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Polyhedron 22 (2003) 1515–1521

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Synthesis, crystal structure and photophysical properties of *N*-heterocyclic carbene Pd(II), Pt(II) complexes and iodine adduct

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Received 22 November 2002; accepted 28 February 2003

Abstract

In the presence of $KOBu^t$, 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1**) is treated with $PdCl_2$ and $Pt(cod)Cl_2$ in acetonitrile and THF to afford the luminescent complexes [1-(9-anthracylmethyl)-3-ethylimidazol-2-ylidene]$_2PdCl_2$ (**2**) and [1-(9-anthracylmethyl)-3-ethylimidazol-2-ylidene]$_2PtCl_2$ (**3**), respectively, and an analogous treatment with iodine affords [1-(9-anthracylmethyl)-3-ethylimidazol-2-ylidene I]$^+$ I_3^- (**4**). In a refluxed CH_2Cl_2 solution imidazolium salt **1** is transformed into another salt 1-(9-anthracylmethyl)-3-ethylimidazol-2-ylidene chloride (**5**). The luminescent emission spectra of **1**, **2**, **3** and **4** are determined.

Keywords: Carbenes; Palladium; Platinum; Iodine; Crystal structures; Luminescence

1. Introduction

In recent years the discovery of stable *N*-heterocyclic carbenes has provided exciting new possibilities for the chemistry of carbene metal complexes [1]. While some of these carbenes are isolable, less stable relatives may be generated and used in situ [2]. *N*-Heterocyclic carbenes metal complexes are usually stable to heat, air, and moisture [3], and therefore the introduction of carbene ligands to metal can be performed under simple and mild conditions. This attractive feature stimulates extensive interest, and many transition metal complexes with *N*-heterocyclic carbenes derived from imidazolium ions have been synthesized [4]. *N*-heterocyclic carbenes are easily accessible and, due to their strong σ-donating character resembling phosphine ligands [5], their transition metal complexes can act as catalysts and catalyst precursors in some important transformations, such as Pd-catalysed Heck Suzuki coupling, CO-ethylene copolymerisation, Ru-catalysed olefin metathesis and Rh-catalysed hydrosilylation [6]. Furthermore, electronic and steric optimization of the catalytic site should be acheivable via ligand design. However *N*-heterocyclic carbene complexes exhibiting fluorescence have not been explored up to now. In this context we wish to report the synthesis, structure and photophysical properties of *N*-heterocyclic carbene Pd(II) and Pt(II) complexes as well as an iodine adduct.

2. Experimental

2.1. General procedures

All manipulations were performed using Schlenk techniques, and solvents were purified by standard procedures. All the reagents for syntheses and analyses were of analytical grade and used without further purification. Melting points were determined with a Boetius Block apparatus. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Mercury Vx 300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts, δ, are reported in parts per million relative to the internal standard TMS for both ^1H and ^{13}C NMR. Elemental analyses were measured using a Perkin–

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doi:10.1016/S0277-5387(03)00268-7

Elmer 2400C Elemental Analyzer. The luminescent intensities of **1**, **2**, **3** and **4** were measured using a Cary Eclipse Fluorescence spectrophotometer.

*2.2. [1-(9-Anthracylmethyl)-3-ethylimidazol-2-ylidene]$_2$PdCl$_2$ (**2**)*

A stirred suspension of KOBu^t (0.056 g, 0.500 mmol), 1-(9-anthracylmethyl)-3-ethylimidazolium iodide (0.200 g, 0.483 mmol) and PdCl$_2$ (0.043 g, 0.242 mmol) in acetonitrile (20 ml) and tetrahydrofuran (20 ml) was refluxed for 8 h, during which time a brown solution formed. After cooling the solvents were removed in vacuo, water (30 ml) was added to the residue, and then the solution was extracted with CH$_2$Cl$_2$ (3 × 20 ml). The extracting solution was dried with anhydrous MgSO$_4$, then concentrated to 10 ml, and hexane (2 ml) was added to give a yellow powder. Yield: 0.089 g (49.3%), m.p.: 294–296 °C. *Anal*. Calc. for $C_{40}H_{36}Cl_2N_4Pd$: C, 64.05; H, 4.84; N, 7.47. Found: C, 64.32; H, 4.53; N, 7.88%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.73 (s, 1H, AnH) (An: anthracene), 8.38 (d, $J = 8.4$, 2H, AnH), 8.10 (d, $J = 8.4$, 2H, AnH), 7.55 (m, 4H, AnH), 7.38 and 7.32 (s, 2 × 1H, 4, 5-imiH) (imi: imidazole), 6.44 (s, 2H, CH$_2$–An), 4.46 (q, $J = 7.2$, 2H, CH$_2$–CH$_3$), 1.59 (t, $J = 7.2$, 3H, CH$_3$). ^{13}C NMR(75 MHz, DMSO-d_6): δ 167.8 (C$_{carbene}$), 130.9, 130.5, 129.1, 127.3 and 125.4 (AnC), 123.9, 122.2 and 120.3 (AnC or 4, 5-imiC), 54.8 (CH$_2$–An), 45.6 (CH$_2$–CH$_3$), 16.0 (CH$_3$).

*2.3. [1-(9-Anthracylmethyl)-3-ethylimidazol-2-ylidene]$_2$PtCl$_2$ (**3**)*

This complex was prepared in a manner analogous to that for **2**. Starting from **1** (0.200 g, 0.483 mmol) and Pt(cod)Cl$_2$ (0.090 g, 0.024 mmol) complex **3** was obtained as a yellow powder (0.218 g, 51%), m.p.: 270–272 °C (dec.). *Anal*. Calc. for $C_{40}H_{36}Cl_{1.5}I_{0.5}N_4Pt$: C, 54.30; H, 4.10; N, 6.34. Found: C, 54.31; H, 4.36; N, 6.79%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.80 (s, 1H, AnH), 8.21 (d, $J = 8.4$, 2H, AnH), 8.12 (d, $J = 8.4$, 2H, AnH), 7.51 (m, 4H, AnH), 7.22 and 7.08 (s, 2 × 1H, 4, 5-imiH), 6.46 (s, 2H, CH$_2$An), 4.44 (q, $J = 7.2$, 2H, CH$_2$CH$_3$), 1.35 (t, $J = 7.2$, 3H, CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 131.7, 129.9, 129.5, 128.1 and 126.1 (AnC), 124.6, 124.3, 121.7 and 119.0 (AnC or 4, 5-imiC), 47.2 (CH$_2$–An), 46.1 (CH$_2$–CH$_3$), 16.0 (CH$_3$), (carbene carbon was not observed).

*2.4. [1-(9-Anthracylmethyl)-3-ethylimidazol-2-ylidene I] I$_3^-$ (**4**)*

A suspension of KOBu^t (0.056 g, 0.500 mmol), precursor **1** (0.200 g, 0.483 mmol) and iodide (0.249 g, 0.980 mmol) in THF (20 ml) and acetonitrile (20 ml) was refluxed for 8 h, after which time a brown solution formed and the solvent was removed with a rotary evaporator. Then water (30 ml) was added to the residue and the solution was extracted with CH$_2$Cl$_2$ (3 × 20 ml). The extracting solution was dried with anhydrous MgSO$_4$, then concentrated to 10 ml, and hexane (2 ml) was added to give a purple red powder. Yield: 0.199 g (52%), m.p.: 214–216 °C. *Anal*. Calc. for $C_{20}H_{18}I_4N_2$: C, 30.26; H, 2.29; N, 3.53. Found: C, 30.17; H, 2.44; N, 3.82%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.87 (s, 1H, AnH), 8.21 (t, $J = 8.7$, 4H, AnH), 7.64 (m, 4H, AnH), 7.80 and 6.78 (d, $J = 2.1$, 2 × 1H, 4, 5-imiH), 6.25 (s, 2H, CH$_2$–An), 4.22 (q, $J = 7.2$, 2H, CH$_2$–CH$_3$), 1.38 (t, $J = 7.2$, 3H, CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 131.0, 130.9, 130.3, 129.4, 127.7, 125.6 (AnC), 124.0, 123.3, 122.2 (AnC or 4, 5-imiC), 109.2 (C$_{carbene}$), 48.4 (CH$_2$–An), 47.1 (CH$_2$–CH$_3$), 14.8 (CH$_3$).

*2.5. 1-(9-Anthracylmethyl)-3-ethylimidazol-2-ylidene chloride (**5**)*

A suspension of KOBu^t (0.056 g, 0.500 mmol), and precursor **1** (0.200 g, 0.483 mmol) in CH$_2$Cl$_2$ (40 ml) was refluxed for 10 h. After cooling, the solution was filtrated, the filtrate was concentrated to 10 ml, and hexane (2 ml) was added to give a yellow powder. Yield: 0.092 g (59%), m.p.: 190–192 °C. *Anal*. Calc. for $C_{20}H_{19}ClN_2$: C, 74.41; H, 5.93; N, 8.68. Found: C, 74.18; H, 5.68; N, 8.33%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.00 (s, 1H, 2-imiH). 8.85 (s, 1H, AnH), 8.35 (d, $J = 8.2$, 2H, AnH), 8.23 (d, $J = 8.2$, 2H, AnH), 7.79 and 7.69 (s, 2 × 1H, 4, 5-imiH), 7.69 (t, $J = 8.2$, 2H, AnH), 7.65 (t, $J = 8.2$, 2H, AnH), 6.48 (s, 2H, CH$_2$–An), 4.10 (q, $J = 7.2$, 2H, CH$_2$–CH$_3$), 1.32 (t, $J = 7.2$, 3H, CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 135.3 (2-imiC), 131.7, 131.0, 130.5, 130.0, 129.3, 127.7, 125.5 (AnC), 123.3, 122.5 and 122.0 (AnC or 4, 5-imiC), 44.7 and 44.1 (CH$_2$–CH$_3$ and CH$_2$–An), 15.1 (CH$_3$).

2.6. X-ray crystallography

For each of compounds **2**, **3**, **4** and **5**, a selected single crystal was mounted on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 20 mA using Mo Kα radiation (0.71073 Å). Data collection and reduction were performed using the SMART and SAINT software [7] with frames of 0.6° oscillation in the θ range $1.8° < \theta < 25°$. An empirical absorption correction was applied using the SADABS program [8]. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL package [9]. All hydrogen atoms were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriated isotropic thermal parameters and included in structure factor calculations. Crystal data and structure refine-

Table 1
Crystallographic data and details of the structure determination for **2**–**5**

Compound	**2**	**3**	**4**	**5**
Empirical formula	$C_{42}H_{40}Cl_6N_4Pd$	$C_{42}H_{40}Cl_{5.50}I_{0.50}N_4Pt$	$C_{20}H_{18}I_4N_2$	$C_{20}H_{21}ClN_2O$
Formula weight	919.88	1054.29	793.96	340.84
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Unit cell dimensions				
a (Å)	10.962(4)	11.005(4)	10.982(4)	9.134(3)
b (Å)	8.568(3)	8.667(3)	9.951(3)	19.925(6)
c (Å)	22.636(9)	22.573(7)	21.886(7)	9.787(3)
α (°)	90	90	90	90
β (°)	96.737(7)	97.130(5)	101.281(6)	97.481(7)
γ (°)	90	90	90	90
V (Å^3)	2111(1)	2136(1)	2346(1)	1766(1)
Z	2	2	4	4
D_{calc} (Mg m^{-3})	1.447	1.639	2.248	1.282
μ (Mo Kα) (cm^{-1})	8.54	40.24	5.321	0.225
$F(0\,0\,0)$	936	1036	1456	720
Crystal size (mm)	0.52 × 0.42 × 0.30	0.30 × 0.25 × 0.20	0.22 × 0.20 × 0.18	0.32 × 0.18 × 0.08
θ_{min}, θ_{max} (°)	1.98, 26.38	1.82, 25.02	2.26, 26.41	2.04, 23.00
T (K)	293(2)	293(2)	293(2)	293(2)
Reflections collected	11 712	8091	13 152	7541
Independent reflections	4315	3588	4787	2452
Observed reflections [$I > 2\sigma(I)$]	3059	2208	236	220
Parameters	241	241	2974	1342
Residuals [a]: R; wR	0.0599, 0.1528	0.0407, 0.0793	0.0404, 0.0863	0.0644, 0.1653
Goodness-of-fit	1.029	0.968	0.964	0.989

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$ where $P = (F_o^2 + 2F_c^2)/3$.

ment details are summarized in Table 1. Selected bond lengths and bond angles are showed in Table 2.

3. Results and discussion

The required precursor, substituted imidazolium iodide **1**, was prepared from imidazole by stepwise alkylations with 9-chloromethylanthracene followed by ethyl iodide in sequence, and obtained as yellow crystals in analogy to a reported procedure [10].

The direct reaction of 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1**) with metal compounds $PdCl_2$ or $Pt(cod)Cl_2$ in the presence of $KOBu^t$ in acetonitrile and THF solution afforded the luminescent complexes [1-(9-anthracylmethyl)-3-ethylimidazol-2-ylidene]$_2$PdCl$_2$ (**2**) and [1-(9-anthracylmethyl)-3-ethylimidazol-2-ylidene]$_2$PtCl$_2$ (**3**), respectively. Complexes **2** and **3** are soluble in DMSO, sparingly soluble in chloroform and insoluble in diethyl ether and hydrocarbon solvents. The complexes are stable in air and moisture, and display high thermal stability. The ^{1}H NMR spectra of **2** and **3** do not show a low-field signal of 9.00 ppm, and the chemical shifts of other hydrogens are similar to those of **1**. In the ^{13}C NMR spectrum the signal for the carbene carbon appears at 167.8 ppm for **2**, which is characteristic for carbene metal complexes [11].

Crystals of **2** and **3** were grown by evaporating slowly their dichloromethane solutions at room temperature. The molecular structure of **2** is depicted in Fig. 1 (**3** is isomorphous **2**). The Pd(II) center and two imidazole rings lie in the same plane. The Cl–Pd–Cl unit is linear and perpendicular to the above mentioned plane. Pairs of 1-(9-anthracylmethyl)-3-ethylimidazol-2-ylidene and Cl^- ligands are in a *trans* configuration. Because both anions Cl^- and I^- are included in the reaction system, 1.5 Cl^- and 0.5 I^- are incorporated in the molecular structure of **3**, but only Cl^- appears in the molecular structure of **2**. The Pd–C bond distance is 2.038(5) Å in complex **2** and the Pt–C one is 2.044(7) Å in complex **3**, which are similar to those in analogous palladium and platinum complexes [12]. Compared to **1,** the bond angles N–C–N in the imidazole ring for **2** and **3** decrease by about 2°. The dihedral angle between the anthracene and imidazole ring planes is 82.3° for **2** and 97.5° for **3**.

1-(9-Anthracenylmethyl)-3-ethylimidazolium iodide (**1**) reacts with iodine in the presence of $KOBu^t$ in acetonitrile and THF solution to give a purple product [1-(9-anthracylmethyl)-3-ethylimidazol-2-ylidene I]$^+$ $I_3{}^-$ (**4**). In the course of the reaction, the carbene intermediate **6** was first formed by deprotonating **1,** then the strong nucleophilicity of **6** led to cleavage of the I–I bond to yield the carbene iodine adduct **4** (Scheme 1). Compound **4** is soluble in DMSO, sparingly soluble in

Table 2
Selected bond lengths (Å) and bond angles (°) for **2**–**5**

Complex 2					
Bond lengths					
Pd(1)–C(1)	2.038(5)	Pd(1)–Cl(1)	2.566(4)	N(1)–C(1)	1.340(6)
N(1)–C(3)	1.382(6)	N(1)–C(4)	1.478(6)	N(2)–C(1)	1.338(6)
N(2)–C(2)	1.383(7)	N(2)–C(19)	1.468(7)	C(2)–C(3)	1.334(8)
Bond angles					
C(3)–N(1)–C(4)	125.1(4)	C(1)–N(1)–C(3)	110.7(4)	C(1)–N(1)–C(4)	124.0(4)
C(2)–N(2)–C(197)	124.6(4)	C(1)–N(2)–C(2)	110.6(4)	C(1)–N(2)–C(19)	124.7(4)
N(1)–C(1)–Pd(1)	127.4(3)	N(2)–C(1)–N(1)	105.3(4)	N(2)–C(1)–Pd(1)	127.3(3)
C(1)–Pd(1)–Cl(1)	91.97(15)	C(3)–C(2)–N(2)	106.7(5)	C(2)–C(3)–N(1)	106.7(5)
Complex 3					
Bond lengths					
Pt(1)–C(1)	2.044(7)	Pt(1)–Cl(1)	2.636(1)	N(1)–C(1)	1.323(8)
N(1)–C(3)	1.376(9)	N(1)–C(4)	1.515(8)	N(2)–C(1)	1.325(8)
N(2)–C(2)	1.381(9)	N(2)–C(19)	1.462(9)	C(2)–C(3)	1.35(1)
Bond angles					
C(3)–N(1)–C(4)	124.5(6)	C(1)–N(1)–C(3)	112.1(6)	C(1)–N(1)–C(4)	123.3(5)
C(2)–N(2)–C(19)	123.4(6)	C(1)–N(2)–C(2)	110.5(6)	C(1)–N(2)–C(19)	126.0(6)
N(1)–C(1)–Pt(1)	128.3(5)	N(2)–C(1)–N(1)	105.3(6)	N(2)–C(1)–Pt(1)	126.3(5)
C(1)–Pt(1)–Cl(1)	87.3(2)	C(3)–C(2)–N(2)	106.9(7)	C(2)–C(3)–N(1)	105.1(7)
Complex 4					
Bond lengths					
I(1)–C(1)	2.070(6)	N(1)–C(1)	1.340(7)	N(1)–C(3)	1.362(7)
N(1)–C(4)	1.493(7)	N(2)–C(1)	1.335(8)	N(2)–C(2)	1.375(8)
N(2)–C(19)	1.54(1)	C(2)–C(3)	1.335(9)		
Bond angles					
C(1)–N(1)–C(3)	108.9(5)	C(1)–N(1)–C(4)	124.4(5)	C(3)–N(1)–C(4)	126.4(5)
C(1)–N(2)–C(2)	109.0(5)	C(1)–N(2)–C(19)	125.7(6)	C(2)–N(2)–C(19)	124.9(6)
(2)–C(1)–N(1)	107.3(5)	N(2)–C(1)–I(1)	126.4(4)	N(1)–C(1)–I(1)	126.3(4)
C(3)–C(2)–N(2)	107.0(6)	C(2)–C(3)–N(1)	107.9(6)		
Complex 5					
Bond lengths					
N(1)–C(18)	1.300(6)	N(1)–C(16)	1.455(7)	N(1)–C(15)	1.522(6)
N(2)–C(18)	1.390(7)	N(2)–C(17)	1.396(7)	N(2)–C(19)	1.465(7)
C(16)–C(17)	1.355(8)				
Bond angles					
C(18)–N(1)–C(16)	107.0(5)	C(18)–N(1)–C(15)	121.9(5)	C(16)–N(1)–C(15)	131.1(5)
C(18)–N(2)–C(17)	112.5(5)	C(18)–N(2)–C(19)	124.2(6)	C(17)–N(2)–C(19)	123.3(6)
N(1)–C(18)–N(2)	107.4(5)				

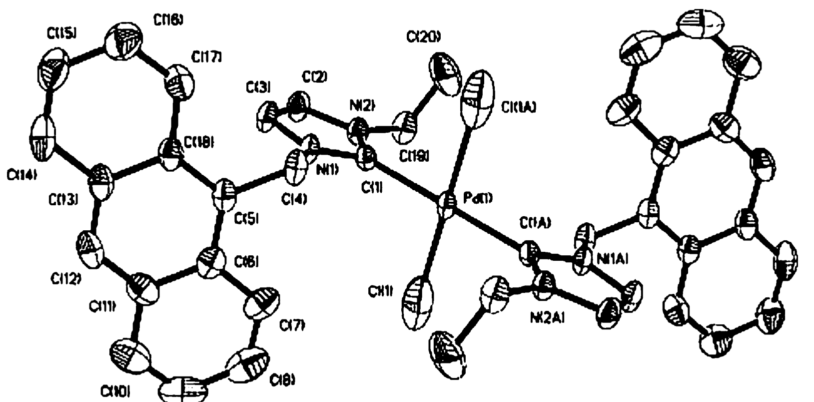
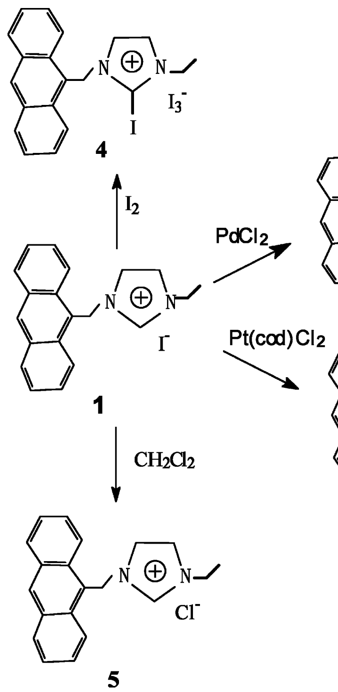


Fig. 1. Perspective view of **2** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.



Scheme 1.

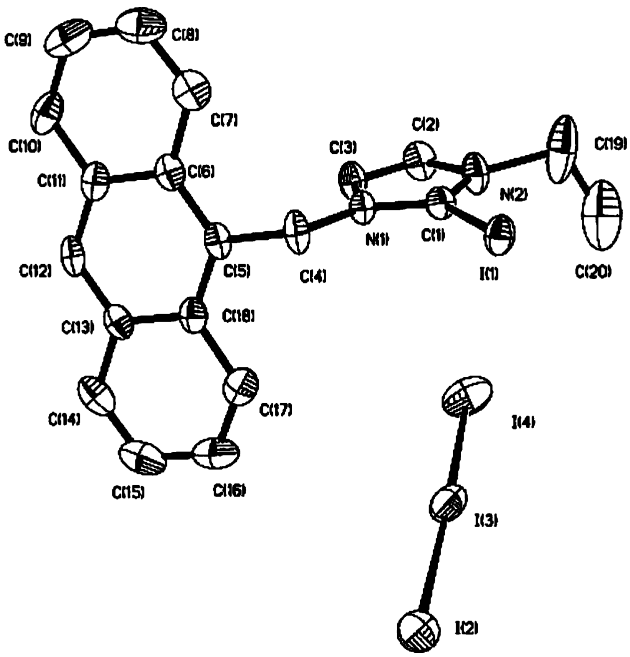
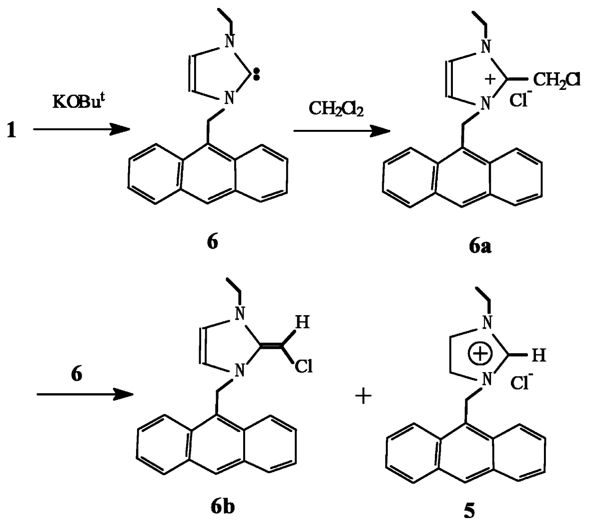


Fig. 2. Perspective view of **4** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.



Scheme 2.

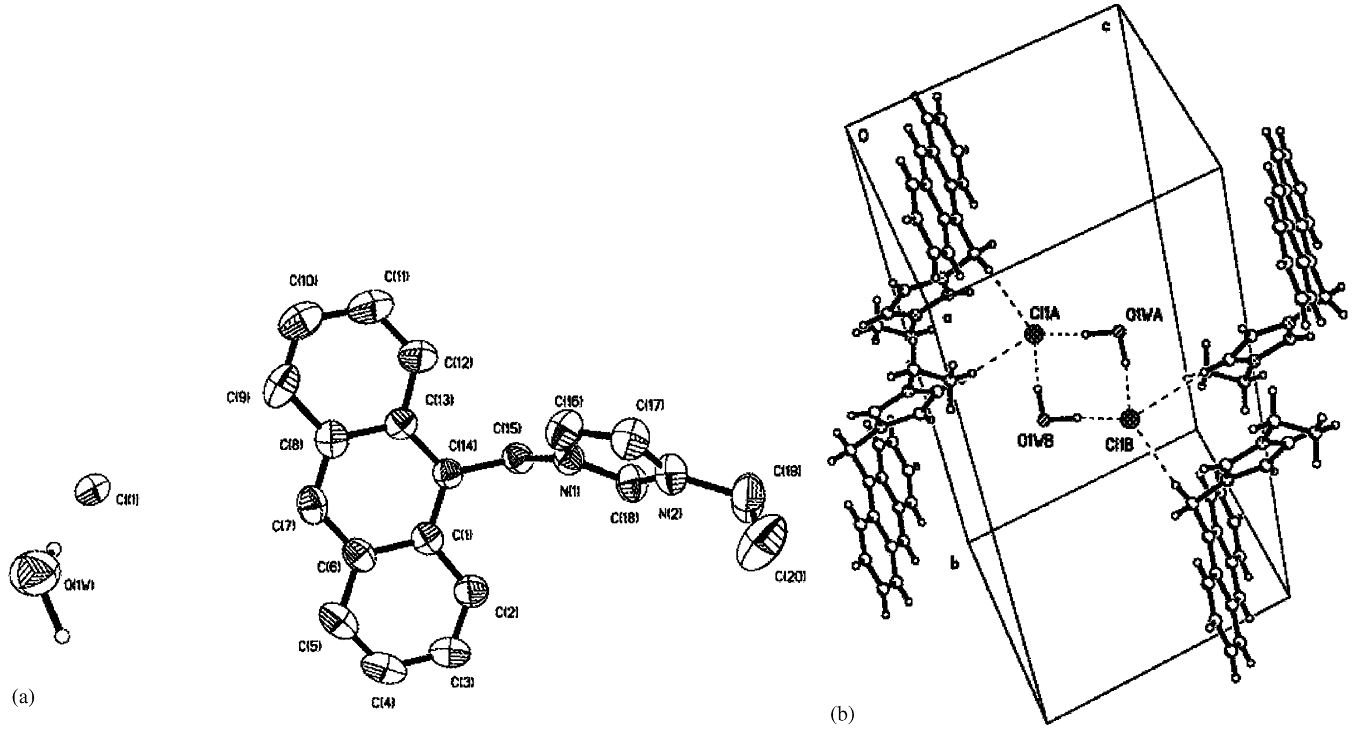
dichloromethane and insoluble in diethyl ether, stable in air and moisture, and displays high thermal stability. The ^{1}H NMR spectrum of **4** does not show the signal in the vicinity of 9.00 ppm, where the imidazolium C_2–H signal of **1** was found, and the chemical shifts of other hydrogens are similar to those of **1**. In the ^{13}C NMR spectrum the signal for the carbene carbon appears at 109.2 ppm [13].

Crystals of **4** were grown by evaporating slowly its dichloromethane/methanol solution at room temperature. The molecular structure of **4** is depicted in Fig. 2. The C–I distance is 2.070(6) Å, which is similar to those in known *N*-heterocyclic carbene iodine adducts (2.104 Å). The internal ring angle (N–C–N) at the carbene center is 107.3°, which is somewhat smaller than that in **1** (108.0°) and those in known carbene iodine adducts (109.5°) [13c]. The dihedral angle between the anthracene and imidazole ring planes is 103.3°.

Precursor **1** in CH_2Cl_2 was refluxed for 10 h in the presence of KOBu^t to form another salt 1-(9-anthracylmethyl)-3-ethylimidazol-2-ylidene chloride **5** (Scheme 1). This was due to carbene **6** derived from **1** reacting with CH_2Cl_2 to lead to the cleavage of the C–Cl bond and to afford the intermediate 2-(chloromethyl) imidazolinium chloride **6a** (Scheme 2). Carbene **6** is sufficiently basic so that it can deprotonate the intermediate **6a** to form **6b** and a new imidazolinium salt **5** [14]. An attempt to isolate monochloroolefin **6b** was unsuccessful. Compound **5** is soluble in DMSO and dichloromethane, sparingly soluble in THF, and insoluble in diethyl ether and hydrocarbon solvents. It is stable in air and moisture and displays high thermal stability.

Crystals of **5** were grown by evaporating slowly its dichloromethane solution at room temperature. The molecular structure of **5** is depicted in Fig. 3a, and its unit cell is depicted in Fig. 3b, showing that H-bonding exists between the anion Cl^- and H atom of the H_2O molecule (distance 2.011 Å) [15]. The ^{1}H and ^{13}C NMR spectra and luminescent emission intensities in **5** and **1** are essentially identical, which suggests that the anions do not play a significant role in the two compounds.

The luminescent emission spectra of **1**, **2**, **3** and **4** are shown in Fig. 4. In dichloromethane **2**, **3** and **4** exhibit



(a)

(b)

Fig. 3. (a) Perspective view of **5** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity. (b) Unit cell structure of **5**.

anthracene fluorescence similar to but stronger than that of **1**. This can be attributed to the electron withdrawing effect of metal(II) in **2** and **3** or iodine in **4**, which inhibits the photoinduced electron transfer process of the lone-pair electron of the nitrogen atom to the anthracene ring [16]. A broad anthracene excimer emission occurs at 512 nm for **3**, 520 nm for **2** and 525 nm for **4**.

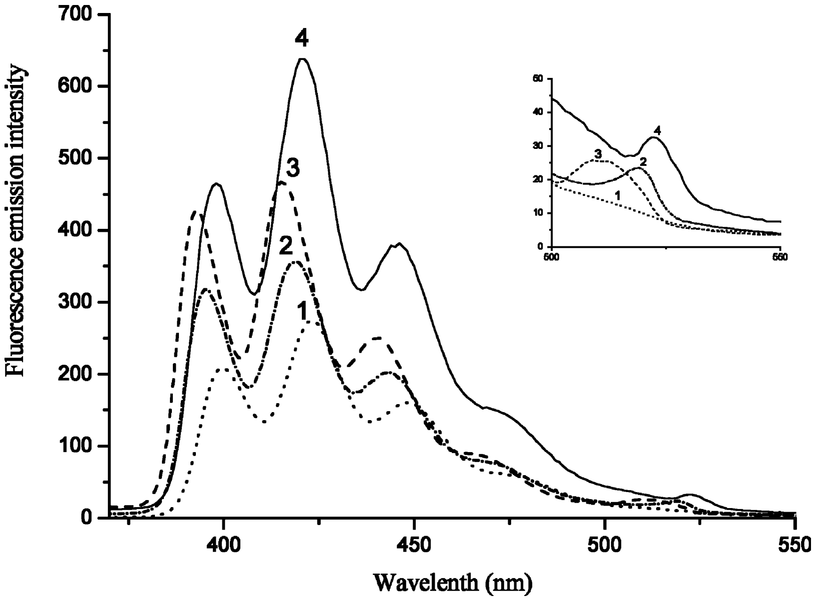


Fig. 4. Emission spectra of precursor **1** (. . .) and compounds **2** (- -), **3** (---) and **4** (—) at 298 K upon excitation at 256 nm in CH_2Cl_2 (5.0×10^{-6} mol l^{-1}).

4. Conclusion

In summary, *N*-heterocyclic carbene Pd(II), Pt(II) complexes and iodine adduct with anthracene fluorophores have been synthetized and the luminescent intensities of these compounds are stronger than that of precursor **1**. Further studies on new luminescent organometallic compounds from precursor **1** and analogous ligands are under investigation.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 194319–194322 for compounds **2**–**5**, respectively. Copies of this 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.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work is supported by the National Science Foundation of China (Project Grant No. 20102003).

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