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Preliminary communication

Syntheses and X-ray crystal structures of neutral *trans*-bis(diamino-carbene)platinum(II) complexes

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Abstract

The first neutral *trans*-bis(diamino-carbene)platinum(II) complex **2** is prepared by the reaction of *trans*-diiodo[bis(*p*-tolylisocyanide)]platinum(II) **1** with a secondary amine, *N*,*N*-dipropylamine, while on applying a primary amine, *N*-propylamine, a neutral *ortho*-metalled *trans*-bis(diamino-carbene)platinum(II) complex **3** is obtained in good yield. The structures of carbene complexes **2** and **3** have been established by X-ray crystallography.

Keywords: Platinum; Neutral *trans*-bis(carbene) complex; *Ortho*-metallation

Since the first stable transition metal carbene complexes were prepared by Fischer and Maasböl in 1964 [1], a whole series of new preparative routes have been developed during the last 30 years. In spite of the variety of methods available, the original preparation by Fischer and Maasböl is probably still the most useful and general procedure for the direct synthesis of carbene complexes from non-carbene precursors. But, because of the highly electrophilic character of the carbene carbon in Fischer-type complex, a nucleophilic anion in excess does not attack the complex at a carbon monoxide ligand but instead at the carbene carbon atom [2]. Therefore, bis(carbene) complex could not, in general, be prepared by this route.

There is a useful method for the preparation of carbene complexes starting from metal complexes containing an isocyanide ligand. However, a neutral *trans*-bis(carbene) metal complex has not been successful so far although some mono or cationic bis(carbene) platinum complexes have been prepared [3]. Here, we report that first neutral *trans*-bis(diamino-carbene)-platinum(II) complex **2** is prepared by the reaction of *trans*-diiodo[bis(*p*-totylisocyanide)]platinum(II) **1** with a secondary amine, *N*,*N*-dipropylamine. Interestingly, we also found that a neutral *ortho*-metallated *trans*-bis(diamino-carbene)platinum(II) complex **3** is obtained by applying a primary amine, *N*-propylamine, instead of the secondary amine under the same reaction conditions (Scheme 1).

The complex **1** (R = CH_3), *trans*-diiodo[bis(*p*-tolylisocyanide)]platinum(II), was synthesized according to a known method [4], that is by the ligand-exchange reaction of PtI_2(COD)[COD: 1,5-cyclooctadiene)] with an appropriate isonitrile such as *p*-tolyl isonitrile in chloroform. To the solution of complex **1** in ether was added a secondary amine, *N*,*N*-dipropylamine. After stirring for 12 h at room temperature, the solvent was evaporated and crystallization from hexane-ether gave complex **2** (R = CH_3, R′ = C_3H_7) as pale yellow crystals (90% yield). That is, both of two isonitrile ligands coordinated to Pt(II) underwent 1,2-addition of the amine to the $N{\equiv}C$ bond with formation of a bis(carbene) complex **2**. Satisfactory analytical and spectroscopic data were obtained for **2**. In the IR spectra, absorptions due to ν(N-H) and ν(N=C) were found around 3330 and 1535 cm^{-1}, respectively, with disappearance of the absorption of $\nu(N{\equiv}C)$ at 2220 cm^{-1} of **1**. Its structure was finally confirmed by X-ray crystallographic studies [5]. Fig. 1 is an ORTEP drawing of **2** (R = CH_3, R′ = C_3H_7) with important interatomic distances and angles noted. The structure shows that **2** is a *trans* square-planar complex having a cen-

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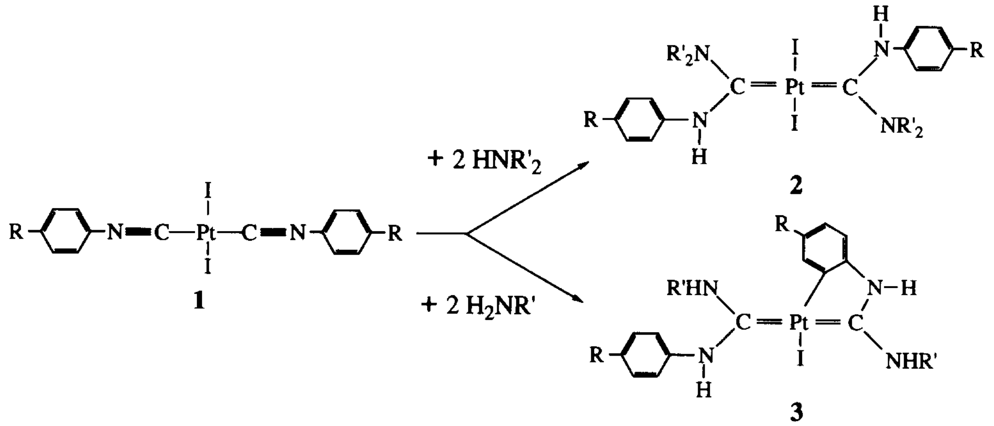

Scheme 1.

tral metal platinum(II) carrying two iodo ligands and two (diamino)carbenes with a typical *trans*-type Pt=C bond distance of 2.051(4) Å [3(a),6].

To our surprise, when a primary amine like *N*-propylamine was applied instead of *N*,*N*-dipropylamine of a secondary amine under the same conditions, complex **3** (Scheme 1, $R = CH_3$, $R' = C_3H_7$) was obtained in good yield (79% yield). The reaction of *N*-hexylamine with complex **1** ($R = C_8H_{17}$) gave complex **3** ($R = C_8H_{17}$, $R' = C_6H_{13}$) in 82% yield. The structure of **3** ($R = C_8H_{17}$, $R' = C_6H_{13}$) was characterized by spectroscopic and X-ray crystallographic data [7]; it contains an iodo ligand, two (diamino)carbenes and a new Pt–C bond formed by an *ortho*-metallation (see Fig. 2).

Dihedral angle between least-squares planes, the aromatic ring and the five-membered ring containing a Pt atom is 5.59°, and thus the two rings are almost in a plane. The metallation of aromatic groups in transition metal complexes is generally induced by reduction [8] or oxidation [9]. Although the intramolecular reaction between a transition metal and an *ortho* C-H bond on an aromatic substituent on a P ligand is well known [8,10], there have been few examples of *ortho*-metallation occurring in carbene complexes to give neutral complexes directly [9(c),11].

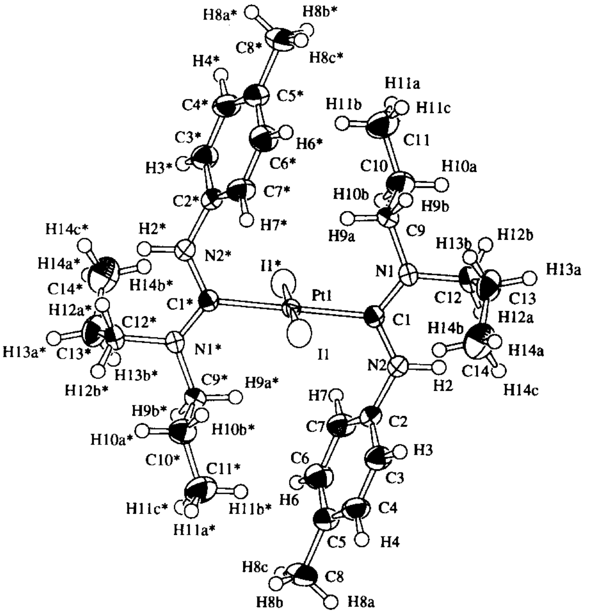

Fig. 1. ORTEP drawing of complex **2** ($R = CH_3$, $R' = C_3H_7$). Selected bond distances (Å) and angles (°): Pt(1)-C(1), 2.051(4); Pt(1)-I(1), 2.609(1); C(1)-N(1), 1.322(6); C(1)-N(2), 1.486(6); I(1)-Pt(1)-I(1)*, 180.0; C(1)-Pt(1)-C(1)*, 180.0; C(1)-Pt(1)-I(1), 94.1(1); N(1)-C(1)-N(2), 115.7(4).

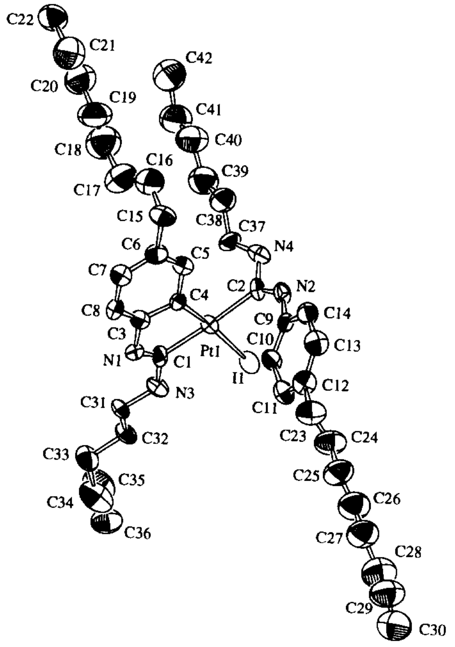

Fig. 2. ORTEP drawing of complex **3** ($R = C_8H_{17}$, $R' = C_6H_{13}$). Selected bond distances (Å) and angles (°): Pt(1)-C(1), 2.07(2); Pt(1)-C(4), 1.90(2); Pt(1)-C(2), 2.12(2); Pt(1)-I(1), 2.709(3); C(1)-N(1), 1.29(2); C(1)-N(3), 1.41(2); C(2)-N(2), 1.27(2); C(2)-N(4), 1.40(2); C(1)-Pt(1)-C(2), 174.1(7); C(1)-Pt(1)-C(4), 77.7(7); I(1)-Pt(1)-C(2), 89.1(5); I(1)-Pt(1)-C(1), 96.8(5); N(1)-C(1)-N(3), 120(1); N(2)-C(2)-N(4), 115(1).

The reasons that the synthesis of neutral bis(carbene) complexes has not been successful until now are perhaps follows: (1) a complex of type L_2MX_2 having *cis* configuration, when attacked by a nucleophilic amine, gives only a *mono*-carbene complex because of steric hindrance of the firstly formed carbene group; (2) previous reports by Belluco and coworkers [12] and our group [13] have shown that there are two possible configurations, *trans* and *cis*, for square-planar $MX_2(CN\text{-}R)_2$, which may be controlled by changing the halogen X (M = Pt and Pd; X = Cl, Br and I). In the case of M = Pt, only $PtI_2(CN\text{-}R)_2$ shows *trans* configuration, while the chloro and bromo derivatives of platinum complexes have *cis* configurations. Most of the studies on (carbene) metal complexes until now have been trending toward applying the complexes with halogen ligand, Cl, not with I. Fortunately we used iodo derivatives because we already prepared a large number of *trans*-$PtI_2(CN\text{-}R)_2$ complexes for a study of liquid–crystalline materials [13].

The complexes prepared in the present work provide the first examples of neutral *trans*-bis(diamino-carbene)platinum(II) complexes as well as neutral *ortho*-metalled *trans*-bis(diamino-carbene)platinum complexes although it remains unclear now why a primary amine gives an *ortho* metallation product, not a secondary amine does. Further studies on the reaction mechanism and reaction scope are in progress.

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[5] Crystal data for **2** ($R = CH_3$, $R' = C_3H_7$): M = 442.79 × 2; crystal dimensions $0.33 \times 0.18 \times 0.15$ mm^3, triclinic, space group $P\bar{1}$; $a = 10.390(6)$, $b = 10.721(7)$, $c = 8.826(4)$ Å, $\alpha = 101.98(5)°$, $\beta = 104.08(4)°$, $\gamma = 117.99(4)°$, $V = 780.5(9)$ Å^3, $Z = 1$, $D_c = 1.884$ g cm^{-3}, $F(000) = 424$, $\mu(\text{MoK}\alpha) = 64.78$ cm^{-1}. The data were collected on a Rigaku AFC5R diffractometer at room temperature. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The final cycle of full-matrix least-squares refinement was based on 4101 observed reflections ($I > 3.00\sigma(I)$) and converged with unweighted and weighted agreement factors of: $R = 0.036$, $R_w = 0.038$.

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[7] Crystal data for **3** ($R = C_8H_{17}$, $R' = C_6H_{13}$): $C_{42}H_{72}N_4I_1Pt_1$, $M = 955.05$; crystal dimensions $0.25 \times 0.25 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$; $a = 12.70(1)$, $b = 16.79(1)$, $c = 10.93(1)$ Å, $\alpha = 98.06(9)°$, $\beta = 92.04(9)°$, $\gamma = 76.42(6)°$, $V = 2242(4)$ Å^3, $Z = 2$, $D_c = 1.415$ g cm^{-3}, $F(000) = 966.0$, $\mu(\text{MoK}\alpha) = 38.36$ cm^{-1}. The data were collected on a Rigaku AFC5R diffractometer at room temperature. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 6147 observed reflections ($I > 3.00\sigma(I)$) and converged with unweighted and weighted agreement factors of: $R = 0.084$, $R_w = 0.097$. The final R value of 0.084 was not particularly precise because large thermal vibration of the long alkyl groups.

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