

# Formation of the Fluorescent Complexes [(carbene)<sub>2</sub>M<sup>II</sup>(CN)<sub>2</sub>] (M = Ni, Pd, Pt) by C–C Bond Cleavage of CH<sub>3</sub>CN

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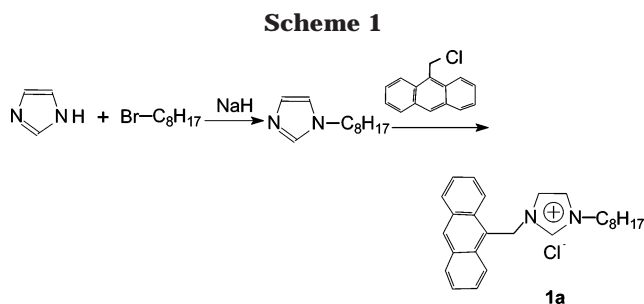
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In the presence of NaH and KOBu<sup>t</sup>, 1-(9-anthracenylmethyl)-3-octylimidazolium chloride (**1a**) or 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1b**) was treated with Ni(OAc)<sub>2</sub>, Pd(OAc)<sub>2</sub>, or Pt(cod)Cl<sub>2</sub> in CH<sub>3</sub>CN/THF solution to afford the fluorescent complexes [1-(9-anthracenylmethyl)-3-alkylimidazol-2-ylidene]<sub>2</sub>M(CN)<sub>2</sub> (**2a**, alkyl = C<sub>8</sub>H<sub>17</sub>, M = Ni; **2b**, alkyl = C<sub>2</sub>H<sub>5</sub>, M = Ni; **3a**, alkyl = C<sub>8</sub>H<sub>17</sub>, M = Pd; **3b**, alkyl = C<sub>2</sub>H<sub>5</sub>, M = Pd; **4a**, alkyl = C<sub>8</sub>H<sub>17</sub>, M = Pt; **4b**, alkyl = C<sub>2</sub>H<sub>5</sub>, M = Pt). The metal(II) center has a square-planar geometry, and pairs of 1-(9-anthracenylmethyl)-3-alkylimidazol-2-ylidene and CN<sup>-</sup> ligands are in a trans configuration. The CN<sup>-</sup> ligand in **2–4** derives from C–C bond cleavage in the CH<sub>3</sub>CN solvent. The fluorescent emission spectra of **1–4** are determined.

## Introduction

Since the discovery of stable N-heterocyclic carbenes,<sup>1</sup> increasing attention has been focused on using these compounds as ancillary ligands for a number of transition-metal-mediated catalytic reactions.<sup>2</sup> A large number of transition-metal complexes with these special types of carbene ligands have been synthesized.<sup>3</sup> In contrast to the widely used phosphine complexes, the complexes formed with these ligands have been shown to be remarkably stable toward heat, air, and moisture.<sup>4</sup> The N-heterocyclic carbene complexes have been applied to a broad spectrum of catalytic reactions, including Heck, Suzuki, and Kumada couplings,<sup>5–7</sup> olefin metathesis,<sup>8</sup> hydrosilylation,<sup>9</sup> etc. We are interested in N-



heterocyclic carbene complexes exhibiting fluorescence.<sup>10</sup> Herein we wish to report the C–C bond cleavage of CH<sub>3</sub>CN and the synthesis, structure, and photophysical properties of [(carbene)<sub>2</sub>M<sup>II</sup>(CN)<sub>2</sub>] type complexes (M = Ni, Pd, Pt).

## Results and Discussion

The required precursor, 1-(9-anthracenylmethyl)-3-octylimidazolium chloride (**1a**), was prepared from imidazole by stepwise alkylation with 1-bromooctane followed by 9-chloromethylanthracene in sequence and was obtained as a yellow powder (Scheme 1). The precursor 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1b**) was prepared according to the method in the literature.<sup>10a</sup>

The complexes [1-(9-anthracenylmethyl)-3-alkylimidazol-2-ylidene]<sub>2</sub>M(CN)<sub>2</sub> (**2a**, alkyl = C<sub>8</sub>H<sub>17</sub>, M = Ni; **2b**, alkyl = C<sub>2</sub>H<sub>5</sub>, M = Ni; **3a**, alkyl = C<sub>8</sub>H<sub>17</sub>, M = Pd; **3b**, alkyl = C<sub>2</sub>H<sub>5</sub>, M = Pd; **4a**, alkyl = C<sub>8</sub>H<sub>17</sub>, M = Pt; **4b**, alkyl = C<sub>2</sub>H<sub>5</sub>, M = Pt) were synthesized by the reaction

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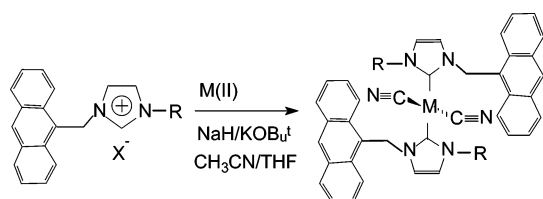
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## Scheme 2



**1a:** R=C<sub>8</sub>H<sub>17</sub>, X<sup>-</sup>=Cl<sup>-</sup>

**1b:** R=C<sub>2</sub>H<sub>5</sub>, X<sup>-</sup>=I<sup>-</sup>

**2a:** R=C<sub>8</sub>H<sub>17</sub>, M=Ni

**2b:** R=C<sub>2</sub>H<sub>5</sub>, M=Ni

**3a:** R=C<sub>8</sub>H<sub>17</sub>, M=Pd

**3b:** R=C<sub>2</sub>H<sub>5</sub>, M=Pd

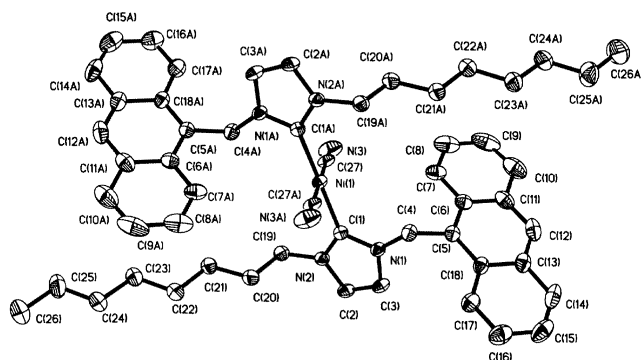
**4a:** R=C<sub>8</sub>H<sub>17</sub>, M=Pt

**4b:** R=C<sub>2</sub>H<sub>5</sub>, M=Pt

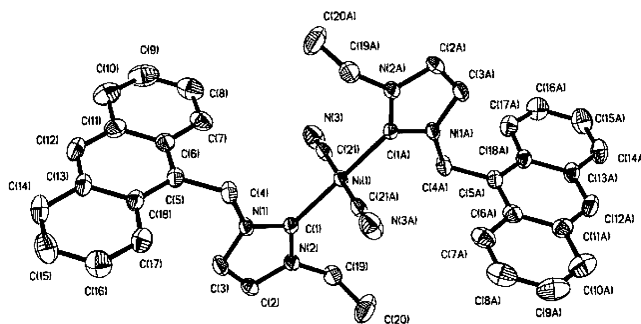
of 1-(9-anthracenylmethyl)-3-octylimidazolium chloride (**1a**) or 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1b**) and Ni(OAc)<sub>2</sub>, Pd(OAc)<sub>2</sub>, or Pt(cod)Cl<sub>2</sub>, respectively, in the presence of NaH and KOBu<sup>t</sup> in the solution of CH<sub>3</sub>CN/THF (Scheme 2).

In these reactions novel results were obtained: namely, although no cyano compounds except CH<sub>3</sub>CN solvent were added to the system of reaction, the CN<sup>-</sup> ligand appears in the molecular structures of **2–4**. To verify the source of CN<sup>-</sup>, the following experiments have been carried out. (1) According to the synthetic method of **2a** (see the Experimental Section), all reactants respectively except CH<sub>3</sub>CN, NaH, and metal salt exist; as a result the CN<sup>-</sup> absorption peak cannot be found in the IR spectra of the products. (2) All reactants except imidazolium salt exist, and the CN<sup>-</sup> absorption peak can be found in the IR spectrum of the solid product. (3) The suspension of CH<sub>3</sub>CN and NaH was refluxed for 8 h, and the CN<sup>-</sup> absorption peak cannot be found in the IR spectrum of the product. From the above experiments we can conclude that only three reactants of CH<sub>3</sub>CN, NaH, and metal salt exist simultaneously, the CN<sup>-</sup> can be generated, and the formation of CN<sup>-</sup> does not relate to the imidazolium salt. Therefore, we think that the CN<sup>-</sup> ligand in **2–4** is derived from the CH<sub>3</sub>CN solvent and the cleavage of the C–C bond in CH<sub>3</sub>CN is plausibly caused by H<sup>-</sup> (from NaH) under the catalysis of M(II) (M = Ni, Pd, Pt), but the detailed mechanism of the cleavage of the C–C bond in CH<sub>3</sub>CN is not clear yet. In the literature only theoretical calculations have been described,<sup>11</sup> and no experimental result has been documented up to now.

The <sup>1</sup>H NMR spectra of complexes **2–4** do not show the signal at 9–11.5 ppm, where the imidazolium C<sub>2</sub>–H signals of precursors are found (9 ppm for **1a** and 11.45 ppm for **1b**), and the chemical shifts of other hydrogens are similar to those of corresponding precursors. In the <sup>13</sup>C NMR spectra the signals for the carbene carbon of complexes **2–4** appear at 170–172 ppm, which is characteristic for a metal carbene signal,<sup>3</sup> and the signals of carbon for the cyano group appear at 109–110 ppm. The IR spectra feature peaks of CN<sup>-</sup> in the range 2100–2300 cm<sup>-1</sup> for **2–4**. The complexes **2a–4a** are soluble in chloroform, sparingly soluble in DMSO and insoluble in diethyl ether and hydrocarbon solvents. The complexes **2b–4b** are soluble in DMSO and in-



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

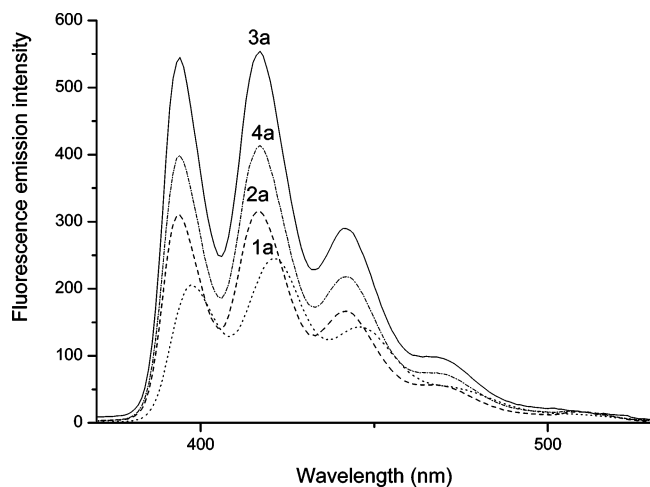


**Figure 2.** Perspective view of **2b** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

soluble in diethyl ether and hydrocarbon solvents. The complexes **2–4** are stable to air and moisture and display high thermal stability.

Molecular structures of the complexes **2–4** were demonstrated by X-ray analysis. Molecular structures of the complexes **2a** and **2b** were shown in Figures 1 and 2, respectively (**2a–4a** have similar molecular structures, and so do **2b–4b**). Pale yellow crystals of **2a**·2CH<sub>3</sub>OH, **3a**·2CH<sub>3</sub>OH, and **4a** as well as yellow crystals of **2b**·2CH<sub>2</sub>Cl<sub>2</sub>, **3b**·2CH<sub>2</sub>Cl<sub>2</sub>, and **4b**·2CH<sub>2</sub>Cl<sub>2</sub> suitable for X-ray diffraction were obtained by evaporating slowly their CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH solutions at room temperature. In these asymmetrically substituted carbene complexes **2–4** the metal(II) center and two imidazole rings lie in the same plane. The NC–M–CN unit is linear and perpendicular to the above-mentioned plane. Pairs of 1-(9-anthracenylmethyl)-3-alkylimidazol-2-ylidene and CN<sup>-</sup> ligands are in a trans configuration, and two 9-anthracenylmethyl groups and two alkyl groups point to opposite directions due to the sterically demands to form a trans-anti geometry. In the same metal complex the M–C<sub>carbene</sub> and M–C<sub>CN</sub> bond distances are similar, i.e. Pd–C<sub>carbene</sub> = 2.026(5) Å and Pd–C<sub>CN</sub> = 2.032(7) Å for **3a**, and in the complexes with different metals the M–C<sub>carbene</sub> and M–C<sub>CN</sub> bond distances are different, i.e. Pt–C > Pd–C > Ni–C (2.030(6) Å (Pt–C<sub>carbene</sub>) > 2.026(5) Å (Pd–C<sub>carbene</sub>) > 1.912(3) Å (Ni–C<sub>carbene</sub>); 2.074(7) Å (Pt–C<sub>CN</sub>) > 2.032(7) Å (Pd–C<sub>CN</sub>) > 1.853(4) Å (Ni–C<sub>CN</sub>) for **2a–4a**). The internal ring angles (N–C–N) at the carbene center are 104–106°, which is somewhat smaller than that in the precursor **1b** (108.0°) and similar to those in some known carbene nickel, palladium, and platinum com-

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**Figure 3.** Emission spectra of **1a** (···), **2a** (---), **3a** (—), and **4a** (— · —) at 298 K upon excitation at 256 nm in  $\text{CH}_2\text{-Cl}_2$  ( $5.0 \times 10^{-6}$  mol/L).

plexes.<sup>12</sup> The dihedral angles between anthracene and imidazole ring planes are  $69.7^\circ$  for **2a**,  $80.8^\circ$  for **2b**,  $70.5^\circ$  for **3a**,  $81.8^\circ$  for **3b**,  $80.5^\circ$  for **4a**, and  $82.5^\circ$  for **4b**, respectively.

The fluorescent emission spectra of **1a–4a** are shown in Figure 3 (the fluorescent emission spectra of **1b–4b** are similar to those of **1a–4a**). In dichloromethane complexes **2–4** exhibit anthracene types of fluorescence emissions similar to but stronger than those of the corresponding precursors **1a** and **1b**. This can be attributed to the electron-withdrawing effect of M(II), which inhibits the photoinduced electron transfer (PET) process of the lone-pair electron of the nitrogen atom to the anthracene ring.<sup>13</sup> Further studies on new fluorescent organometallic complexes from precursors **1a** and **1b** are being carried out, and it is expected that the nitrogen atoms of the cyano group in the complexes might coordinate further with other metals, so that they can be assigned to fluorescent sensors.

### Conclusion

In summary, our work demonstrates that the C–C bond in  $\text{CH}_3\text{CN}$  solvent can be cleaved easily by  $\text{H}^-$  (from NaH) under the catalysis of M(II). The  $\text{CN}^-$  from  $\text{CH}_3\text{CN}$  and the free N-heterocyclic carbene formed in situ from precursor **1a** or **1b** can be captured by M(II) to form  $[(\text{carbene})_2\text{M}^{\text{II}}(\text{CN})_2]$  type complexes.

### Experimental Section

**General Comments.** 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 were used without further purification. FI-IR spectra were measured on a Bruker FI-IR Equinox-55 infrared spectrophotometer. Melting points were determined with a Boetius Block apparatus.  $^1\text{H}$  and  $^{13}\text{C}$ -

$\{^1\text{H}\}$  NMR spectra were recorded on a Varian Mercury Vx 300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts,  $\delta$ , are reported in ppm relative to the internal standard TMS for both  $^1\text{H}$  and  $^{13}\text{C}$  NMR;  $J$  values are given in Hz. Elemental analyses were measured using a Perkin-Elmer 2400C elemental analyzer. The luminescent intensities of **1–4** were measured using a Cary Eclipse fluorescence spectrophotometer.

**1-(9-Anthracenylmethyl)-3-octylimidazolium chloride (1a).** A 1,4-dioxane solution of imidazole (7.829 g, 0.12 mol) was added to a suspension of oil-free sodium hydride (3.036 g, 0.13 mol) in 1,4-dioxane (150 mL) and the mixture stirred for 1 h at  $90^\circ\text{C}$ . Then a 1,4-dioxane (100 mL) solution of 1-bromooctane (22.210 g, 0.12 mol) was added dropwise to the above solution. The mixture was kept stirring for 48 h at  $90^\circ\text{C}$ , and a yellow solution was obtained. The solvent was removed with a rotary evaporator, and  $\text{H}_2\text{O}$  (500 mL) was added to the residue. Then the solution was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 100$  mL), and the extracting solution was dried with anhydrous  $\text{MgSO}_4$ . After  $\text{CH}_2\text{Cl}_2$  was removed, the yellow liquid 9-octylimidazole was obtained by distillation. Yield: 6.413 g (80%). Bp:  $125\text{--}127^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.88 (t,  $J = 6.6$ , 3H,  $\text{CH}_3$ ), 1.27 (m, 10H,  $5\text{CH}_2$ ), 1.78 (m, 2H,  $\text{CH}_2$ ), 3.94 (t,  $J = 7.2$ , 2H,  $\text{CH}_2$ ), 6.92 (s, 1H, 4-imi H), 7.06 (s, 1H, 5-imi H), 7.55 (s, 1H, 2-imi H).

A solution of 9-octylimidazole (3.965 g, 0.02 mol) and 9-chloromethylanthracene (4.983 g, 0.02 mol) in 1,4-dioxane (150 mL) was stirred for 3 days under refluxing, and a yellow precipitate was formed. The product was filtered and washed with 1,4-dioxane to give a pale yellow powder of **1a**. Yield: 8.169 g (91%). Mp:  $166\text{--}168^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{31}\text{ClN}_2$ : C, 76.73; H, 7.68; N, 6.88. Found: C, 76.34; H, 7.68; N, 6.62.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.87 (t,  $J = 6.0$ , 3H,  $\text{CH}_3$ ), 1.25 (m,  $J = 6.0$ , 10H,  $\text{CH}_2$ ), 1.85 (m,  $J = 6.0$ , 2H,  $\text{CH}_2$ ), 4.29 (t,  $J = 6.0$ , 2H,  $\text{CH}_2$ ), 6.68 (s, 2H,  $\text{CH}_2\text{An}$ ) (An = anthracene), 6.94 (s, 1H, An H), 7.00 (s, 1H, 4- or 5-imi H) (imi = imidazole), 7.57 (t,  $J = 8.0$ , 2H, An H), 7.65 (t,  $J = 8.0$ , 2H, An H), 8.10 (d,  $J = 8.0$ , 2H, An H), 8.38 (d,  $J = 8.0$ , 2H, An H), 8.61 (s, 1H, 4- or 5-imi H), 11.45 (s, 1H, 2-imi H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 14.1 ( $\text{CH}_3$ ), 22.5 ( $\text{CH}_2$ ), 26.2 ( $\text{CH}_2$ ), 28.9 ( $\text{CH}_2$ ), 29.0 ( $\text{CH}_2$ ), 30.2 ( $\text{CH}_2$ ), 31.6 ( $\text{CH}_2$ ), 45.5 ( $\text{CCH}_2\text{N}$ ), 50.2 (An  $\text{CH}_2\text{N}$ ), 121.1, 121.5, 122.1 and 122.8 (An C or 4,5-imi C), 125.6, 128.3, 129.5, 130.5, 130.9, and 131.2 (An O), 137.5 (2-imi C).

**[1-(9-Anthracenylmethyl)-3-octylimidazol-2-ylidene]<sub>2</sub>Ni(CN)<sub>2</sub> (2a).** A suspension of oil-free sodium hydride (0.013 g, 0.54 mmol),  $\text{KOBU}^t$  (0.006 g, 0.05 mmol), precursor **1a** (0.200 g, 0.49 mmol), and anhydrous nickel(II) acetate (0.044 g, 0.25 mmol) in THF (20 mL) and acetonitrile (20 mL) was refluxed for 8 h. A brown solution was formed, and the solvent was removed with a rotary evaporator. The water (30 mL) was added to the residue and the solution extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20$  mL). The extracting solution was dried with anhydrous  $\text{MgSO}_4$ , then the solution was concentrated to 10 mL, and hexane (2 mL) was added; as a result a pale yellow powder was obtained. Yield: 0.115 g (54%). Mp:  $262\text{--}264^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{54}\text{H}_{60}\text{N}_6\text{Ni}$ : C, 76.14; H, 7.10; N, 9.87. Found: C, 76.31; H, 7.21; N, 9.60.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.60 (t,  $J = 7.2$ , 3H,  $\text{CH}_3$ ), 0.81 (m,  $J = 7.2$ , 10H,  $\text{CH}_2$ ), 1.27 (m,  $J = 7.2$ , 2H,  $\text{CH}_2$ ), 2.22 (m,  $J = 7.2$ , 10H,  $\text{CH}_2$ ), 4.57 (t,  $J = 7.2$ , 2H,  $\text{CH}_2$ ), 6.63 (s, 2H,  $\text{CH}_2\text{An}$ ), 6.66 (s, 1H, An H), 7.08 (s, 1H, imi H), 7.50 (t,  $J = 8.0$ , 2H, An H), 7.60 (t,  $J = 8.0$ , 2H, An H), 8.02 (d,  $J = 8.0$ , 2H, An H), 8.35 (d,  $J = 8.0$ , 2H, An H), 8.51 (s, 1H, imi H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 14.1 ( $\text{CH}_3$ ), 14.3 ( $\text{CH}_2$ ), 22.6 ( $\text{CH}_2$ ), 27.3 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 31.6 ( $\text{CH}_2$ ), 32.1 ( $\text{CH}_2$ ), 47.7 ( $\text{CCH}_2\text{N}$ ), 51.8 (An  $\text{CH}_2\text{N}$ ), 109.4 (CN), 120.7, 120.9, 121.5, 121.8 and 124.2 (An C or 4,5-imi C), 125.7, 127.9, 129.4, 129.9, 131.6 and 133.5 (An C), 171.8 ( $\text{C}_{\text{carbene}}$ ). IR (KBr):  $\nu_{\text{CN}}$  2109  $\text{cm}^{-1}$ .

**[1-(9-Anthracenylmethyl)-3-octylimidazol-2-ylidene]<sub>2</sub>-Pd(CN)<sub>2</sub> (3a).** This complex was prepared in a manner analogous to that for **2a**, only with  $\text{Pd}(\text{OAc})_2$  instead of  $\text{Ni}(\text{OAc})_2$ . Yield: 0.11 g (52%). Mp:  $264\text{--}266^\circ\text{C}$ . Anal. Calcd for

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2–4

2a		3a		4a	
Ni(1)–C(27)	1.853(4)	Pd(1)–C(27)	2.032(7)	Pt(1)–C(27)	2.074(7)
Ni(1)–C(1)	1.912(3)	Pd(1)–C(1)	2.026(5)	Pt(1)–C(1)	2.030(6)
C(27)–Ni(1)–C(27)#1	180.0(3)	C(27)#1–Pd(1)–C(27)	180.0(7)	C(27)–Pt(1)–C(27)#1	180.0(2)
C(27)–Ni(1)–C(1)	89.6(1)	C(1)–Pd(1)–C(27)	89.8(2)	C(1)–Pt(1)–C(27)	90.3(2)
C(27)#1–Ni(1)–C(1)	90.4(1)	C(1)–Pd(1)–C(27)#1	90.2(2)	C(1)–Pt(1)–C(27)#1	89.7(2)
C(1)–Ni(1)–C(1)#1	180.0(1)	C(1)#1–Pd(1)–C(1)	180.0(2)	C(1)#1–Pt(1)–C(1)	180.0(2)
2b		3b		4b	
Ni(1)–C(21)	1.861(4)	Pd(1)–C(21)	1.977(8)	Pt(1)–C(21)	2.009(1)
Ni(1)–C(1)	1.903(3)	Pd(1)–C(1)	2.031(6)	Pt(1)–C(1)	2.035(7)
C(21)#1–Ni(1)–C(21)	180.0(3)	C(21)#1–Pd(1)–C(21)	180.0(6)	C(21)#1–Pt(1)–C(21)	180.0(3)
C(21)#1–Ni(1)–C(1)	90.5(1)	C(21)#1–Pd(1)–C(1)	90.0(3)	C(21)#1–Pt(1)–C(1)	90.7(3)
C(21)–Ni(1)–C(1)	89.5(1)	C(21)–Pd(1)–C(1)	90.0(3)	C(21)–Pt(1)–C(1)	89.3(3)
C(1)–Ni(1)–C(1)#1	180.0(1)	C(1)–Pd(1)–C(1)#1	180.0(3)	C(1)–Pt(1)–C(1)#1	180.0(2)

Table 2. Summary of Crystallographic Data for 2a–4a

	2a	3a	4a
chem formula	C <sub>56</sub> H <sub>68</sub> N <sub>6</sub> –NiO <sub>2</sub>	C <sub>56</sub> H <sub>68</sub> N <sub>6</sub> –PdO <sub>2</sub>	C <sub>54</sub> H <sub>60</sub> N <sub>6</sub> Pt
fw	915.87	963.56	988.17
cryst syst	triclinic	triclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	8.315(4)	8.4526(18)	11.024(3)
<i>b</i> /Å	12.634(6)	12.530(3)	26.777(8)
<i>c</i> /Å	12.828(6)	12.852(3)	8.148(3)
<i>α</i> /deg	102.198(8)	101.837(5)	90
<i>β</i> /deg	104.316(8)	105.436(4)	101.626(5)
<i>γ</i> /deg	93.127(9)	92.855(5)	90
<i>V</i> /Å <sup>3</sup>	1268.1(10)	1276.3(5)	2355.9(13)
<i>Z</i>	1	1	2
<i>D</i> <sub>calcd</sub> , Mg/m <sup>3</sup>	1.199	1.254	1.393
abs coeff, mm <sup>−1</sup>	0.429	0.410	3.020
<i>F</i> (000)	490	508	1008
<i>θ</i> <sub>min</sub> , <i>θ</i> <sub>max</sub> /deg	1.68, 25.03	1.69, 25.00	2.42, 26.41
<i>T</i> /K	293(2)	293(2)	293(2)
no. of data collected	5262	6747	13257
no. of unique data	4450	4476	4797
no. of refined params	295	295	278
goodness of fit on <i>F</i> <sup>2</sup> <sup>a</sup>	0.959	0.992	1.201
final <i>R</i> indices <sup>b</sup>			
( <i>I</i> > 2σ( <i>I</i> ))			
<i>R</i> 1	0.0549	0.0705	0.0548
w <i>R</i> 2	0.1233	0.1058	0.1072
<i>R</i> indices (all data)			
<i>R</i> 1	0.0947	0.1372	0.0933
w <i>R</i> 2	0.1420	0.1262	0.1161

<sup>a</sup> GOF = [Σw(*F*<sub>o</sub><sup>2</sup> − *F*<sub>c</sub><sup>2</sup>)/(*n* − *p*)]<sup>1/2</sup>, where *n* is the number of reflections and *p* is the number of parameters refined. <sup>b</sup> *R*1 = Σ(|*F*<sub>o</sub> − |*F*<sub>c</sub>||)/Σ|*F*<sub>o</sub>|; w*R*2 = 1/σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0691*P*) + 1.4100*P*, where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3.

C<sub>54</sub>H<sub>60</sub>N<sub>6</sub>Pd: C, 72.10; H, 6.72; N, 9.34. Found: C, 71.88; H, 6.53; N, 9.22. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.56 (t, *J* = 7.2, 3H, CH<sub>3</sub>), 0.86 (m, *J* = 7.2, 10H, CH<sub>2</sub>), 1.27 (m, *J* = 7.2, 2H, CH<sub>2</sub>), 2.22 (m, *J* = 7.2, 10H, CH<sub>2</sub>), 4.57 (t, *J* = 7.2, 2H, CH<sub>2</sub>), 6.63 (s, 2H, CH<sub>2</sub> An), 6.66 (s, 1H, An *H*), 7.08 (s, 1H, imi *H*), 7.50 (t, *J* = 8.0, 2H, An *H*), 7.60 (t, *J* = 8.0, 2H, An *H*), 8.02 (d, *J* = 8.0, 2H, An *H*), 8.35 (d, *J* = 8.0, 2H, An *H*), 8.51 (s, 1H, imi *H*). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 13.9 (CH<sub>3</sub>), 22.4 (CH<sub>2</sub>), 27.1 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 31.5 (CH<sub>2</sub>), 47.6 (CCH<sub>2</sub>N), 51.6 (An CH<sub>2</sub>N), 109.6 (CN), 120.0, 121.1, 124.0, 124.2, and 125.0 (An *C* or 4,5-imidazole), 125.5, 127.7, 129.2, and 131.3 (An *C*), 170.0 (C<sub>carbene</sub>). IR (KBr): ν<sub>CN</sub> 2127 cm<sup>−1</sup>.

**[1-(9-Anthracenylmethyl)-3-octylimidazol-2-ylidene]<sub>2</sub>Pt(CN)<sub>2</sub> (4a)**. This complex was prepared in a manner analogous to that for **2a**, only with Pt(cod)Cl<sub>2</sub> instead of Ni(OAc)<sub>2</sub>. Yield: 0.105 g (43%). Mp: 269–271 °C. Anal. Calcd for C<sub>54</sub>H<sub>60</sub>N<sub>6</sub>Pt: C, 65.64; H, 6.12; N, 8.51. Found: C, 65.32; H, 6.01; N, 8.37. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.58 (t, *J* = 7.2, 3H, CH<sub>3</sub>), 0.88

Table 3. Summary of Crystallographic Data for 2b–4b

	2b	3b	4b
chem formula	C <sub>44</sub> H <sub>40</sub> Cl <sub>4</sub> –N <sub>6</sub> Ni	C <sub>44</sub> H <sub>40</sub> Cl <sub>4</sub> –N <sub>6</sub> Pd	C <sub>44</sub> H <sub>40</sub> Cl <sub>4</sub> –N <sub>6</sub> Pt
fw	853.33	901.02	989.71
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	10.938(4)	10.946(4)	10.927(9)
<i>b</i> /Å	8.364(3)	8.545(3)	8.539(9)
<i>c</i> /Å	22.721(8)	22.645(7)	22.646(10)
<i>α</i> /deg	90	90	90
<i>β</i> /deg	95.648(7)	96.486(6)	96.257(19)
<i>γ</i> /deg	90	90	90
<i>V</i> /Å <sup>3</sup>	2068.7(13)	2104.3(12)	2100(3)
<i>Z</i>	2	2	2
<i>D</i> <sub>calcd</sub> , Mg/m <sup>3</sup>	1.370	1.422	1.565
abs coeff, mm <sup>−1</sup>	0.767	0.734	3.634
<i>F</i> (000)	884	920	984
<i>θ</i> <sub>min</sub> , <i>θ</i> <sub>max</sub> , deg	1.80, 26.45	2.17, 25.00	1.99, 25.00
<i>T</i> /K	293(2)	293(2)	293(2)
no. of data collected	11 586	10 502	7973
no. of unique data	4258	3698	3329
no. of refined params	251	250	250
goodness of fit on <i>F</i> <sup>2</sup> <sup>a</sup>	1.052	1.027	0.954
final <i>R</i> indices <sup>b</sup>			
( <i>I</i> > 2σ( <i>I</i> ))			
<i>R</i> 1	0.0555	0.0650	0.0426
w <i>R</i> 2	0.1535	0.1721	0.0836
<i>R</i> indices (all data)			
<i>R</i> 1	0.0801	0.1082	0.0918
w <i>R</i> 2	0.1694	0.1984	0.0969

<sup>a</sup> GOF = [Σw(*F*<sub>o</sub><sup>2</sup> − *F*<sub>c</sub><sup>2</sup>)/(*n* − *p*)]<sup>1/2</sup>, where *n* is the number of reflections and *p* is the number of parameters refined. <sup>b</sup> *R*1 = Σ(|*F*<sub>o</sub> − |*F*<sub>c</sub>||)/Σ|*F*<sub>o</sub>|; w*R*2 = 1/σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0691*P*) + 1.4100*P*, where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3.

(m, *J* = 7.2, 10H, CH<sub>2</sub>), 1.26 (m, *J* = 7.2, 2H, CH<sub>2</sub>), 2.09 (m, *J* = 7.2, 10H, CH<sub>2</sub>), 4.40 (t, *J* = 7.2, 2H, CH<sub>2</sub>), 6.63 (s, 2H, CH<sub>2</sub> An), 6.66 (s, 1H, An *H*), 7.08 (s, 1H, imi *H*), 7.50 (t, *J* = 8.0, 2H, An *H*), 7.60 (t, *J* = 8.0, 2H, An *H*), 8.02 (d, *J* = 8.0, 2H, An *H*), 8.35 (d, *J* = 8.0, 2H, An *H*), 8.51 (s, 1H, imi *H*). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 14.1 (CH<sub>3</sub>), 22.6 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 47.5 (NCH<sub>2</sub>CH<sub>2</sub>), 51.7 (NCH<sub>2</sub> An), 109.9 (CN), 120.0, 121.1 and 123.9 (An *C* or 4,5-imidazole), 124.7, 125.5, 127.7, 129.2, 129.5, and 131.2 (An *C*), 161.9 (C<sub>carbene</sub>). IR (KBr): ν<sub>CN</sub> 2113 cm<sup>−1</sup>.

**[1-(9-Anthracenylmethyl)-3-ethylimidazol-2-ylidene]<sub>2</sub>Ni(CN)<sub>2</sub> (2b)**. This complex was prepared in a manner analogous to that for **2a**, only with 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1b**) instead of **1a** as starting material. Yield: 0.091 g (55%). Mp: 258–260 °C. Anal. Calcd for C<sub>42</sub>H<sub>36</sub>N<sub>6</sub>Ni: C, 73.81; H, 5.31; N, 12.30. Found: C, 73.49; H, 5.02; N, 12.38. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): 1.68 (t, *J* = 7.2, 3H, CH<sub>3</sub>), 4.60 (q, *J* = 7.2, 2H, CH<sub>2</sub>), 5.74 (s, 2H, CH<sub>2</sub>An), 6.70 (s, 1H,

imi *H*), 7.29 (s, 1H, imi *H*), 7.52 (t,  $J = 8.4$ , 2H, An *H*), 7.64 (t,  $J = 8.4$ , 2H, An *H*), 8.12 (d,  $J = 8.4$ , 2H, An *H*), 8.60 (d,  $J = 8.4$ , 2H, An *H*), 8.71 (s, 1H, An *H*).  $^{13}\text{C}$  NMR (300 MHz, DMSO- $d_6$ ): 16.0 (CH<sub>3</sub>), 45.2 (NCH<sub>2</sub>CH<sub>3</sub>), 46.6 (NCH<sub>2</sub> An), 109.2 (CN), 120.3, 122.2, and 123.9 (An *C* or 4,5-imi *C*), 125.4, 127.2, 127.5, 129.1, 130.5, 130.9, and 131.5 (An *C*), 171.8 (*C*<sub>carbene</sub>). IR (KBr):  $\nu_{\text{CN}}$  2113 cm<sup>-1</sup>.

**[1-(9-Anthracenylmethyl)-3-ethylimidazol-2-ylidene]<sub>2</sub>-Pd(CN)<sub>2</sub> (3b)**. This complex was prepared in a manner analogous to that for **2b**, only with Pd(OAc)<sub>2</sub> instead of Ni(OAc)<sub>2</sub>. Yield: 0.093 g (52%). Mp: 308–310 °C. Anal. Calcd for C<sub>42</sub>H<sub>36</sub>N<sub>6</sub>Pd: C, 69.00; H, 4.96; N, 11.49. Found: C, 68.77; H, 4.83; N, 11.53.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ): 1.58 (t,  $J = 7.2$ , 3H, CH<sub>3</sub>), 4.42 (q,  $J = 7.2$ , 2H, CH<sub>2</sub>), 5.75 (s, 2H, CH<sub>2</sub>An), 6.48 (s, 1H, imi *H*), 7.36 (s, 1H, imi *H*), 7.56 (t,  $J = 8.4$ , 2H, An *H*), 7.65 (t,  $J = 8.4$ , 2H, An *H*), 8.16 (d,  $J = 8.4$ , 2H, An *H*), 8.62 (d,  $J = 8.4$ , 2H, An *H*), 8.70 (s, 1H, An *H*).  $^{13}\text{C}$  NMR (300 MHz, DMSO- $d_6$ ): 16.0 (CH<sub>3</sub>), 45.6 (NCH<sub>2</sub>CH<sub>3</sub>), 46.8 (NCH<sub>2</sub> An), 109.2 (CN), 120.3, 122.3 and 123.9 (An *C* or 4,5-imi *C*), 125.4, 127.4, 128.1, 129.2, 130.5, and 131.0 (An *C*), 167.8 (*C*<sub>carbene</sub>). IR (KBr):  $\nu_{\text{CN}}$  2124 cm<sup>-1</sup>.

**[1-(9-Anthracenylmethyl)-3-ethylimidazol-2-ylidene]<sub>2</sub>Pt(CN)<sub>2</sub> (4b)**. This complex was prepared in a manner analogous to that for **2b**, only with Pt(cod)Cl<sub>2</sub> instead of Ni(OAc)<sub>2</sub>. Yield: 0.097 g (49%). Mp: 355–356 °C. Anal. Calcd for C<sub>42</sub>H<sub>36</sub>N<sub>6</sub>Pt: C, 61.53; H, 4.43; N, 10.25. Found: C, 61.23; H, 4.67; N, 10.58.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ): 1.55 (t,  $J = 7.2$ , 3H, CH<sub>3</sub>), 4.42 (q,  $J = 7.2$ , 2H, CH<sub>2</sub>), 6.51 (s, 2H, CH<sub>2</sub> An), 7.36 (s, 1H, imi *H*), 7.57 (s, 1H, imi *H*), 8.15 (t,  $J = 8.4$ , 2H, An *H*), 8.68 (t,  $J = 8.4$ , 2H, An *H*), 8.12 (d,  $J = 8.4$ , 2H, An *H*), 8.60 (d,  $J = 8.4$ , 2H, An *H*), 8.71 (s, 1H, An *H*).  $^{13}\text{C}$  NMR (300 MHz, DMSO- $d_6$ ): 16.0 (CH<sub>3</sub>), 45.2 (NCH<sub>2</sub>CH<sub>3</sub>), 46.6 (NCH<sub>2</sub> An), 109.2 (CN), 120.6, 122.7 and 124.6 (An *C* or 4,5-imi *C*), 126.1, 128.1, 129.9, and 131.6 (An *C*), 173.1 (*C*<sub>carbene</sub>). IR (KBr):  $\nu_{\text{CN}}$  2113 cm<sup>-1</sup>.

**X-ray Crystallography.** For each of compounds **2–4** a selected single crystal was mounted on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 20 mA using Mo K $\alpha$  radiation (0.710 73 Å). Data collection and reduction were performed using the SMART and SAINT software,<sup>14</sup> with frames of 0.6° oscillation in the  $\theta$  range  $1.8 < \theta < 25^\circ$ . An empirical absorption correction was applied using the SADABS program.<sup>15</sup> 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.<sup>16</sup> 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. Selected bond lengths and angles are given in Table 1, and crystallographic data are summarized in Tables 2 and 3 for **2–4**.

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**Supporting Information Available:** Crystallographic data for **2–4** as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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