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ELECTROCHEMICAL PREPARATION OF ISOCYANIDE COMPLEXES OF LOW-VALENT PLATINUM CONTAINING A METAL-METAL BOND

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The potentiostatic reduction of cis-$PtCl_2(RNC)_2$ (**3a**:R = 2,4-t-Bu_2-6-MeC_6H_2; **3b**: R = 2,4,6-t-$Bu_3C_6H_2$; **3c**: R = 2,6-$Me_2C_6H_3$) were carried out on a mercury pool electrode in CH_3CN. The one-electron reduction (96.5 kC/mol) of **3a** and **3b** gave $[PtCl(RNC)_2]_2$ (**4a** and **4b**). An X-ray analysis of **4a** showed that the two $PtCl(RNC)_2$ planes jointed by a Pt-Pt bond were perpendicular. The two-electron reductions (2x96.5 kC/mol) of **3a** and **3b** gave $Hg[Pt_3(RNC)_6]_2$ and $Pt_3(RNC)_6$, respectively. Electrolysis of **3c** gave only $Hg[Pt_3(2,6\text{-}MeC_6H_3NC)_6]_2$.

Recently we reported that the reaction of dichlorobis(2,6-xylyl isocyanide)platinum(II) with sodium amalgam gave new homo- and mixed clusters, $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$ (1)$^{1)}$ and $Hg[Pt_3(2,6\text{-}Me_2C_6H_3NC)_6]_2$ (**2c**)$^{2)}$.

Electrochemical studies give useful information on the electronic configuration of complexes and the mechanism of reactions. Furthermore, electrochemical methods can be used for selective preparation of transition metal complexes in higher or lower oxidation state. Several polarographic studies have been made for square planar complexes of nickel, palladium and platinum. Recently, Lemoine and his coworkers reported that electroreduction of cis and trans-dihalobis(alkyl isocyanide)platinum(II) on platinum electrode took place as two irreversible processes.$^{3)}$ Zanello et al. described that cis-$MCl_2(p\text{-}XC_6H_4NC)(PMePh_2)$ (M = Pd, Pt; X = Cl, MeO) was electrochemically reduced to give zerovalent species.$^{4)}$ However, the two groups could not isolate any discrete complexes.

The present paper reports electrochemical preparation of new platinum(I) dimeric complexes containing a metal-metal bond.

Figure 1 shows polarograms of cis-$PtCl_2(RNC)_2$ (**3a**; R=2,4-t-Bu_2-6-MeC_6H_2, **3b**; R=2,4,6-t-$Bu_3C_6H_2$, and **3c**; R=2,6-$Me_2C_6H_3$).$^{5)}$ Two reduction waves defined by regions of A and B appeared in the polarograms. The waves in A whose wave-heights are independent of the concentrations of Pt(II) complexes, are attributed to a reduction of strongly absorbed species of Pt(II) complexes.

The waves in B correspond to a main reduction of Pt(II) complexes and can be analyzed as the diffusion control with a two electron reduction process. However, the shape of the slopes of the waves indicates that the reaction is not a simple polarographic reversible process, but a more complicated process.

The potentiostatic electrolysis of **3a** in CH_3CN containing 0.1 M n-Bu_4NClO_4 (TBAP) was carried out by means of a mercury pool electrode at -1.70 V.$^{6)}$

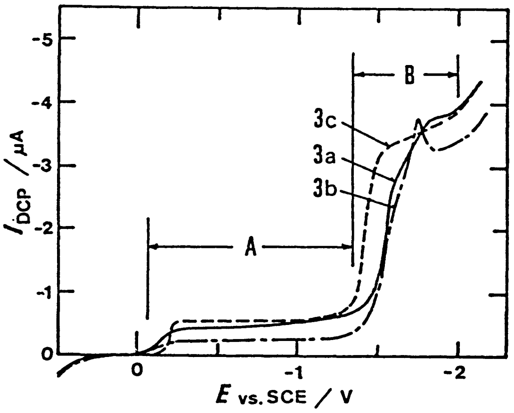

Fig. 1. Polarograms of $PtCl_2(RNC)_2$ in CH_3CN. (**3a**: R=2,4-t-Bu_2-6-Me-C_6H_2; **3b** R=2,4,6-t-$Bu_3C_6H_2$; **3a** R=2,6-$Me_2C_6H_3$.

After the electrolysis with charge (96.5 kC/mol) corresponding to the one electron reduction of Pt(II) + e $\longrightarrow$ Pt(I), a yellow complex **4a**, formulated as $[Pt(2,4\text{-t-}Bu_2\text{-}6\text{-}MeC_6H_2NC)_2Cl]_2$,7) was obtained in a 90% yield. The IR spectrum of **4a** showed a peak at 2142 cm^{-1}, attributable to terminal isocyanide groups.

The crystal structure analysis of **4a** shows that the complex unit comprises two independent molecules, as depicted in Fig. 2.8) The molecule involves two Pt atoms, each possessing an essentially square-planar coordination jointed by a Pt-Pt bond, where the Pt atom occupies one of the coordination sites. This type of complex has not been obtained in the chemical reduction with Na-Hg, and **4a** is the first neutral Pt(I) dimer which does not contain bridging ligands. The average of the dihedral angles between the two coordination planes are 88°, nearly perpendicular. A similar geometry has been observed in the cationic $[Pd(MeNC)_3]_2^{2+}$ complex **5**.9)

The Pt-Pt bond lengths of 2.563(2) and 2.561(2) Å are shorter by ca. 0.1-0.2 Å than those found in some zerovalent platinum clusters.1,2,10) The averages for Pt-C and Pt-Cl bonds are 1.95 and 2.38 Å, and resemble those found in other related complexes.11) The mean value of the Pt-C-N bond angle is 176.3°, being almost linear. The equatorial isocyanide ligands bend away from the axial Cl atoms giving rise to values of 93.8° for the mean C-Pt-Cl angle and 85.5° for mean Pt-Pt-C angle. A similar type of distortion has been observed in **5**.

The electrochemical reaction is considered as a reductive coupling one containing a cis-trans isomerization. This isomerization may proceed either via a 17 electron species $[PtCl_2(RNC)_2]^-$ or a 15 electron one $PtCl(RNC)_2\cdot$, since the chemical isomerization from cis-$PtCl_2(RNC)_2$ to trans-one has not been observed.

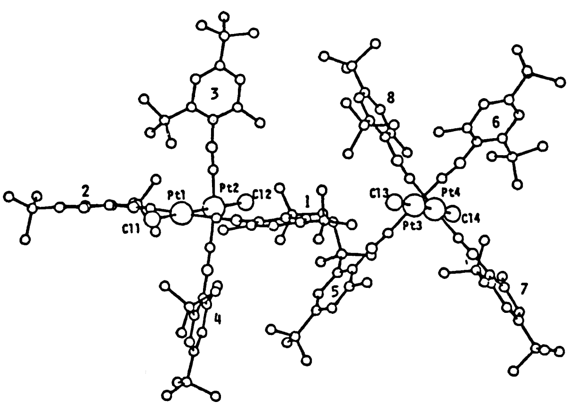

Fig. 2. Crystal structure of **4a**.

The potential energy curve of a dimer, $[PtCl(HNC)_2]_2$, was calculated as a function of dihedral angles between the two $PtClC_2$ planes, using the EHMO calculations.12) The perpendicular geometry was estimated to be more stable by 3.7 eV than that with dihedral angle of 0° (a planar structure), in agreement with the crystal structure of **4a**.

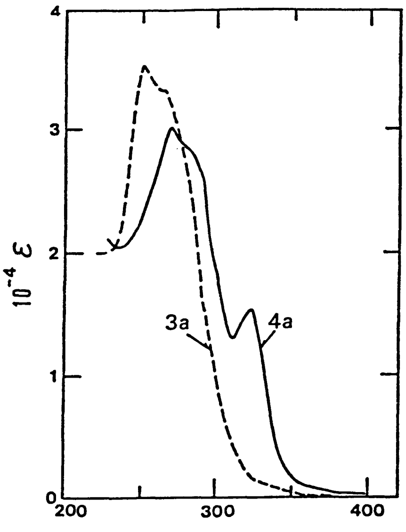

Fig. 3. Electronic spectra of 3a and 4a in CH_2Cl_2.

The electronic spectrum of **4a** shows a peak at 324 nm (ε 15320) assignable to a σ-σ* transition, in the same range as $[Pd(MeNC)_3]_2^{2+}$ (**5**) (307 nm).

The two electron reduction (2x96.5 kC/mol) of **3a** at -2.00 V gave a dark yellowish green solution, from which a green solid was obtained by evaporation. The electronic spectrum of the green solid in CH_3CN was similar to that found in known **2c**. An attempt to purify the green solid has failed because of decomposition during the processes, but orange yellow crystals of triangular $Pt_3(2,4\text{-t-}Bu_2\text{-}6\text{-}MeC_6H_2NC)_6$ (**6a**)[13] were obtained in ca. 90% yield. These results suggest the initial formation of $Hg[Pt_3(2,4\text{-t-}Bu_2\text{-}6\text{-}MeC_6H_2NC)_6]_2$ (**2a**), followed by the formation of **6a**.

When **3a** was electrolyzed with charge of 2x96.5 kC/mol at -1.70 V, **4a** and **6a** were isolated in yields of 20 and 41%, respectively, suggesting that the electrolysis of **3a** is proceed via two successive one electron reduction processes, and r_1 is larger than r_2.

$$\mathrm{Pt(II)} \xrightarrow[r_1]{e} \mathrm{Pt(I)} \xrightarrow[r_2]{e} \mathrm{Pt(0)}$$

In the case of the reduction at -2.00 V, both of the reaction rates r_1 and r_2, are fast, and therefore the Pt(0) complex was produced in a rate determining step of a mass-transport of the Pt(II) complex.

One and two electron reductions of **3b** consumed 96.5 and 2x96.5 kC/mol at -1.70 V gave $[PtCl(2,4,6\text{-t-}Bu_3C_6H_2NC)_2]_2$ (**4b**)[14] in a 92% yield and $Pt_3(2,4,6\text{-t-}Bu_3C_6H_2NC)_6$ (**6b**)[15] in a 86% yield, respectively. In the latter reaction, the formation of a mixed cluster containing a mercury atom has not been observed. Bulky ligands have sterically prevented the inclusion of a mercury atom into a platinum cluster.

Similar charge-controlled electrolyses of **3c** at -1.50 V were carried out and the only isolated product was identified as **2c**, whose yields were 24 and 77% for the electrolyses with 96.5 and 2x96.5 kC/mol, respectively. In the former reaction, the starting complex **3c** was recovered in a 45% yield without giving the expected Pt(I) dimer, suggesting $r_1 < r_2$ or a two electron-one step reduction taking place.

The mechanistic study is now in progress.

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crystallographic analysis of **4a**.

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5) Cis-configuration of Pt(II) isocyanide complexes is suggested by the presence of two $\nu_{N\equiv C}$ bands in the infrared spectra: 2224, 2189 cm^{-1} for **3a** and 2197, 2205 cm^{-1} for **3b**, 2205, 2172 cm^{-1} for **3c**. They gave good elemental analyses.
6) The potentials are indicated against a saturated calomel electrode (SCE), although a $Ag/AgNO_3$-TBAP-CH_3CN electrode was employed.
7) Found: C, 57.01; H, 7.03; N, 3.9%. Calcd for $C_{64}H_{92}N_4Cl_2Pt_2$: C, 57.09; H, 6.76; N, 3.92%. NMR($CDCl_3$):δ 1.19(p-t-Bu), 1.53(o-t-Bu), 2.56(o-Me), ca. 7.0(aromatic protons).
8) Crystal data: space group $P\bar{1}$. a= 14.507(3), b=34.212(6), c= 14.502(6)A, α= 99.29(3), β = 91.49(3), γ = 98.60(2) . Z= 4. R = 0.097.
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12) The Pt-Pt, Pt-C, and Pt-Cl lengths were set as 2.56, 1.96, and 2.37 Å, respectively. The Pt-C-N-H bond was idealized to be linear. The Pt-Pt-C and Pt-Pt-Cl angles were set as 86 and 180°, respectively. The parameters used in the EHMO calculations were taken from the literature (A.Dedieu and R.Hoffmann, J.Am.Chem.Soc. 100, 2074(1978)).
13) Found: C, 58.99; H, 7.31; N, 4.22%. Calcd for $C_{96}H_{138}N_6Pt_3$: C, 58.79; H, 7.09; N, 4.28%. IR(nujol): 2108, 2088, 1720 cm^{-1}. NMR($CDCl_3$):δ 1.00, 1.15(o-t-Bu), 1.41, 1.56(p-t-Bu), 2.30, 2.59(o-Me), ca. 7.0(aromatic protons). The detail will be reported elsewhere.
14) Found: C, 59.42; H, 7.66; N, 3.52%. Calcd for $C_{76}H_{116}N_4Cl_2Pt_2$: C, 59.01; H, 7.56; N, 3.62%. IR(nujol): 2165, 2136 cm^{-1}. NMR($CDCl_3$): δ 1.34(o-t-Bu), 1.57(p-t-Bu), ca. 7.3(aromatic protons). Electronic spectrum(CH_2Cl_2): λ 333sh, 271(ε 39930).
15) Found: C, 61.85; H, 8.01; N, 3.66%. Calcd for $C_{114}H_{174}N_6Pt_3$: C, 61.85; H, 7.92; N, 3.80%. IR(nujol): 2099, 1826 cm^{-1}. NMR($CDCl_3$): δ 1.32(o-t-Bu), 1.51(p-t-Bu), ca. 7.33(aromatic protons).

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