	133.8(2)
C(7)–Pt(1)–I(2)	92.49(9)	N(5)–C(22)–N(6)	104.6(3)
N(1)–C(7)–Pt(1)	134.2(3)	C(22)–N(5)–C(19)	124.6(3)
N(1)–C(7)–N(2)	105.0(3)	C(22)–N(5)–C(20)	110.6(3)
C(7)–N(1)–C(5)	110.3(3)	C(21)–C(20)–N(5)	107.5(3)
C(7)–N(1)–C(4)	125.4(3)	C(22)–N(6)–C(21)	111.3(3)
C(6)–C(5)–N(1)	107.4(3)	C(22)–N(6)–C(23)	122.3(3)
C(5)–C(6)–N(2)	106.4(3)	C(20)–C(21)–N(6)	106.1(3)
C(7)–N(2)–C(6)	110.9(3)	N(7)–C(23)–N(6)	108.1(3)
C(7)–N(2)–C(8)	121.5(3)		
N(2)–C(8)–N(3)	107.2(3)		

Table 3
Crystal data and structure refinement for **2**

Compound	**2**
Empirical formula	$C_{15.5}H_{24.5}C_{11.5}I_2N_4Pt$
Formula weight	769.8
Temperature (K)	100(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.614(1)
b (Å)	15.259(2)
c (Å)	14.393(1)
α (°)	90
β (°)	102.937(2)
γ (°)	90
V (Å^3)	2271.9(4)
Z	4
D_{calc} (Mg m^{-3})	2.248
Crystal size (mm)	0.06 × 0.03 × 0.02
θ Range (°)	1.97–25.00
Reflections collected	15 924
Reflections unique (R_{int})	3998
Data/restraint/parameters	3998/0/228
R_1, wR_2 [$I > 2\delta(I)$]	0.0398, 0.0858
R_1, wR_2 (all data)	0.0693, 0.0918
Goodness-of-fit	1.039

complex, Pt(1) is square planar with both the carbene and iodide ligands in a *cis* conformation. The C(7)–Pt(1)–I(1) and C(11)–Pt(1)–I(2) bond angles are 174.7(1) and 171.9(1)°, respectively. The Pt(1)–C(7) and Pt(1)–C(11) carbene distances are 1.983(3) and 1.991(3) Å, which compare well with previously reported Pt–carbene distances [3]. The C(7)–Pt(1)–C(11) bond angle of 84.2(1)° deviates from idealized angles, presumably due to the restraint imposed by the chelating nature of the ligand. The Pt(1)–I(1) and Pt(1)–I(2) distances are 2.6563(3) and 2.6641(3) Å, respectively. The I(1)–Pt(1)–I(2) angle is as expected for a square planar geometry at 89.89(1)°.

Compound **3** (Fig. 2) is a cationic complex of Pt(II). The Pt is surrounded by two methylene-linked N-heterocyclic carbenes, and the charge is balanced by two non-coordinating iodide anions. The coordination around Pt(2) is square planar with the metal located on an inversion center. The Pt(2)–C(22) and Pt(2)–C(26) distances are 2.026(3) and 2.030(3) Å, respectively. The C(22)–Pt(2)–C(27) bond angle is 84.0(1)°, which corresponds well with that of **2**. The alkyl chains of the respective ligands point away from one another in order to minimize the steric interactions.

In conclusion, we have demonstrated the synthesis of two new chelating N-heterocyclic carbene complexes of Pt(II). They are the first of their kind to be prepared in a non-inert atmosphere using a conventional solvent.

2. Experimental

2.1. General procedures

The *n*-butyl imidizole, CH_2I_2, and Me_2SO were purchased from Aldrich and used as received. $PtCl_2$ was purchased from Strem and also used as received.

Mass spectrometric analysis was performed by the mass spectrometry facility at our university. ^{1}H- and ^{13}C-NMR spectra were obtained on a Varian 300 MHz instrument. Elemental analyses were performed by E & R Microanalytical Laboratories, Inc. The X-ray analyses were performed in our laboratory

The full sphere of data was collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The reflections were collected using psi and omega scans. Unit cell determination was achieved by using reflections from three different orientations. An empirical absorption correction and other corrections were done using multi-scan SADABS. Structure solution, refinement and modeling were accomplished using the Bruker SHELXTL package [9]. The structure was obtained by full-matrix least-squares refinement of F^2 and the selection of appropriate atoms from the generated difference map. Hydrogen atom positions for the structure of **2** were calculated and their β values fixed accordingly. Hydrogen atoms for the co-crystallized structure of **2** and **3** were found from the difference map and their positions refined.

2.1.1. 1,1′-Methylene bis(3-n-butylimidizolium)diiodide (1)

To a solution of 10.0 g (80.5 mmol) of *n*-butyl imidazole in 150 ml of THF was added 10.27 g (38.3 mmol) of CH_2I_2. This solution was stirred at reflux temperature for 72 h. The solution was then cooled and filtered to give **1** as a fine white powder in 83% yield (16.4 g). ^{1}H-NMR 300 MHz (Me_2SO-d_6): δ 0.91 (t, 3H, CH_3), 1.29 (sextet, 2H, CH_2), 1.79 (quintet, 2H, CH_2), 4.23 (t, 2H, CH_2), 6.63 (s, 1H, CH_2), 7.92 (d, 1H, CH), 8.00 (d, 1H, CH), 9.46 (s, 1H, CH). ^{13}C-NMR 60 MHz (Me_2SO-d_6): δ 13.29 (CH_3), 18.71 (CH_2), 30.97 (CH_2), 49.06 (CH_2) 58.28 (N–CH_2–N), 122.09 (CH), 123.14 (CH), 137.40 (carbonium C). MS m/z^+ ESI Calculated: 642.91. Found: 642.9. Anal. Calc. for $C_{15}H_{26}I_2N_4$: C, 34.9; H 5.08; N, 10.85. Found: C, 34.8; H, 4.98; N, 10.74%.

2.1.2. Bis(1,1′-n-butylimidazolium)-3,3′-methylenePtI$_2$ (2) and bis[bis(1,1′-n-butylimidazolium)-3,3′-methylene]PtI$_2$ (3)

To a solution of 1.07 g (2.07 mmol) of **1** in 50 ml of Me_2SO was added 0.50 g (1.88 mmol) of $PtCl_2$ and 0.57 g (4.14 mmol) of sodium acetate. The solution was stirred at 90 °C for 1.5 h, and the solvent was removed in vacuo. The residue was taken up in $CHCl_3$ and washed several times with water. Removal of the solvent in vacuo afforded **2** (0.995 g) and **3** (0.6366 g) in 50 and 16% yields, respectively. In order to optimise the yield of **2** under the exact same reaction conditions, the volume of solvent was increased to 500 ml. This bypassed the synthesis of **3** and afforded 1.250 g (69.2%) of **2**. For **2**: ^{1}H-NMR (Me_2SO-d_6): δ 0.85 (t, 3H, CH_3), 1.15 (sextet, 2H, CH_2), 1.72 (quintet, 2H, CH_2), 3.97 (m, 1H, CH_2), 4.72 (m, 1H, CH_2), 6.05 (2d, 2H, CH_2), 7.39 (d, 1H, CH), 7.53 (d, 1H, CH). ^{13}C-NMR (Me_2SO-d_6): δ 14.16 (CH_3), 19.70 (CH_2), 32.52 (CH_2), 51.13 (CH_2) 62.83 (N–CH_2–N), 121.26 (CH), 122.02 (CH), 149.61 (carbene C). MS m/z^+ ESI $(-I)^-$ Calculated: 582.6. Found: 582.2.

For **3**: ^{1}H-NMR (Me_2SO-d_6): δ 0.85 (t, 3H, CH_3), 1.15 (sextet, 2H, CH_2), 1.72 (quintet, 2H, CH_2), 4.22 (m, 1H, CH_2), 4.48 (m, 1H, CH_2), 6.34 (2d, 1H, CH_2), 7.60 (br. s, 1H, CH), 7.79 (br. s, 1H, CH). MS m/z^+ ESI $(-I)^-$ Calculated: 842.3. Found: 843.3.

3. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 190035 and 190036 for the compounds $C_{32}H_{51}I_3N_9Pt_{1.50}$ and $C_{15.5}H_{24.5}Cl_{1.5}I_2N_4Pt$, respectively. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk).

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