Bull. Chem. Soc. Jpn., **60**, *2665—2666 (1987)*

Electrochemical Preparation of Tetrakis(isocyanide)-dipalladium(I) Dichloride[1)]

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(Received January 8, 1987)

Synopsis. The electrochemical behavior of $PdCl_2(RNC)_2$ (**1**) has been investigated in acetonitrile at Pt and Hg electrodes. The cyclic voltammogram of **1** showed a reduction wave at ca. −1.2 V, corresponding to a two-electron transfer. Coulometric reduction of **1** at the Pt electrode gave a binuclear complex, $Pd_2Cl_2(RNC)_4$ (**2**). A similar reaction at the Hg electrode gave **2** in a relatively low yield. A Pt electrode was superior to a Hg one in the electrochemical synthesis of **2**. The polarogram of **1** at a Hg electrode suggested a CE mechanism of the electrode reaction.

Binuclear complexes having a metal-metal bond are of interest in areas of photo- and catalytic chemistry.[2)] Recently we described electrochemical preparation of $Pt_2Cl_2(RNC)_4$ from $PtCl_2(RNC)_2$.[3)] Analogous binuclear palladium(I) complexes of isocyanide have been prepared by the metathesis reactions between Pd(II) and Pd(0) complexes.[4)] We report here the electrochemical preparation of dichlorotetrakis(isocyanide)dipalladium(I).

The cyclic voltammogram (CVM) of $PdCl_2(2,6\text{-}Me_2C_6H_3NC)_2$ (**1a**) was measured in acetonitrile by means of a Pt electrode to determine the preparative condition of a macroscopic electroreduction (Fig. 1). The CVM showed reduction waves at ca. − 1.1 V (current peak potential, E_{pc}) for aryl isocyanide complexes and at ca. −1.4 V for alkyl isocyanide complex. In comparison with the CVM of $PtCl_2(RNC)_2$,[5)] these waves were assigned to a two-electron reduction of the Pd(II) complexes.

When a charge-controlled electrolysis of **1a** consumed 1F (1F=96.5 kC) of charge per mole of the Pd(II) complex at −1.5 V, binuclear complex, $Pd_2Cl_2(2,6\text{-}Me_2C_6H_3NC)_4$ **2a** was obtained in a 73% yield. Similar binuclear complexes were obtained in a relatively high yield by the electroreduction of $PdCl_2(RNC)_2$ (R=2,6-Me_2-4-BrC_6H_2, 2,4-*t*-Bu_2-6-MeC_6H_2, 2,4,6-*t*-$Bu_3C_6H_2$, and *t*-Bu), as shown in Table 1.

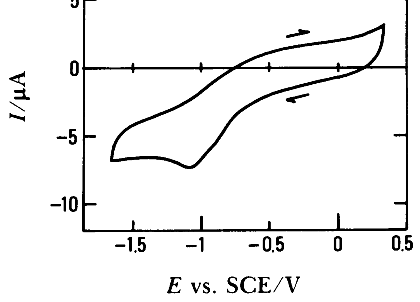
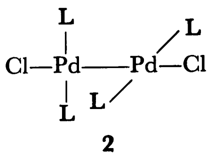


Fig. 1. Cyclic voltammogram of $PdCl_2(2,6\text{-}Me_2C_6H_3NC)_2$ (0.2 mM) on a Pt-tip electrode (surface area= 0.078 cm^2) in a 0.1 M *n*-Bu_4NClO_4-CH_3CN solution at 22 °C. Sweep rate=0.1 Vs^{-1}.



2

L=RNC

The charge-controlled electrolysis of **1a** consumed 1 F of charge per mole of complex at −1.4 V carried out at a mercury pool electrode and gave **2a** in a 23% yield. In this reaction, palladium metal was liberated as a precipitate, showing decomposition of a part of the palladium complexes. Yields of **2** at a mercury electrode were lower than those at a platinum one. In an attempt to reveal the origin of the low yields of **2** at a mercury electrode, a d.c. polarogram of **1a** was measured in a 0.1 M (mol dm^{-3}) *n*-Bu_4NClO_4-CH_3CN solution, using a dropping mercury electrode (Fig. 2). The polarogram showed a reduction wave at $E_{1/2}$ = 0.05 V where $E_{1/2}$ is an apparent halfwave potential. This was significantly different from that at the CVM. The shape of this wave and the reduction potential agreed resonably with those of the polarogram of $HgCl_2$ (Fig. 1).

These results suggest that the CE (chemical-electrochemical) reaction is operative at the Hg electrode surface, in which an initial chemical reaction of 1a with Hg proceeds to give $HgCl_2$ (Eq. 1), followed by an electrochemical reduction of $HgCl_2$ to Hg(0)

Table 1. Cathodic Current Peak Potential (E_{pc}) of $PdCl_2(RNC)_2$ (**1**) on the CVM and Yields of $Pd_2Cl_2(RNC)_4$ (**2**)$^{a)}$

	R	Electrode	E_{pc}/V$^{b)}$	Yield/%
1a	2,6-$Me_2C_6H_3$	Pt	−1.19	73
		Hg		23
1b	2,6-Me_2-4-BrC_6H_2	Pt	−1.13	83
		Hg		38
1c	2,4-*t*-Bu_2-6-MeC_6H_2	Pt	−1.18	87
		Hg		49
1d	2,4,6-*t*-$Bu_3C_6H_2$	Pt	−1.15	70
		Hg		52
1e	*t*-Bu	Pt	−1.41	69

a) Reactions were carried out at −1.5 V except **1e** (−1.6 V) in a 0.1 M $NaClO_4$-CH_3CN solution (ca. 30 cm^3) containing ca. 0.25 mmol of a sample. Charge, ca. 1 F per mole of a sample, was passed. b) A Pt-tip electrode was used for the CVM measurement in a 0.1 M *n*-Bu_4NClO_4-CH_3CN solution. The potentials are shown against a saturated calomel electrode. Sample concentration: ca. 0.1—0.5 mM; scan rate: 0.2 Vs^{-1}.

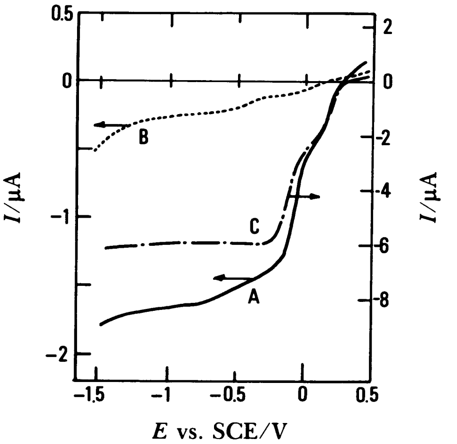


Fig. 2. d.c. Polarograms on a dropping mercury electrode (m=0.864 mg s^{-1}, drop time=4 s) in a 0.1 M n-Bu_4NClO_4-CH_3CN solution at 23 °C. A: $PdCl_2(2,6$-$Me_2C_6H_3NC)_2$ (0.2 mM). B: Blank (suppoting electrolyte solution). C: $HgCl_2$ (0.5 mM).

(Eq. 2).[6]

$$\mathrm{Hg(metal)} + \mathrm{Pd(II)} \longrightarrow \mathrm{Hg(II)} + \mathrm{Pd(metal)} \qquad (1)$$

$$\mathrm{Hg(II)} + 2e \longrightarrow \mathrm{Hg(metal)} \qquad (2)$$

Relatively high yields of complexes having bulky isocyanide ligands showed less interaction with mercury than that in the complex **1a**.

In conclusion, a Pt electrode was superior to a Hg electrode in the electrochemical synthesis of the Pd complex (Table 1).

The reaction path leading to the formation of $Pd_2Cl_2(RNC)_4$ was considered to be similar to that in a platinum complex.[5] The electrochemical reaction was initiated by a two-electron transfer to **1** to give a zerovalent species **3**. The chemical reaction of the zerovalent species (or a trinuclear complex, $Pd_3(RNC)_6$) and **1** led to a formation of **2**.

$$\mathrm{PdCl_2(RNC)_2} \xrightarrow{2e} \underset{\mathbf{3}}{\text{“}\mathrm{Pd(RNC)_2}\text{” (or } \mathrm{Pd_3(RNC)_6})}$$

$$\xrightarrow{\mathrm{PdCl_2(RNC)_2}} \underset{\mathbf{2}}{\mathrm{Pd_2Cl_2(RNC)_4}}$$

Experimental

The electrochemical apparatus has been already descrbed.[5] 2,6-Xylyl, 2,6-dimethyl-4-bromophenyl, 2,4,6-tri-*t*-butylphenyl, and *t*-butyl isocyanides were prepared according to the literature.[7] $PdCl_2(RNC)_2$ (R = 2,6-$Me_2C_6H_3$, 2,6-Me_2-4-BrC_6H_2) was prepared according to the literature.[3]

2,4-Di-*t*-methylphenyl isocyanide was prepared by a modification of the method described in the literature.[7b] IR (Nujol) 2109 cm^{-1},

^{1}H NMR($CDCl_3$) δ = 1.32 (s, 4-*t*-Bu), 1.52 (s, 2-*t*-Bu), 2.43 (s, 6-Me), ca. 7.2 (aromatic protons). Anal. ($C_{16}H_{23}N$) C, H, N.

$PdCl_2(2,4,6$-*t*-$Bu_3C_6H_2NC)_2$: IR (Nujol) 2229, 2195 cm^{-1}. Anal. ($C_{38}H_{58}N_2Cl_2Pd$) C, H, N.

$PdCl_2(2,4$-*t*-Bu_2-6-$MeC_6H_2NC)_2$: IR (Nujol) 2205 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 1.30 (4-*t*-Bu), 1.48 (2,-*t*-Bu), 2.50 (6-Me), ca. 7.3(aromatic protons). Anal. ($C_{32}H_{46}N_2Cl_2Pd$) C, H, N.

$Pd_2Cl_2(2,4,6$-*t*-$Bu_3C_6H_2NC)_4$: IR (Nujol) 2144 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 1.29 (s, 4-*t*-Bu), 1.65 (bs, 2 and 6-*t*-Bu), 7.32 (s, aromatic protones, 3- and 4-H). Found: C, 66.66: H, 8.54; N, 4.09%. Calcd for $C_{76}H_{116}N_4Cl_2Pd_2$: C, 66.71; H, 8.91; N, 3.90%.

$Pd_2Cl_2(2,4$-*t*-Bu_2-6-$MeC_6H_2NC)_4$: IR (Nujol): 2187, 2147 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 1.27 (4-*t*-Bu), 1.46 (2-*t*-Bu), 2.47 (6-Me), ca. 7.3(aromatic protons). Anal. ($C_{64}H_{92}N_4Cl_2Pd_2$) C, H, N.

The authors (Y.Y and K.T) with to express their thanks for a Grant-in-Aid for Scientific Research 59540332 from the Ministry of Education, Science and Culture.

References

1) A part of this paper was presented at the 32nd Symposium on Organometallic Chemistry, November (1985), Osaka. Electrochemical studies of organometallic compounds, Part 4. Part 1: Y. Yamamoto, K. Takahashi, and H. Yamazaki, *Chem. Lett.*, **1984**, 201. Part 2: Y. Yamamoto, K. Takahashi, and H. Yamazaki, *J. Am. Chem. Soc.*, **108**, 2458 (1986). Part 3: Y. Yamamoto, K. Takahashi, K. Matsuda, and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, in press.

2) G. L. Geoffroy and M. S. Wrighton, "Organometallic Photochemistry," Academic Press (**1979**); M. P. Brown, J. R. Fisher, S. J. Franklin, R. J. Puddephatt, M. A. Thomson, *Adv. Chem. Ser.*, **196**, 231 (1982) and references therein.

3) Y. Yamamoto, K. Takahashi, and H. Yamazaki, *Chem. Lett.*, **1985**, 201.

4) Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, **58**, 1843 (1985).

5) Y. Yamamoto, K. Takahashi, K. Matsuda, and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, in press.

6) Mechanistic study of the electrochemical reactions is now in progress and details will be reported in the future.

7) H. M. Walborsky and G. E. Niznik, *J. Org. Chem.*, **37**, 187 (1972); Y. Yamamoto, K. Aoki, and H. Yamazaki, *Inorg. Chem.*, **18**, 1681 (1979).