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# Unsymmetrically substituted bis(carbene)platinum(II) complexes☆

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**Abstract**

Consecutive nucleophillic attack by an alcohol and then an amine to a *trans*-diiodo[bis(isocyanide)]platinum(II) complex **1** gives an unsymmetrically substituted neutral bis(carbene)platinum complex, *trans*-diiodo{[diaminocarbene][(alkoxy)(amino)carbene]} platinum(II) **4**, some of which, bearing a long alkyl substituent on the carbene ligand, exhibit a liquid crystalline property. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Platinum; Hetero-bis(carbene); Mesomorphic property

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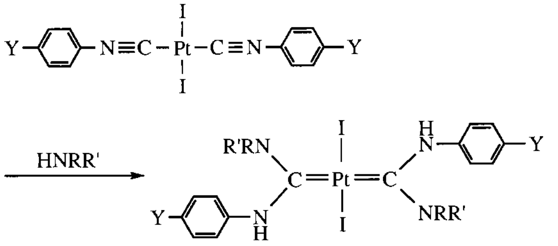
## 1. Introduction

The preparation of Fischer-type carbene complexes involves the effective addition of nucleophiles to transition metal acetylide and isocyanide complexes, in which nucleophiles HQ attack the positively charged $\alpha$-carbon atom of M–C≡CR and M–C≡NR to give carbene complexes. The preparation of the type M=CQ–CHR (M = Pt, Pd and Ni) carbene complexes from M–C≡CR complexes has extensively been studied by Clark [1] and Okawara [2]. On the other hand, carbene complexes of the type M=CQ–NHR with a variety of transition metals were prepared from M–C≡NR complexes [3,4]. We also applied this method to the synthesis of liquid-crystalline gold(I)-carbene complexes from chloro(isocyanide)gold(I) [5,6]. Furthermore, we have prepared first neutral *trans*-bis(diaminocarbene)platinum complexes by the nucleophilic addition of amines to both of the C≡N bonds in bis(isocyanide)platinum complexes (Eq. (1)) [7]. These complexes have two symmetrically substituted diaminocarbene ligands and showed a reactivity for intramolecular metalation, but they did not exhibit mesomorphic properties because of their high melting temperature (decomposition at about 180°C), although chloro(carbene)gold complexes form stable liquid crystals around 120°C.



(1)

We have now found that treatment of *trans*-diiodo[bis(isocyanide)]platinum(II) complex **1** with alcohol and then amine nucleophiles results in formation of a new type of platinum carbene complexes, *trans*-diiodo {[diaminocarbene][(alkoxy)(amino)]carbene]}platinum(II) 4 (Eq. (2)). This is the first example of unsymmetrically substituted bis(carbene)metal complexes although some symmetrical bis(carbene)metal complexes are known [8]. We also found that comlexes **4** showed a mesomorphic property when they have long alkyl substituents on the carbene ligands.

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☆ Dedicated to the memory of the late Professor Rokuro Okawara.

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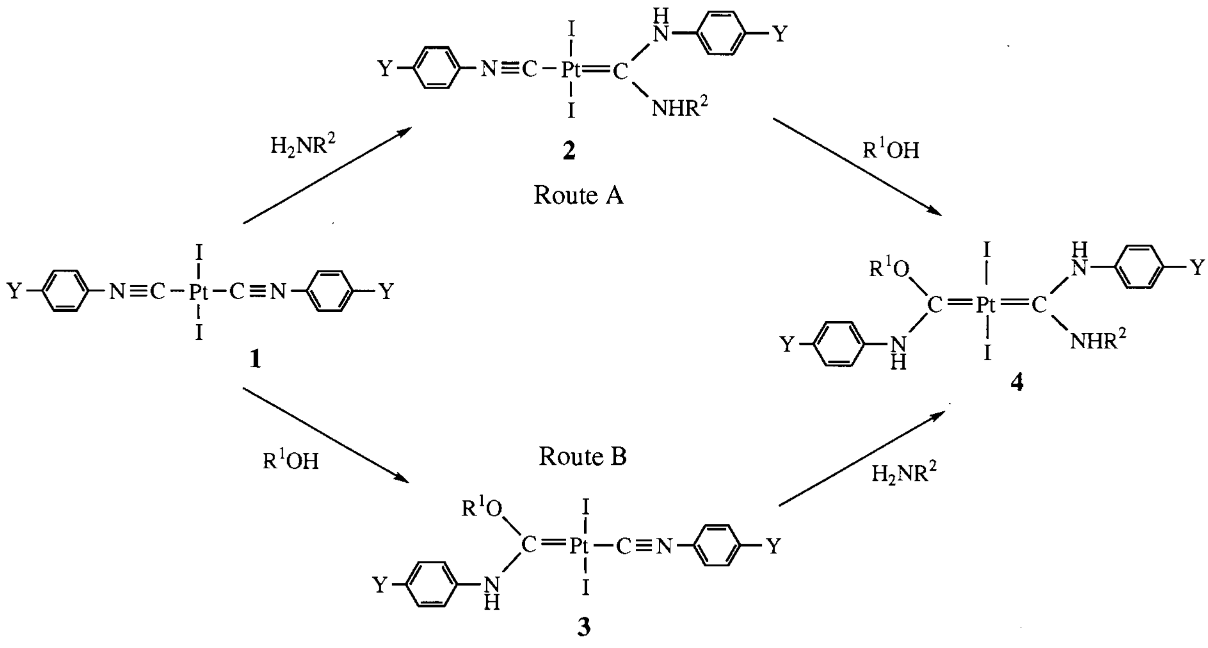
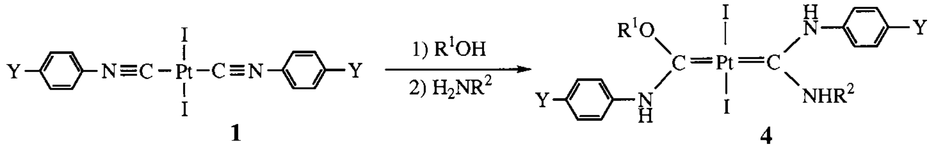


Scheme 1.



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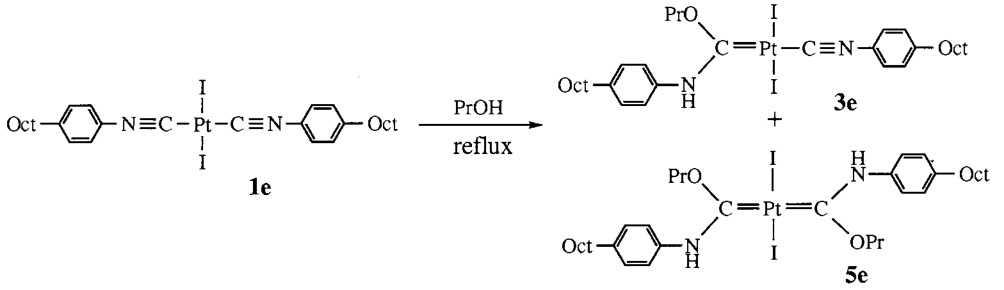
## 2. Results and discussion

Two possible synthetic routes to unsymmetrically substituted bis(carbene)platinum, *trans*-diiodo{[diaminocarbene][(alkoxy)(amino)carbene]}platinum(II) **4**, can be considered (Scheme 1). One is route A, in which the nucleophilic attack of an amine to one of the C≡N bonds of **1** leads to mono-[(diamino)carbene]platinum complex **2**, and then the addition of an alcohol to the other C≡N bond of **2** would result in the formation of **4**. In route B, the addition of an alcohol to **1** may form monocarbene **3** and then the addition of an amine to **3** gives **4**. At first according to route A we reacted complex **1** ($Y = C_8H_{17}$ or $C_4H_7$) with propylamine (one equivalent) in benzene at room temperature and isolated monocarbenes **2** in 90% yields. However, no reaction occurred when propanol was added to the solution of monocarbene **2** at room temperature in various kinds of solvents. When **2** was heated in propanol under reflux, a mixture of products was obtained but we could not isolate definite products. Then, we adopted route B and found two kinds of methods for the synthesis of bis{[diaminocarbene][(alkoxy)(amino)carbene]}platinum(II) **4**.

### 2.1. Synthesis of diiodo{[isocyanide][(alkoxy)(amino)carbene]}-platinum(II) complexes

Propanol did not react with *trans*-diiodo[bis(4-octylphenyl isocyanide)]platinum(II) **1e** in solvents such as benzene and dichloromethane even if the reaction was carried out at the reflux temperature. However, when a solution of complex **1e** in propanol was heated for 24 h at reflux temperature (89°C), a mixture of complexes **3e** and **5e** were obtained in a ratio of 4:1 (Eq. (3)).



(3)

Table 1
Reaction of complex **1e** with propanol[a]

| Entry | Reaction time (h) | Conversion of **1e** (%) | Ratio of products **3e**:**5e**[b] |
|---|---|---|---|
| 1 | 0.5 | 11 | 1:1 |
| 2 | 3 | 55 | 2:1 |
| 3 | 16 | 84 | 4:1 |
| 4 | 20 | 92 | 4:1 |
| 5 | 24 | 100 | 4:1 |
| 6 | 48 | 100 | 4:1 |

[a] Complex **1e** (0.1 mmol), propanol (5 ml), reflux.

[b] Determined by HPLC and $^1$H-NMR analysis.

Complex **3e** was identified to be a mono(carbene) complex, diiodo{[isocyanide][(alkoxy)(amino)carbene]}-platinum(II), while complex **5e** is a bis(carbene) complex, diiodo-bis[(alkoxy)(amino)carbene]platinum(II). As shown in Table 1, the production of **3e** was always accompanied with the formation of **5e** although we tried to find the reaction conditions for the selective synthesis of mono(carbnene) **3e**. Although the conversion of substrate **1e** reached 100% after 24 h, the reaction gave a mixture of **3e** and **5e** with a ratio of 4:1, and the ratio of **3e**/**5e** was held constant at 4:1 even after the reaction for 48 h. All the reactions of complex **1** with several kinds of alcohols gave a mixture of complexes **3** and **5** (Table 2). For example, complex **1a** reacted with propanol, ethanol and methanol to give the corresponding products **3** and **5** (entries 1, 2 and 3), but we could not find a suitable method to isolate **3** from the product mixtures. Although most of complexes **3** have not been isolated from the mixture of **3** and **5**, complexes **3b**–**e** were successfully separated by means of recrystallization from hexane–dichloromethane (entries 4, 7, 10 and 13). On the other hand, we found that the reaction of isolated complex **3e** with propanol also gave a mixture of **3e** and **5e** with a ratio of 4:1 (Eq. (4)), suggesting that there may be an equilibrium between **3** and **5** in the reaction of **3** with propanol in spite of the presence of large excess of propanol.

$$\mathbf{3e} \xrightarrow[\text{reflux, 24 h}]{\text{PrOH}} \underset{(\mathbf{3e} : \mathbf{5e} = 4:1)}{\mathbf{3e} + \mathbf{5e}} \qquad (4)$$

### 2.2. Synthesis of trans-diiodo{[diaminocarbene][(alkoxy)(amino)carbene]}platinum 4 by the reaction of monocarbene 3 with propylamine

To synthesize unsymmetrical bis(carbene) complexes, we examined the reaction of mono(carbene) complex **3** with an amine and successfully obtained [diaminocarbene][(alkoxy)(amino)carbene] complexes **4** in an excellent yield. Thus, isolated mono(carbene) complex **3b** was reacted with propylamine in benzene at room temperature for 24 h to give complex **4b**, after recrystallization from hexane–dichloromethane, as pale yellow powders in 97% yield (Eq. (5)).

Table 2
Reactions of complex **1** with alcohols[a]

| Entry | | Complex **1** Y | Alcohol R$^1$ | Conversion of **1** (%) | Ratio of products **3** and **5** (**3**:**5**)[b] | Isolated yield of **3** (%) |
|---|---|---|---|---|---|---|
| 1 | **a** | Me | Pr | 100 | 3:1 | –[c] |
| 2 | | | Et | 100 | 5:1 | –[c] |
| 3 | | | Me | 65 | 2:1 | –[c] |
| 4 | **b** | OMe | Pr | 100 | 8:3 | 33 |
| 5 | | | Et | 100 | 2:1 | –[c] |
| 6 | | | Me | 67 | 1:1 | –[c] |
| 7 | **c** | Bu | Pr | 100 | 4:1 | 29 |
| 8 | | | Et | 100 | 4:1 | –[c] |
| 9 | | | Me | 60 | 8:3 | –[c] |
| 10 | **d** | OHex | Pr | 100 | 4:1 | 34 |
| 11 | | | Et | 100 | 4:1 | –[c] |
| 12 | | | Me | 63 | 2:1 | –[c] |
| 13 | **e** | Oct | Pr | 100 | 4:1 | 54 |
| 14 | | | Et | 100 | 4:1 | –[c] |
| 15 | | | Me | 65 | 4:1 | –[c] |

[a] Complex **1** (0.1 mmol), alcohol (5 ml), reflux for 24 h.

[b] Determined by HPLC and $^1$H-NMR analysis.

[c] Not isolated from the mixture of complexes **3** and **5**.

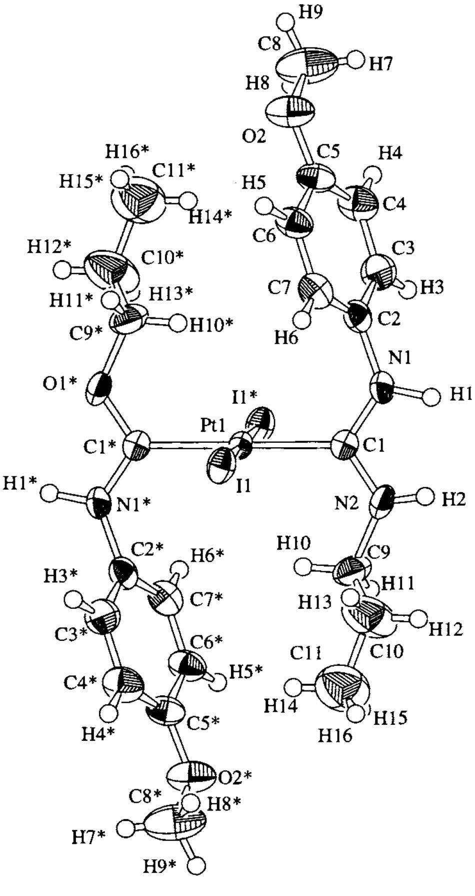
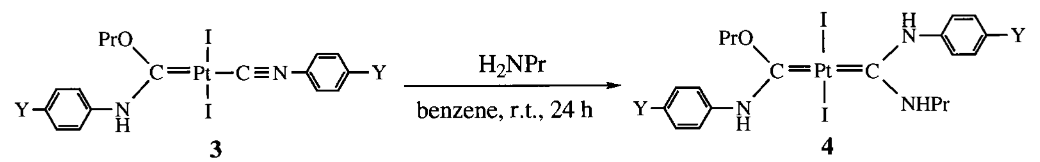


Fig. 1. ORTEP drawing of complex **4b** ($Y = OCH_3$, $R = R' = C_3H_7$). Selected bond distances (Å) and angles (°): Pt(1)–C(1), 2.027(1); Pt(1)–I(1), 2.627(1); C(1)–O(1), 1.329(7); C(1)–N(1), 1.336(8); C(1)–N(2), 1.329(6); I(1)–Pt(1)–I(1)*, 180.0; C(1)–Pt(1)–C(1)*, 180.0; C(1)–Pt(1)–I(1), 89.9(2); C(1)–Pt(1)–I(1)*, 90.1(2); N(1)–C(1)–N(2), 113.3(5); O(1)–C(1)*–N(1)*, 113.3(5).

The similar reaction of **3c**, **3d** and **3e** gave the corresponding heterobis(carbene) complexes **4c**, **4d** and **4e**. Consequently, both of two isocyanide ligands coordinated to Pt(II) underwent consecutive 1,2-addition of propanol and propylamine to the N≡C bonds with the formation of heterobis(carbene) complex **4**. In the IR spectra of **4**, absorptions due to ν(N–H) and ν(N=C) were found around 3276 and 1548 $cm^{-1}$, respectively, with complete disappearance of the absorption due to ν(N≡C) at about 2186 $cm^{-1}$ in **3**. The structure of **4b** was finally confirmed by an X-ray crystallographic study (Fig. 1) (see Section 4) as well as the results of elemental analysis. The molecular structure shows that **4b** possesses a *trans* square-planar configuration having central metal platinum, which carries two iodo and two carbene ligands with a typical bond distance of 2.027(1) Å for *trans* Pt=C ([3]c, [7,8]). It is a $C_2$ symmetrical structure irrespective of the two different carbene ligands, diaminocarbene and (alkoxy)(amino)carbene. This is the first example of neutral heterobis(carbene)metal complexes by a simple sequential nucleophilic additions of alcohol and amine to bis(isocyanide)platinum complexes.

### 2.3. *Direct synthesis of trans-diiodo{[diaminocarbene][(alkoxy)(amino)carbene]}platinum* **4** *by the reaction of complex* **1** *with alcohol and then amine*

Due to the difficulties in separating mono(carbene) complexes **3** from the mixture of **3** and **5**, we tried to convert **3** to **4** by directly adding amine to the mixture of **3** and **5**. Successfully, a mixture of **4e** and **5e** was obtained by the addition of propylamine (two equivalents to **1e**) to the mixture of **3e** and **5e** (**3e**:**5e** = 4:1) which was produced by the reaction of **1e** with propanol at reflux temperature (Eq. (6)). Heterobis(carbene) complex **4e** can be easily separated from the mixture of **4e** and **5e** by means of recrystallization from hexane–dichloromethane. Surprisingly, on adding a large excess of propylamine (20 equivalents to **1e**) to the mixture of **3e** and **5e**, heterobis(carbene) complex **4e** was obtained as a single product and no remaining homobis[(alkoxy)(amino)carbene] complex **5e** was de-

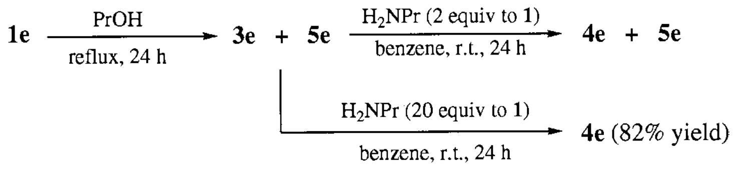


**3**

**4**

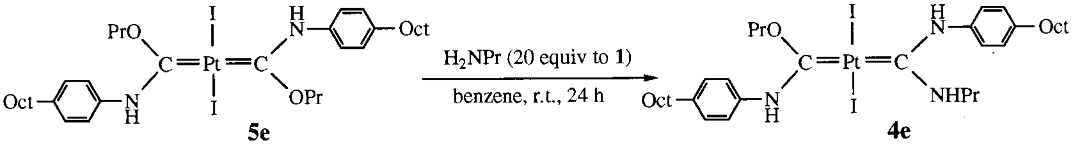
**4b**: Y = OMe, 97% yield
**4c**: Y = Bu, 97% yield
**4d**: Y = OHex, 98% yield
**4e**: Y = Oct, 98% yield

(5)



(6)

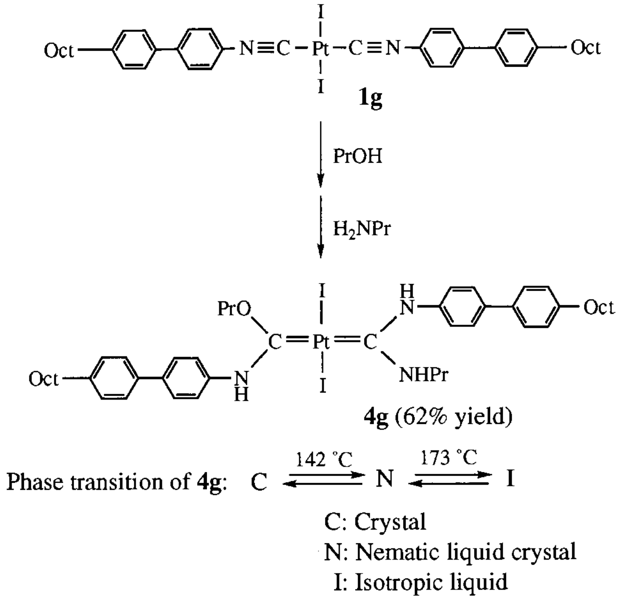
tected (Eq. (6)). On the other hand, **5e** which was isolated from a mixture of **4e** and **5e** reacted with propylamine (20 equivalents to **5e**) in benzene to give **4e** quantitatively and no further reaction occurred (Eq. (7)). These experimental facts show that only one alkoxy substituent on the two carbene ligands was replaced by the amine to form a diaminocarbene ligand although the reason why the other does not undergo replacement with amine is not clear at present.



(7)

As shown in Table 3, the reactions of *trans*-diiodo[bis(isocyanide)]platinum **1a–e** with propanol and then propylamine gave the corresponding unsymmetrically substituted neutral bis(carbene)platinum complexes **4a–e** in good yields (entries 1–5). The reaction of **1e** (Y = Oct) with propanol and then ethylamine gave diiodo{[(4-octylphenylamino)(ethylamino)carbene][(4-octylphenylamino)(propoxy)carbene]}platinum(II) **4f** in 84% yield.

Similarly, **1g** reacted with propanol and then propylamine to give **4g** in 62% yield, which has a long alkoxy-substituented biphenyl group on the carbene ligands (Eq. (8)). Heterobis(carbene) complex **4g** melts at a lower temperature than the corresponding homobis(carbene) complex and has been firstly demonstrated to exhibit a mesomorphic property. Now a further effort is being made to synthesize liquid crystalline heterobis(carbene)platinum complexes having long alkyl substituents on the carbene ligands by the present methodology.



(8)

## 3. Conclusion

Two kinds of methods for synthesizing unsymmetrically substituted neutral bis(carbene)platinum complex, *trans* - diiodobis{[diaminocarbene][(alkoxy)(amino)carbene]}platinum(II) have been developed. One of them is the consecutive nucleophilic attack by an alcohol and then an amine to a *trans*-diiodo[bis(isocyanide)]platinum(II) complex, which provides a simple and versatile methodology for the synthesis of heterobis(carbene)metal complexes.

## 4. Experimental section

Melting points were recorded on a Yamato melting point apparatus MP21 and are not corrected. Elemental microanalyses were performed by the Material Analysis Center, ISIR, Osaka University. IR spectra were obtained with a Perkin Elmer 2000 FT-IR system. $^1$H-NMR spectra were recorded on a JNM-LA400 FT NMR system in $CDCl_3$ with tetramethylsilane as an internal standard.

### *4.1. Materials*

Platinum–isonitrile complexes, *trans*-diiodo[bis(isocyanide)]platinum(II), were prepared by the known methods [7]. Solvents such as dichloromethane and benzene were distilled before used. Amines and alcohols were used as received from commercial sources.

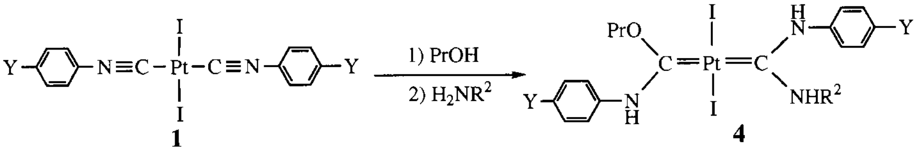
### *4.2. General procedure for preparation of mono(diaminocarbene)platinum complexes **3** by reaction of bis(isocyanide)platinum(II) complexes **1** with alcohols*

A solution of *trans*-bis(isocyanide)platinum **1** (0.3 mmol) in propanol (15 ml) was stirred for 20 h at reflux temperature under argon. After the solvent was evaporated, the resultant residue containing **3** and **5** was purified by a short column. Recrystallization from $CH_2Cl_2$/hexane gave monocarbenes 3.

#### *4.2.1. Diiodo[(4-methoxyphenylamino)(propoxy)carbene][4-methoxyphenylisocyanide]platinum(II) (**3b**)*

The general procedure was followed using *trans*-bis(4-methoxyphenylisocyanide)platinum (0.215 g, 0.3 mmol) (**1b**) and propanol (15 ml). **3b** was obtained as pale yellow

Table 3
Reactions of complex **1** with propanol and amines[a]



| Entry | | Complex **1**<br>Y | Amine<br>$R^2$ | Isolated yield of **4**<br>(%) |
|---|---|---|---|---|
| 1 | **a** | Me | Pr | 86 |
| 2 | **b** | OMe | Pr | 84 |
| 3 | **c** | Bu | Pr | 78 |
| 4 | **d** | Ohex | Pr | 79 |
| 5 | **e** | Oct | Pr | 82 |
| 6 | **f** | Oct | Et | 84 |

[a] (1) Complex **1** (0.3 mmol), propanol (15 ml), reflux for 24 h. (2) Amine (6.0 mmol) in benzene for 24 h.

crystals (0.077 g, 33% yield). M.p. 75.1–75.6°C; IR(KBr): 3325 ν(N–H), 2193 ν(C≡N), 1540 ν(C=N) $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H, N*H*Ar), 7.42 (d, 2H, $J = 9.0$ Hz, Ar), 7.23 (d, 2H, $J = 9.2$ Hz, Ar), 6.93–6.87 (m, 4H, Ar′), 4.93 (t, 2H, $J = 6.7$ Hz, $OCH_2C_2H_5$), 3.85 (s, 3H, $OCH_3$), 3.82 (s, 3H, $OCH_3$), 1.90–1.80 (m, 2H, $OCH_2CH_2CH_3$), 0.97 (t, 3H, $J = 7.3$ Hz, $OC_2H_4CH_3$); Mass ($M^+$) 775.

### 4.2.2. Diiodo[(4-butylphenylamino)(propoxy)carbene][4-butylphenylisocyanide]platinum(II) (3c)

Yellow powders, 29% yield. M.p. 70.5–71.2°C; IR(KBr): 3294 ν(N–H), 2194 ν(C≡N), 1540 ν(C=N) $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H, N*H*Ar), 7.39 (d, 2H, $J = 8.5$ Hz, Ar), 7.27–7.18 (m, 6H, Ar and Ar′), 4.96 (t, 2H, $J = 6.7$ Hz, $OCH_2C_2$H5), 2.67–2.60 (m, 4H, 2 × $CH_2C_3H_7$), 1.92–1.83 (m, 2H, $OCH_2CH_2CH_3$), 1.64–1.56 (m, 4H, 2 × $CH_2CH_2C_2H_5$), 1.40–1.31 (m, 4H, 2 × $C_2H_4CH_2CH_3$), 1.01 (t, 3H, $J =$ 7.4 Hz, $OC_2H_4CH_3$), 0.96–0.92 (m, 6H, 2 × $C_3H_6CH_3$); Mass ($M^+$) 827.

### 4.2.3. Diiodo[(4-hexyloxyphenylamino)(propoxy)-carbene][4-hexyloxyphenylisocyanide]platinum(II) (3d)

Yellow powders, 34% yield. M.p. 71.2–71.5°C; IR(KBr): 3280 ν(N–H), 2191 ν(C≡N), 1548 ν(C=N) $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H, N*H*Ar), 7.39 (d, 2H, $J = 9.0$ Hz, Ar), 7.21 (d, 2H, $J = 8.8$ Hz, Ar), 6.90 (d, 2H, $J = 9.3$ Hz, Ar), 6.87 (d, 2H, $J = 9.0$ Hz, Ar), 4.92 (t, 2H, $J = 6.7$ Hz, $OCH_2C_2H_5$), 3.97 (t, 2H, $J = 6.6$ Hz, $OCH_2C_5H_{11}$), 3.95 (t, 2H, $J = 6.6$ Hz, $OCH_2C_5H_{11}$), 1.88–1.74 (m, 4H, 2 × $OCH_2CH_2C_4H_9$), 1.48–1.42 (m, 2H, $OCH_2CH_2CH_3$), 1.36–1.34 (m, 12H, 2 × $OC_2H_4$ $C_3H_6CH_3$), 0.97 (t, 3H, $J = 7.4$ Hz, $OC_2H_4CH_3$), 0.91 (t, 3H, $J = 6.7$ Hz, $OC_5H_{10}CH_3$); Mass ($M^+$) 915; Anal. Calc. for $C_{29}H_{42}N_2O_3I_2Pt$: C, 38.16; H, 4.64; N, 2.82; I, 27.45. Found: C, 38.04; H, 4.63; N, 3.06; I, 27.72%.

### 4.2.4. Diiodo[(4-octylphenylamino)(propoxy)carbene][4-octylphenylisocyanide]platinum(II) (3e)

Yellow powders, 54% yield. M.p. 67.3–68.0°C; IR(KBr): 3263 ν(N–H), 2186 ν(C≡N), 1538 ν(C=N) $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H, N*H*Ar), 7.38 (d, 2H, $J = 8.3$ Hz, Ar), 7.26–7.17 (m, 6H, Ar), 4.95 (t, 2H, $J = 6.6$ Hz, $OCH_2C_2H_5$), 2.66–2.58 (m, 4H, 2 × $CH_2C_7H_{15}$), 1.91–1.82 (m, 2H, $OCH_2CH_2CH_3$), 1.60–1.53 (m, 4H, 2 × $CH_2CH_2C_6H_{13}$), 1.30–1.26 (m, 20H, 2 × $C_2H_4C_5H_{10}H_3$), 0.96 (t, 3H, $J = 7.3$ Hz, $OC_2H_4CH_3$), 0.88 (m, 6H, 2 × $C_7H_{14}CH_3$); Mass ($M^+$) 939; Anal. Calc. for $C_{33}H_{50}N_2O_1I_2Pt$: C, 42.41; H, 5.16; N, 2.77; I, 26.85. Found: C, 42.18; H, 5.36; N, 2.98; I, 27.10%.

### 4.3. General procedures for preparation of [diaminocarbene][(alkoxy)(amino)carbene]platinum complexes 4

### 4.3.1. Synthesis of 4 (4b–e) by the reaction of isolated mono(diaminocarbene)platinum complexes 3 (3b–e) with propylamine

To a solution of **3e** (94 mg, 0.1 mmol) in benzene (5 ml) was added propylamine (12 mg, 0.2 mmol). After stirring for 24 h at room temperature under argon, the solvent was evaporated and the resultant residue was recrystallization from $CH_2Cl_2$/hexane to give **4e** (99 mg, 98% yield) as yellow powders. In analogous manners, **4b**, **4c** and **4d** were obtained in 97, 98 and 97% yield, respectively.

### 4.3.2. Direct synthesis of 4 by the reaction of complex 1 with alcohol and then amine

A solution of **1a** (170 mg, 0.3 mmol) in propanol (15 ml) was stirred for 24 h at reflux temperature (89°C) under argon. After the solvent was evaporated, the resultant residue was resolved in benzene (10 ml) and then propylamine (360 mg, 6.0 mmol) was added to the solution. After stirring for 24 h at room temperature under argon, the solvent was evaporated and the resultant residue was recrystallized from $CH_2Cl_2$/hexane to give **4a** (210 mg, 86% yield) as yellow powders. In analogous manners, **4b**–**h** were obtained.

### 4.3.3. Diiodo{[(4-methylphenylamino)(propylamino)carbene][(4-methylphenylamino)(propoxy) carbene]}platinum(II) **4a**

Yellow powders, 86% yield. M.p. 188.2–189.0°C; IR(KBr): 3242 $\nu$(N–H), 1553 $\nu$(C=N) cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.35 (bs, 1H, $N\mathit{H}Ar$), 8.16 (bs, 1H, $N\mathit{H}Ar$), 7.22–7.10 (m, 4H, Ar), 6.95–6.83 (m, 4H, Ar), 6.93–6.81 (m, 4H, Ar′), 5.94 (sb, 1H, $N\mathit{H}C_3H_7$), 5.07 (m, 2H, $OC\mathit{H}_2C_2H_5$), 3.81 (m, 2H, $NHC\mathit{H}_2C_2H_5$), 2.35 (bs, 6H, $2\times C\mathit{H}_3$), 1.86 (m, 2H, $OCH_2C\mathit{H}_2CH_3$), 1.68 (m, 2H, $NHCH_2C\mathit{H}_2CH_3$), 0.96 (t, 3H, $J=7.6$ Hz, $NHC_2H_4C\mathit{H}_3$), 0.89 (t, 3H, $J=7.3$ Hz, $OC_2H_4C\mathit{H}_3$); Mass ($M^+$) 803; Anal. Calc. for $C_{22}H_{31}N_3O_1I_2Pt$: C, 33.22; H, 3.94; N, 5.29; I, 31.85. Found: C, 32.93; H, 3.89; N, 5.24; I, 31.63%.

### 4.3.4. Diiodo {[(4-methoxyphenylamino)(propylamino)carbene][(4-methoxyphenylamino)(propoxy)carbene]} platinum(II) **4b**

Yellow powders, 84% yield. M.p. 186.0–186.7°C; IR(KBr): 3250 $\nu$(N–H), 1548 $\nu$(C=N) cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.37 (bs, 1H, $N\mathit{H}Ar$), 8.18 (bs, 2H, $N\mathit{H}Ar$), 7.25–7.12 (m, 4H, Ar), 6.96–6.83 (m, 4H, Ar), 6.93–6.87 (m, 4H, Ar′), 5.96 (sb, 1H, $N\mathit{H}C_3H_7$), 5.05 (m, 2H, $OC\mathit{H}_2C_2H_5$), 3.83–3.79 (m, 8H, $2\times OC\mathit{H}_3+NHC\mathit{H}_2C_2H_5$), 1.88 (m, 2H, $OCH_2C\mathit{H}_2CH_3$), 1.66 (m, 2H, $NHCH_2C\mathit{H}_2CH_3$), 0.98 (t, 3H, $J=7.6$ Hz, $NHC_2H_4C\mathit{H}_3$), 0.90 (t, 3H, $J=7.3$ Hz, $OC_2H_4C\mathit{H}_3$); Anal. Calc. for $C_{22}H_{31}N_3O_3I_2Pt$: C, 31.94; H, 3.56; N, 4.83; I, 30.24. Found: C, 31.66; H, 3.75; N, 5.04; I, 30.42%.

Crystal data for **4b** ($Y=OCH_3$, $R=R'=C_3H_7$): $C_{22}H_{31}N_3O_3I_2Pt$, $M=834.40$; crystal dimensions $0.25\times 0.25\times 0.30$ mm, orthorhombic, space group *Pccn*(#56); $a=12.51(5)$, $b=25.3(1)$, $c=8.47(6)$ Å, $V=2684(20)$ Å$^3$, $Z=4$, $D_{\mathrm{calc}}=2.065$ g cm$^{-3}$, $F(000)=1568.00$, $\mu(\mathrm{Mo{-}K}_\alpha)=75.34$ cm$^{-1}$. The data were collected on a Rigaku AFC7R diffractometer at −81.0°C. The structure was solved by heavy-atom Patterson methods (PATTY) and expanded using Fourier techniques. Hydrogen atoms were included but not refined. The range of transmission factors is 0.667–1.000. The method used for correction is Lorentz-polarization absorption. The final cycle of full-matrix least-squares refinement was based on 2330 observed reflections ($I>3.00\sigma(I)$) and 142 variable parameters and converged with unweighted and weighted agreement factors of: $R=0.029$, $R_w=0.029$. Since **4b** is exactly centrosymmetric, only 142 parameters were used to model $C_{11}H_{16}N_2OIPt$. A final difference-Fourier map possessed some peaks near the platinum atom with the largest peak, $-1.13\leq\Delta\rho\leq 0.57$ e Å$^{-3}$

### 4.3.5. Diiodo {[(4-buthylphenylamino)(propylamino)carbene][(4-buthylphenylamino)(propoxy)carbene]} platinum(II) **4c**

Yellow powders, 78% yield. M.p. 139.4–140.0°C; IR(KBr): 3272 $\nu$(N–H), 1563 $\nu$(C=N) cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.21 (bs, 2H, $N\mathit{H}Ar$), 7.28–7.09 (m, 8H, Ar), 6.11 (bs, 1H, $N\mathit{H}C_3H_7$), 5.05 (m, 2H, $OC\mathit{H}_2C_2$H5), 3.82 (m, 2H, $NHC\mathit{H}_2C_2H_5$), 2.62 (m, 4H, $2\times C\mathit{H}_2C_3H_7$), 1.89 (m, 2H, $OCH_2C\mathit{H}_2CH_3$), 1.62 (m, 2H, $NHCH_2C\mathit{H}_2CH_3$), 1.39–1.30 (m, 8H, $2\times CH_2C_2\mathit{H}_4CH_3$), 1.11–0.87 (m, 12H, $NHC_2H_4C\mathit{H}_3+OC_2H_4C\mathit{H}_3+2\times C_3H_6C\mathit{H}_3$); Anal. Calc. for $C_{28}H_{42}N_3O_1I_2Pt$: C, 38.30; H, 4.64; N, 4.47; I, 28.72. Found: C, 37.93; H, 4.89; N, 4.74; I, 28.63%.

### 4.3.6. Diiodo {[(4-hexyloxyphenylamino)(propylamino)carbene][(4-hexyloxyphenylamino)(propoxy)carbene]} platinum(II) **4d**

Yellow powders, 79% yield. M.p. 96.9–97.6°C; IR(KBr): 3273 $\nu$(N–H), 1552 $\nu$(C=N) cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.14 (s, 1H, $N\mathit{H}Ar$), 7.21 (d, 2H, $J=9.0$ Hz, Ar), 7.31 (sb, 1H, $N\mathit{H}Ar$), 7.17 (d, 2H, $J=8.8$ Hz, Ar), 6.85 (d, 2H, $J=9.0$ Hz, Ar), 6.82 (d, 2H, $J=8.8$ Hz, Ar), 5.96 (sb, 1H, $N\mathit{H}C_3H_7$), 5.00 (t, 2H, $J=6.7$ Hz, $OC\mathit{H}_2C_2H_5$), 3.97–3.91 (m, 4H, $2\times OC\mathit{H}_2C_5H_{11}$), 3.83 (m, 2H, $NHC\mathit{H}_2C_2H_5$), 1.89–1.74 (m, 6H, $OCH_2C\mathit{H}_2CH_3+2\times OCH_2C\mathit{H}_2C_4H_9$), 1.65 (m, 2H, $NHCH_2C\mathit{H}_2CH_3$), 1.53–1.46 (m, 4H, $2\times OC_2H_4C\mathit{H}_2C_2H_5$), 0.97 (t, 3H, $J=7.4$ Hz, $OC_2H_4C\mathit{H}_3$), 0.93–0.87 (m, 9H, $NHC_2H_4CH_3+2\times OC_5H_{10}C\mathit{H}_3$); Mass ($M^+$) 975; Anal. Calc. for $C_{32}H_{51}N_3O_3I_2Pt$: C, 39.20; H, 5.08; N, 4.20; I, 25.93. Found: C, 39.43; H, 5.27; N, 4.31; I, 26.04%.

### 4.3.7. Diiodo{[(4-octylphenylamino)(propylamino)carbene][(4-octylphenylamino)(propoxy)carbene]} platinum(II) **4e**

Yellow powders, 82% yield. M.p. 123.4–124.0°C; IR(KBr): 3276 $\nu$(N–H), 1548 $\nu$(C=N) cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.19 (bs, 2H, $N\mathit{H}Ar$), 7.30–7.09 (m, 8H, Ar), 6.12 (bs, 1H, $N\mathit{H}C_3H_7$), 5.10 (m, 2H, $OC\mathit{H}_2C_2H_5$), 3.85 (m, 2H, $NHC\mathit{H}_2C_2H_5$), 2.61 (m, 4H, $2\times C\mathit{H}_2C_7H_{15}$), 1.89 (m, 2H, $OCH_2C\mathit{H}_2CH_3$), 1.69–1.52 (m, 6H, $NHCH_2CH_2CH_3+2\times CH_2C\mathit{H}_2C_6H_{13}$), 1.30–1.26 (m, 20H, $2\times C_2H_4C_5\mathit{H}_{10}CH_3$), 1.00 (t, 3H, $J=7.4$ Hz, $OC_2H_4C\mathit{H}_3$), 0.93–0.87 (m, 9H, $NHC_2H_4C\mathit{H}_3+2\times C_7H_{14}C\mathit{H}_3$); Mass ($M^+$) 999;

Anal. Calc. for $\mathrm{C_{36}H_{59}N_3O_1I_2Pt}$: C, 43.45; H, 5.77; N, 4.19; I, 25.32. Found: C, 43.29; H, 5.95; N, 4.21; I, 25.41%.

### *4.3.8. Diiodo{[(4-octylphenylamino)(ethylamino)carbene][(4-octylphenylamino)(propoxy) carbene]}platinum(II)* **4f**

Yellow powders, 84% yield. M.p. 130.5–131.5°C; IR(KBr): 3297 $\nu$(N–H), 1557, 1539 $\nu$(C=N) cm$^{-1}$; $^1$H-NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta$ 8.20 (bs, 2H, $\mathrm{N}H\mathrm{Ar}$), 7.25–7.13 (m, 8H, Ar), 6.04 (sb, 1H, $\mathrm{N}H\mathrm{C_2H_5}$), 5.29 (m, 2H, $\mathrm{OC}H_2\mathrm{C_2H_5}$), 3.94 (m, 2H, $\mathrm{NHC}H_2\mathrm{CH_3}$), 2.60 (m, 4H, $2\times\mathrm{C}H_2\mathrm{C_7H_{15}}$), 1.89 (m, 2H, $\mathrm{OCH_2C}H_2\mathrm{CH_3}$), 1.55 (m, 4H, $2\times\mathrm{CH_2C}H_2\mathrm{C_6H_{13}}$), 1.30–1.25 (m, 23H, $\mathrm{NHC_2H_4C}H_3+2\times\mathrm{C_2H_4C_5}H_{10}\mathrm{CH_3}$), 1.00 (t, 3H, $J=$ 7.5 Hz, $\mathrm{OC_2H_4C}H_3$), 0.93–0.87 (m, 6H, $2\times\mathrm{C_7H_{14}C}H_3$); Mass (M$^+$) 985.

### *4.3.9. Diiodo {[(4-(4-octylphenyl)phenylamino)(propylamino)carbene][(4-(4-octylphenyl)phenylamino) (propoxy)carbene]}platinum(II)* **4g**

Yellow powders, 62% yield. M.p. C---144°C---N---173---I; IR(KBr): 3196 $\nu$(N–H), 1577 $\nu$(C=N) cm$^{-1}$; $^1$H-NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta$ 8.39 (bs, 2H, $\mathrm{N}H\mathrm{Ar}$), 7.87–7.36 (m, 12H, Ar), 7.26–6.95 (m, 4H, Ar), 6.20 (bs, 1H, $\mathrm{N}H\mathrm{C_3H_7}$), 5.05 (m, 2H, $\mathrm{OC}H_2\mathrm{C_2H_5}$), 4.51–3.99 (m, 6H, $2\times\mathrm{OC}H_2\mathrm{C_7H_{18}}+\mathrm{NHC}H_2\mathrm{C_2H_5}$), 1.88 (m, 2H, $\mathrm{OCH_2C}H_2\mathrm{CH_3}$), 1.52–1.44 (m, 4H, $2\times\mathrm{OCH_2C}H_2\mathrm{C_6H_{13}}$), 1.30 (m, 2H, $\mathrm{NHCH_2CH_2CH_3}$), 1.07–1.02 (m, 20H, $2\times\mathrm{OC_2H_4(C}H_2\mathrm{)_5CH_3}$), 0.93 (m, 3H, $\mathrm{OC_2H_4C}H_3$), 0.89–0.83 (m, 9H, $\mathrm{NHC_2H_4C}H_3+2\times\mathrm{OC_7H_{14}C}H_3$); Anal. Calc. for $\mathrm{C_{48}H_{67}N_3O_3I_2Pt}$: C, 48.73; H, 5.72; N, 3.55; I, 21.45. Found: C, 49.00; H, 5.74; N, 3.31; I, 21.61%.

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## References

[1] M.H. Chisholm, H.C. Clark, Accounts Chem. Res. 6 (1973) 202, and references cited therein.

[2] K. Oguro, M. Wada, R. Okawara, J. Organomet. Chem. 159 (1978) 417.

[3] (a) M. Keeton, R. Mason, D.R. Russell, J. Organomet. Chem. 33 (1971) 259. (b) U.T. Struchkov, G.G. Aleksandrov, S.P. Sushchinskaya, M.G. Voronkov, J. Organomet. Chem. 172 (1979) 269. (c) D.J. Cardin, B. Cetinkaya, M.F. Lappert, Chem. Rev. 72 (1992) 545, and references therein. (d) T. Kaharu, S. Takahashi, Chem. Lett. (1992) 1515.

[4] (a) M.H. Chisholm, H.C. Clark, Inorg. Chem. 10 (1971) 1711. (b) E.M. Badley, J. Chatt, R.L. Richards, G.A. Sim, J. Chem. Soc., Chem. Commun. (1969) 1322. (c) F. Bonati, G. Minghetti, J. Organomet. Chem. 24 (1970) 251. (d) J.S. Miller, A.L. Balch, Inorg. Chem. 11 (1972) 2069. (e) J.E. Parks, A.L. Balch, J. Organomet. Chem. 71 (1974) 453. (f) G. Banditelli, F. Bonati, S. Calogero, G. Valle, J. Organomet. Chem. 275 (1984) 153.

[5] (a) F. Bonati, G. Minghetti, Synth. Inorg. Metal-Org. Chem. 1 (1971) 299. (b) F. Bonati, G. Minghetti, J. Organomet. Chem. 59 (1973) 403.

[6] (a) R. Ishii, T. Kaharu, N. Pirio, S.-W. Zhang, S. Takahashi, J. Chem. Soc., Chem. Commun. (1995) 1215. (b) S.-W. Zhang, R. Ishii, S. Takahashi, Organometallics 16 (1997) 20.

[7] (a) S.-W. Zhang, T. Kaharu, N. Pirio, R. Ishii, M. Uno, S. Takahashi, J. Organomet. Chem. 489 (1995) C62. (b) S.-W. Zhang, R. Ishii, F. Motoori, S. Takahashi, Inorg. Chim. Acta (1997).

[8] (a) M.E.M. Badley, J. Chatt, R.L. Richards, G.A. Sim, Chem. Commun. (1969) 1322. (b) G.A. Larkin, R.P. Scott, M.G.H. Wallbridge, J. Organomet. Chem. 37 (1972) C21. (c) J.S. Miller, A.L. Balch, Inorg. Chem. 11 (1972) 2069. (d) G. Rouschias, B.L. Shaw, J. Chem. Soc. A 2097 (1971). (e) A. Burke, A.L. Balch, J.H. Enemark, J. Am. Chem. Soc. 92 (1970) 2555.